Birla Central Library

PILANI (Jaipur State)

Class No: 546.13

Book No .- 4494 P

Accession No - 33231

-			
		•	

THE PREPARATION, PROPERTIES, CHEMICAL BEHAVIOR, AND IDENTIFICATION OF ORGANIC CHLORINE COMPOUNDS

By Ernest Hamlin Huntress

A Brief Introduction to the Use of Beilstein's Handbuch der organischen Chemie

The Preparation, Properties, Chemical Behavior, and Identification of Organic Chlorine Compounds Tables of Data on Selected Compounds of Order III

By Ernest Hamin Huntress and the late Samuel Parsons Mulliken Identification of Pure Organic Compounds
Tables of Data on Selected Compounds of Order I
(Compounds of Carbon with Hydrogen or with Hydrogen and Oxygen)

THE PREPARATION, PROPERTIES, CHEMICAL BEHAVIOR, AND IDENTIFICATION OF

ORGANIC CHLORINE COMPOUNDS

Tables of Data on Selected Compounds of Order III

By

ERNEST HAMLIN HUNTRESS

Professor of Organic Chemistry Massachusetts Institute of Technology

NEW YORK · JOHN WILEY & SONS, INC. LONDON · CHAPMAN & HALL, LIMITED 1948

COPYRIGHT 1948, BY JOHN WILDS & SONS, INC.

All Rights Reserved

This book of any part thereof must not be reproduced in any form without the written permission of the publisher.

COPYRIGHT CANAJA, 1948, INTERNATIONAL COPYRIGHT, 1948

JOHN WILEY & SONS, INC., Proprietor

All Foreign Rights Reserved Reproduction in whole or in part forbidden

PREFACE

This volume represents the second to appear in the series of Tables of Data prepared by the present author. It presents in organized and conveniently usable form a summary of data on a selected list of organic compounds containing carbon and chlorine, or carbon, oxygen, and chlorine, or carbon, hydrogen, and chlorine, or carbon, hydrogen, and chlorine. Such compounds may more briefly be described as comprising Order 3.

Although users of its predecessor will immediately recognize many aspects of similarity in this book, they will also note in this volume certain differences. These distinctions are more fully discussed in Chapter I, but certain general aspects may be noted here.

Whereas the treatment of Order 1 compounds was directed mainly toward the aspect of identification, and though this point of view is vigorously continued, the present treatment of compounds of Order 3 has been expanded to include also the preparation, properties, and general chemical behavior of the individuals selected for treatment.

A second major difference from the earlier volume is in the extent of reference to the original literature or the corresponding abstracts thereof. This documentation is carried to a degree which may suggest to organic chemists that this volume comprises a Beilstein. The author hastens to disclaim any such degree of completeness for this work but does admit that for each compound selected a meticulous search of the literature through 1945 has furnished the basis for appropriate selection and systematic grouping of the aspects to be treated.

A third important difference from the earlier volume is the inclusion of references to patents as well as scientific articles. Though such patent references are treated with reserve, it is believed that they will be of interest to all users and of special value to industrial chemists. Throughout the book emphasis is given to industrial aspects since the rapid growth of this field during the last two decades, particularly in the United States, has resulted in the production and large-scale utilization of many individual compounds of this order (3).

A fourth type of difference in the present treatment as compared with that of Order 1 is seen in the tabulation of physical constants. In the earlier volume an attempt was made to select the "best" values. This process tended to conceal the magnitude and nature of the available constants from

PREFACE vi

which such selection was made and thus somewhat to weaken the degree of reliance to which the final selection was entitled. In the present volume all the relevant data on boiling points, melting points, densities, and refractive indices have been included, thus permitting the user to make such interpretation of their consonance (or lack of it) as his particular needs may require. With certain exceptions, the amount of such physical data is surprisingly small, and no attempt to assess its reliability has been made except that instances where little effort to obtain pure products was demonstrated have usually been disregarded.

A merely superficial inspection of this volume by a nonchemical user might give the erroneous impression that the text comprised only a compilation of reported data. Careful examination by organic chemists, however, will immediately disclose that its form of organization and mode of treatment are largely influenced by the nature of the chemistry involved. conspicuously shown by what might be called "negative entries." Definite knowledge that a particular reaction has not been reported or that an individual compound does not appear in the systematic literature is often of real value. Many entries of this type appear in the current record. connection the dependence of chemists upon adequate and complete indexes to their original and especially to their abstract journals deserves emphasis. The term "unreported" as used in this book signifies that the compound in question cannot be found by systematic use of the usual index sources. Undoubtedly, instances will arise in which a substance so characterized will be found to have been embedded in details of work with other principal objectives and thus to have escaped proper indexing in the abstract journals. The author will be grateful for information on any cases of this sort.

An extended exposition of the principles involved in the formulation of this volume will be found in Chapter I. Special attention, however, may be directed to the exceptional care taken to facilitate the use of this book. For example, the volume includes (as Chapter XXIII) five kinds of indexes. These comprise not only the conventional alphabetical name index but also indexes of compounds by empirical formulas, by chemical types, and even by percentage chlorine and molecular weights. Moreover, throughout the text of the individual compounds there are inserted extremely frequent references to the related compounds which are necessarily involved. If these other compounds are themselves given detailed treatment in either this book (Order 3) or its precursor (Order 1), they are indicated by appropriate serial numbers so that no reference to either index is necessary. If, however, such secondary compounds are not themselves treated in either book, reference to the corresponding volume and page of Beilstein's Handbuch der organischen Chemie is made instead.

A brief statistical survey of the content of this volume may be of interest.

vii PREFACE

The 1320 individual compounds of Order 3 to which detailed text treatment is given are distributed among 366 groups of isomers. Of these 1320 compounds 366, i.e., 26.7% of the group, have been prepared so recently that they do not appear in the Fourth Edition of Beilstein at all. A total of 164 cross-reference headings facilitate recognition of the melting points of high-boiling liquids, or the boiling points of compounds normally met with as solids.

The total number of literature references in this volume is more than 22,000, of which total 67% represent publications since 1919 (the last year for which both the main and first supplementary series of Beilstein's *Handbuch* are complete), and 47% represent publications since 1929. The number of references associated with a given compound naturally varies widely. The highest number of references (621) is given for chloroacetic acid, followed by 405 each for trichloroacetaldehyde and ethylene chlorohydrin. More than 50 references are associated with each of 68 numbered compounds.

The preparation of this volume has been a long and laborious operation. The author wishes to place on permanent record his deep appreciation of the conscientious, faithful, and accurate secretarial assistance given him over long periods by both Miss Shirley Ridgway and Miss Mildred Capodilupo and for a shorter period by Miss Ruth Volinn.

The author is keenly aware that he cannot hope to satisfy in full the particular interests of every user. There must necessarily exist differences of opinion on the relative importance of this or that compound, reaction, or derivative. However, if all possible objections were first to be overcome nothing would ever be accomplished, and the author hopes that any deficiencies of this volume may to some extent be compensated by its merits.

Furthermore, in a work of this kind and magnitude it is inevitable that, despite every good intention and every earnest and painstaking effort, actual errors of fact will still have escaped detection and correction. The author invites the friendly cooperation of all who discover any such flaws, meanwhile being consoled by the view expressed by the ancient Chinese writer Tai T'ung, who, some seven hundred years ago, issued his History of Chinese Writing with this statement: "Were I to await perfection my book would never be finished.... The book awaits a wise and lofty spirit to correct and suppress where the text is in error, to add where it is defective, and to supply new facts where it is altogether silent."

ERNEST HAMLIN HUNTRESS

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
July 15, 1946

CONTENTS

Preface				PAGES V—vii
TABLE OF CONTENTS		• • • • • • • • • • • • • • • • • • • •		ix-x
TABLE OF ABBREVIATIONS				xi-xv
MEMORANDUM OF CERTAIN 1946-19 REGULAR TEXT		ENCES NOT INCO		xvii–xxv
	Снар	rer I		
Introduction		• • • • • • • • • • • • • • • • • • • •	• • • • • • • • • • • • • • • • • • • •	1–19
DATA ON I	INDIVID	UAL COMPOUR	NDS	
	Division A	. Solids		
CHAPTER II	PAGES	Снарт	ER VII	PAGES
Serial numbers 3:0000-3:0499	20-84	Serial numbers	3:2500-3:2999	277 –299
CHAPTER III		Снарті	er VIII	
Serial numbers 3:0500-3:0999	85-125	Serial numbers	3:3000-3:3499	300-334
CHAPTER IV		Снарт	rer IX	
Serial numbers 3:1000-3:1499 1	26-205	Serial numbers	3:3500-3:3999	335–3 59
Chapter V		Снарт	er X	
Serial numbers 3:1500-3:1999 20	06-252	Serial numbers	3:4000-3:4499	360-409
CHAPTER VI		Снарть	er XI	
Serial numbers 3:2000-3:2499 2	53-276	Serial numbers	3:4500-3:4999	410-506
Division B. Liquids wi	th boiling p	points reported at a	rdinary pressure	
_	Снарте	r XII		PAGES
Section 1. D_4^{20} greater than 1.	1500; Se	rial numbers	3:5000-3:5499	507-700
	CHAPTER	XIII		
Section 1. D_4^{20} greater than 1.		erial numbers	3:5500-3:5999	701-789

					PAGES	
		Сная	TER XIV			
Section 1.	D_4^{20}	greater than 1.1500;	Serial numbers	3:6000-3:6499	7 90–8 7 5	
		Сн	APTER XV			
Section 1.	D_4^{20}	greater than 1.1500;	Serial numbers	3:6500-3:6999	876-929	
		Сни	APTER XVI			
Section 2.	D_4^{20}	less than 1.1500;	Serial numbers	3:7000-3:7499	930-1044	
		Сна	PTER XVII			
Section 2.	D_4^{20}	less than 1.1500;	Serial numbers	3:7500-3:7999	1045-1095	
CHAPTER XVIII						
Section 2.	D_{4}^{20}	less than 1.1500;	Serial numbers	3:8000-3:8499	1096-1153	
	CHAPTER XIX					
Section 2.	D_4^{20}	less than 1.1500;	Serial numbers	3:8500-3:8999	1154-1227	
Div	ision C.	Liquids with boiling p	points reported only t	under reduced press	sure	
		Сн	APTER XX			
Serial numb	ers 3	3:9000-3:9299			1228-1279	
		Сна	PTER XXI			
Serial numb	ers 3	3:93 00–3 :9599			1280-1322	
•		Сна	PTER XXII			
Serial numb	ers 3	3:9600-3:9999			1323-1358	
		Снар	TER XXIII			
I. Index	of com	oounds according to en	npirical formulas		1359-1379	
II. Index	of emp	oirical formulas accord	ling to percentage	chlorine content	1380-1382	
	_	rical formulas accordin	-	ghts	1383-1385	
		oounds according to ch			1386-1422	
V. Index	of comp	pounds by names in al	phabetical sequence	•	1423-1443	

ABBREVIATIONS

	A	aq.	water or aqueous
$[lpha]_{ m D}^{20}$	specific rotation at 20°	arom.	aromatic
	for D line	assoc.(d)(n)	associate(s) (associated)
Ā	represents acid residue		(association)
	in whose description		В
	it occurs	B	represents a molecule of
abs.	absolute; absolutely	D	the "basic" salt-
abt.	about		forming compound in
abund.	abun dant		whose description it
abv.	above		occurs
Ac	acetyl radical, i.e., CH ₃ .CO—	B.B.No.	bromide-bromate num- ber
AcOEt	ethyl acetate	bibl.	bibliography
AcOH	acetic acid (glacial ace-	bkn.	"broken" (cf. color ter-
	tic acid when unmodi-	DAII.	minology)
	fied)	boilg.	boiling
Ac ₂ O	acetic anhydride	b.p.	boiling point (at atm.
ac.	acid	p.	pressure unless speci-
acc.	according		fied)
acid.	acidify, acidified, acidi-	Bu	n-butyl
	fication	bril.	brilliant
act.	active	brn.	brown
addn.(l)	addition (additional)	$\mathbf{B}\mathbf{z}$	benzoyl, i.e., C6H5.CO-
adj.	adjacent (e.g., 1,2,3)	BzOH	benzoic acid
alc.	alcohol (95% unless		C
	otherwise stated); al-	•	
	coholic	C Č	Centigrade degrees
ald.	aldehyde	C	used to designate the
alk.(y)	alkali; alkaline; (alka-		compound in whose
	linity)	1- (1) (-)	description it occurs
alm.	almost	calc.(d) (n)	calculate(d)
Am	amyl		(calculation)
ammon.	ammoniacal	cap.	capillary
amorph.	amorphous	cat.	catalyst; catalytic; catalyzed
amt.(s)	amount(s)	••	cubic centimeter(s)
anal.	analysis; analyses	cc.	• • •
anhyd.	anhydrous	cf.	compare centigram(s)
anti-	anti (stereomeric oppo-	cg. charac.	characteristic
	site of syn-)	chem.	chemical
apprec.	appreciable; appreci-	ciem.	stereochemical opposite
	ably	C16-	of trans-
approx.	approximate; approxi- mately	cm.	centimeter(s)

ABBREVIATIONS

coeff.	coefficient	diam.	diameter
col.(n)	color (coloration)	dif.	different; difference; difficultly
comb.(d)_(n) (g)	combine(d) (combina- tion) (combining)	dil.(td) (tg) (n)	dilute (diluted) (dilu-
comml.	commercial	() (-8) ()	ting) (dilution)
compd.	compound	dimin.	diminish; diminishing;
compn.	composition		diminished; diminu-
conc.(d) (n)	concentrate(d) (concen-		tive
	tration)	dis.(lvd)	dissolve (dissolved)
condens.	condensation	dissoc.(d) (g) (n)	dissociate(d) (dissociat-
cond.	condition(s)		ing) (dissociation)
confrm.(n)	confirm; confirmatory (confirmation)	dist.(d) (g) (n)	distil(led) (distilling) (distillation)
const.	constant	distrib.(n)	distribute (distribution)
cont.(s) (g)	contain(s) (containing)	div.(n)	divide (division)
conv.(n)	convert (conversion)	dk.	dark
cor.	corrected	d, l -	racemic (by external
corresp.	corresponding		compensation as con-
C.P.	chemically pure		trasted with meso)
epd.	compound	D.V.	Duclaux Value
crit.	critical		
cryst.(n) (d)	crystal(s); crystallize(s)		${f E}$
	(d); crystalline (crys-	eas.	easily
	tallization)	efferv.	effervesce(s); efferves-
C.S.T.	critical solubility tem-		cent
	perature	equiv.	equivalent
	D	espec.	especially
_	_	est.(d) (g) (n)	estimate(s) (estimated)
•	derivative (used to intro-		(estimating) (estima-
	duce important de-		tion)
	rivatives for specific	Et	ethyl, i.e., CH ₃ .CH ₂ —
	characterizations)	EtOH	ethyl alcohol (generally
(D)	dark (following name of		refers to 95% if un-
7 20	a broken color)	-41	modified)
D_4^{20}	density at 20° referred to	eth.	ether (generally means
,	water at 4°	(d) (m) (m)	ordinary diethylether)
d-	dextrorotatory	evap.(d) (g) (n)	evaporate(d) (evaporat-
dec.(d) (n)	decompose(s) (decom- posed) (decomposi-	evol.(n)	ing) (evaporation)
	tion)	* *	evolve(s) (evolution)
deliq.	deliquesce(s), deliques-	exam.(d) (n)	examine(d) (examina- tion)
denq.	cent	expt.(l)	•
depolym.(d) (n)	depolymerize(s) (depoly-	ext.(d) (g) (n)	experiment(al) extract(s) (extracted)
deporym.(d) (ii)	merized) (depolymer-	ext.(tt) (g) (tt)	extract(s) (extracted) (extracting) (extrac-
	ization)		tion)
deriv.(s) (d) (n)	derivative(s) (derived)		violi)
(c) (u) (u)	(derivation)		F
desic.	desiccator; desiccated	filt.(n)	filter(s); filtrate (fil-
detectn.	detection		tration)
detn.(d)	determine: determina-	floc.	flocculate; flocculent
	tion (determined)	fluores.	fluoresce(s); fluorescent

f.p. freq. fract.(n) (nl)	freezing point frequently fraction; fractionate (fractionation) (frac- tional) fumaroid (stereochemi-	insol.(y) irreg. irrit.(n) isom.(d) (n)	insoluble (insolubility) irregular irritating (irritation) isomer; isomerize (isomerized) (isomerization)
•	cal opposite of maleinoid)		K
fumg. fus.(n)	fuming fuse(s), melt(s); fusi- ble; fusing (fusion)	k	ionization constant
			L
	G	(L)	Light (modifying name of a broken color)
g.	gram(s)	l-	
gem.	geminate (said of two		laevorotatory
	like groups attached	l.	liter(s)
	to same atom)	lft(s).	leaflet(s)
geom.	geometrical	lgr.	ligroin
glac.	glacial	liq.	liquid; liquefy
gr.	green	lt.	light (of a color)
grad.	graduate; graduated; gradually		M
gran.	granular; granulated	(3.E)	
		(M)	medium (modifying
	н		name of a broken
			color)
H.E.	hydrolysis equivalent	m.	melt(s)
H.E. hexag.	hydrolysis equivalent hexagon; hexagonal	m-	meit(s) meta
	hydrolysis equivalent hexagon; hexagonal hour(s)		• • •
hexag. hr.(s)	hexagon; hexagonal	m-	meta
hexag. hr.(s) ht.(d) (g)	hexagon; hexagonal hour(s) heat(ed) (heating)	m-	meta maleinoid (stereochemi-
hexag. hr.(s)	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis;	m-	meta maleinoid (stereochemi- cal opposite of
hexag. hr.(s) ht.(d) (g)	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro-	m- mal.	meta maleinoid (stereochemical opposite of fumaroid) maximum
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd)	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed)	m- mal. max.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ —
hexag. hr.(s) ht.(d) (g)	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro-	m- mal. max. Me	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd)	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic	m- mal. max. Me MeOH m.e.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd)	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed)	m- mal. max. Me MeOH m.e. mg.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent milligram(s)
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros.	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic	m- mal. max. Me MeOH m.e. mg. mic.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent milligram(s) micro
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros. ibid.	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic I in the same place	max. Me MeOH m.e. mg. mic. microcryst.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent milligram(s) micro microcrystalline
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros. ibid. ident.	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic I in the same place identical; identity	m- mal. max. Me MeOH m.e. mg. mic. microcryst. min.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent milligram(s) micro microcrystalline minute(s); minimum
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros. ibid.	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic I in the same place identical; identity identify (identified)	m- mal. max. Me MeOH m.e. mg. mic. microcryst. min. minl.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH millieguivalent milligram(s) micro microcrystalline minute(s); minimum mineral
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros. ibid. ident. identif.(d) (n)	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic I in the same place identical; identity identify (identified) (identification)	m- mal. max. Me MeOH m.e. mg. mic. microcryst. min. minl. misc.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent milligram(s) micro microcrystalline minute(s); minimum mineral miscellaneous; miscible
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros. ibid. ident. identif.(d) (n) i.e.	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic I in the same place identical; identity identify (identified) (identification) that is	m- mal. max. Me MeOH m.e. mg. mic. microcryst. min. minl. misc. mixt.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent milligram(s) micro microcrystalline minute(s); minimum mineral miscellaneous; miscible mixture(s)
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros. ibid. ident. identif.(d) (n) i.e. immed.	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic I in the same place identical; identify identified) (identification) that is immediate; immediately	m- mal. max. Me MeOH m.e. mg. mic. microcryst. min. minl. misc. mixt. mod.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent milligram(s) micro microcrystalline minute(s); minimum mineral miscellaneous; miscible mixture(s) moderate
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros. ibid. ident. identif.(d) (n) i.e. immed. impt.	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic I in the same place identical; identity identify (identified) (identification) that is immediate; immediately important	max. Me MeOH m.e. mg. mic. microcryst. min. minl. misc. mixt. mod. modifn.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent milligram(s) micro microcrystalline minute(s); minimum mineral miscellaneous; miscible mixture(s) moderate modification
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros. ibid. ident. identif.(d) (n) i.e. immed. impt. inact.	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic I in the same place identical; identity identify (identified) (identification) that is immediate; immediately important inactive; inactivated	max. Me MeOH m.e. mg. mic. microcryst. min. minl. misc. mixt. mod. modifn.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH3— methanol, i.e., CH3OH milliequivalent milligram(s) micro microcrystalline minute(s); minimum mineral miscellaneous; miscible mixture(s) moderate modification molecular
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros. ibid. ident. identif.(d) (n) i.e. immed. impt. inact. indef.	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic I in the same place identical; identity identify identified) (identification) that is immediate; immediately important inactive; inactivated indefinite	max. Me MeOH m.e. mg. mic. microcryst. min. minl. misc. mixt. mod. modifn. mol. monoclin.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent milligram(s) micro microcrystalline minute(s); minimum mineral miscellaneous; miscible mixture(s) moderate modification molecular monoclinic
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros. ibid. ident. identif.(d) (n) i.e. immed. impt. inact.	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic I in the same place identical; identity identify (identified) (identification) that is immediate; immediately important inactive; inactivated indefinite indicate; indicator; in-	max. Me MeOH m.e. mg. mic. microcryst. min. minl. misc. mixt. mod. modifn. mol. monoclin. ml.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent milligram(s) micro microcrystalline minute(s); minimum mineral miscellaneous; miscible mixture(s) moderate modification molecular monoclinic milliliter
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros. ibid. ident. identif.(d) (n) i.e. immed. impt. inact. indef. indic.	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic I in the same place identical; identity identify (identified) (identification) that is immediate; immediately important inactive; inactivated indefinite indicate; indicator; in- dicated	max. Me MeOH m.e. mg. mic. microcryst. min. minl. misc. mixt. mod. modifn. mol. monoclin.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent milligram(s) micro microcrystalline minute(s); minimum mineral miscellaneous; miscible mixture(s) moderate modification molecular monoclinic
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros. ibid. ident. identif.(d) (n) i.e. immed. impt. inact. indef.	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic I in the same place identical; identity identify (identified) (identification) that is immediate; immediately important inactive; inactivated indefinite indicate; indicator; in- dicated infinite	max. Me MeOH m.e. mg. mic. microcryst. min. minl. misc. mixt. mod. modifn. mol. monoclin. ml.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent milligram(s) micro microcrystalline minute(s); minimum mineral miscellaneous; miscible mixture(s) moderate modification molecular monoclinic milliliter
hexag. hr.(s) ht.(d) (g) hydrol.(g) (zd) hygros. ibid. ident. identif.(d) (n) i.e. immed. impt. inact. indef. indic.	hexagon; hexagonal hour(s) heat(ed) (heating) hydrolyze; hydrolysis; (hydrolyzing) (hydro- lyzed) hygroscopic I in the same place identical; identity identify (identified) (identification) that is immediate; immediately important inactive; inactivated indefinite indicate; indicator; in- dicated	m- mal. Me MeOH m.e. mg. mic. microcryst. min. minl. misc. mixt. mod. modifn. mol. monoclin. ml.	meta maleinoid (stereochemical opposite of fumaroid) maximum methyl, i.e., CH ₃ — methanol, i.e., CH ₃ OH milliequivalent milligram(s) micro microcrystalline minute(s); minimum mineral miscellaneous; miscible mixture(s) moderate modification molecular monoclinic milliliter millimeter

	N	pr.	prism(s)
N	normal (equivalents per	pract.	practically
••	liter)	prep.(d) (g) (n)	prepare(d) (preparing)
n	normal		(preparation)
n_{D}^{20}	refractive index at 20°	pres.	presence
•	for D line of sodium	press.	pressure
ndl.(s)	needle(s)	prim.	primary
neg.	negative	prin.	principal
Neut. Eq.	neutralization equiva-	prismat.	prismatic
-	lent	prob.	probably
neut.(zd)	neutral (neutralized)	proc.	procedure
no. ·	number	prod.	product; produce; pro-
non-fus.	non-fusible		duced
non-vol.	non-volatile	prop.	property; properties
		pt.(s)	part(s)
	О	pulv.(d)	pulverize(d)
0-	ortho	pung.	pungent
obs.(d) (n)	observe(d) (observa-	purif.(d) (g) (n)	purify (purified) (puri-
	tion)		fying) (purification)
obt.(d)	obtain(ed)		_
opt.	optical		Q
optim.	optimum	quad.	quadratic
or.	orange	qual.	qualitative; qualita-
ord.	ordinary		tively
orig.	original; originally	quant.	quantity; quantitative;
org.	organic		quantitatively
oxid.(g) (n)	oxidize(s) (oxidizing)	quat.	quaternary
	(oxidation)	q.v.	quod vide (which see)
	P		R
®	preliminary test	rac.	racemic
<i>p</i> -	para	rap.	rapid; rapidly
perm.	permanent	reactn.	reaction(s)
pet. Ph	petroleum	reagt.(s)	reagent(s)
phys.	phenyl, i.e., C ₆ H ₅ —	rearr.	rearrange(s); rearrange-
physiol.	physical	•	ment
Pk	physiological	recommd.	recommend; recom-
- A	picryl, i.e., 2,4,6-tri-		mended
PkOH	nitrophenyl-	recryst.(d) (g) (n)	(, (
pl.	pierie acid		tallizing) (recrystal-
polym.(n)	plate(s)	i	lization)
potym.(n)	polymer; polymerize; polymerized (poly-	rect.	rectangular
	polymerized (poly- merization)	redis.	redissolve
pos.	positive	reduc.(d) (g) (n)	reduce(d) (reducing)
powd.	positive powder; powdered		(reduction)
ppt.(d) (g) (n)		ref.	reference
	precipitate(d) (precipitating) (precipita-	reminis.	reminiscent
	tion)	reppt.(d) (g) (tn)	reprecipitate(d) (repre-
Pr	propyl		cipitating) (reprecipi-
	E57.		tation)

resid.	residue; residual		T
resin.	resinify; resinification	Т	Numbered Test
resp.	respectively	tbl.(s)	tablet(s) > tabular
rhomb.	rhombic	tech.	technical
	S	temp.	temperature
a 15		theor.	theoretical
Sap. Eq.	saponification equiva-	therm.	thermometer
(1) (-) (-)	lent	T.N.B.	1,3,5-trinitrobenzene
sapon.(d) (g) (n)	saponify (saponified)	T.N.T.	2,4,6-trinitrotoluene
	(saponifying) (saponi- fication)	ter-	tertiary
ant (d) (m) (m)	,	trans-	stereochemical opposite
sat.(d) (g) (n)	saturate(d) (saturating) (saturation)		of cis-
sec.	second(s)	transf.	transfer; transform
8ec.	secondary	tt.	test tube
sect.	section		
sep.(d) (g) (n)	separate(d) (separating)		U
sep.(u) (g) (n)	(separation)		O
sft.(n)(s)	soft; soften(s)	u.c.	uncorrected
shak.(g) (n)	shake (shaking) (shaken)	undec.	undecomposed
sint.(d)	sinter(s) (sintered)	undislvd.	undissolved
sl.	slightly	unoxid.	unoxidized
sld. cap.	sealed capillary	unsat.	unsaturated
S.N.	system number (Beil-	unsym.	unsymmetrical
	stein)	U.S.P.	United States Pharma-
spar.	sparing; sparingly		copœia
sol.(n)(y)	soluble (solution) (solu-	u.v.	ultra violet
	bility)		
solv.	solvent(s)		v
sp.gr.	specific gravity	770.0	
sq.	square	vac. vap.	vacuum vapor; vaporize
subl.(g)	sublimes; sublimate;	vap. var.	vapor, vaporize variable
	subliming; sublima-	vic.	variable vicinal (adjacent)
	tion	vig.	vigorous; vigorously
subl. w.m.	sublimes without melt-	viol.	violent; violently; vio-
	ing	7-02.	let
subseq.	subsequent	visc.	viscous
subst.	substance; substanti-	volat.(g) (n)	volatile (volatilizing)
suff.	ally; substituted		(volatilization)
sun. supersat. $(d)(g)(n)$	suffices; sufficient supersaturate(d)(super-	volumin.	voluminous
arbergar.(g)(R)(H)	saturating) (super-		
	saturation)		***
st.	steam		W
s.t.	sealed tube	warm.	warming
stdg.	standing	wh.	white
sym.	symmetrical	wt.	weight
81/n-	stereochemical opposite		-
- 	of anti-		77
syst.	system; systematic;		Y
•	systematically	yel.	yellow

	•		

MEMORANDUM OF CERTAIN 1946-1947 REFERENCES NOT INCORPORATED IN REGULAR TEXT

The regular text of this book is made up of references selected from the chemical literature through the year 1945. Owing to the disturbed postwar conditions of the publishing and printing trades, and also to the exceptional difficulty and magnitude of this work, almost three years have elapsed since the termination of the period of writing of the organized text. Inevitably, there have appeared during this period many scientific papers whose content would gladly have been incorporated appropriately in the regular text. For practical reasons, however, such continuous adjustment was obviously impossible.

In an effort to avoid so far as possible complete loss of such material, however, certain of the more important papers which have come to the attention of the author during the 1946–1947 period have been listed in the following supplementary bibliography. Articles relevant to more than a single numbered compound are cited under the first in such a numerical series, cross-references being given under subsequent compounds to avoid excess duplication of references. In the interests of brevity, clarity, and consistency of nomenclature, slight modifications of the actual titles of the original papers have sometimes been made for purposes of this listing.

General

(1) Table of azeotropes and nonazeotropes

Horsley, Ind. Eng. Chem., Anal. Ed. 19, 508-600 (1947)

This extraordinary 92-page compilation with its accompanying formula index and bibliography of 172 references is so generally valuable and includes so many of the serially numbered compounds of this book that it is placed at the head of this supplementary reference list without further cross-reference to it from subsequent entries below.

3:0075 δ-Chloro-n-valeric acid

(2) Isomeric chlorinated long-chain esters

Guest, J. Am. Chem. Soc. 69, 300-302 (1947)

—Methyl δ -chloro-n-valerate: b.p. 89–92° at 18 mm. [From δ -chloro-n-valeronitrile 80% H_2SO_4 refluxed 50 hr.]

3:0235 α-Chloroisobutyric acid

(3) The chloro- and bromoisobutyronitriles

Stevens. J. Am. Chem. Soc. 70, 166 (1948)

 \bigcirc α -Chloroisobutyramide: cryst. from EtOAc, m.p. 115–118°; from aq., m.p. 117–119°. [From α -chloroisobutyryl chloride (3:5385) with conc. NH₄OH at 10° in 70% yield.]

3:0280 Chloromaleic anhydride

(4) Use of C in determination of conjugated diolefins

Putnam, Moss, Hall, Ind. Eng. Chem., Anal. Ed. 18, 628-630 (1946)

3:0460 8-Chloropropionic acid

(5) Convenient synthesis of β -chloropropionitrile (from acrylonitrile with hydrogen chloride) Stewart, Clark, J. Am. Chem. Soc. 69, 713-714 (1947)

3:0885 α-Chloro-diphenylacetyl chloride

C as reagent for preparation of benzilic acid esters of tertiary amino alcohols (6) King, Holmes, J. Chem. Soc. 1947, 164-168; C.A. 41, 5121 (1947)

3:1150 Trichloroacetic acid

(7) Kinetics of the decomposition of certain salts of \overline{C} in ethanol-water mixtures Hall, Verhoek, J. Am. Chem. Soc. 69, 613-616 (1947)

(8) Kinetics of the decomposition of $\overline{\mathbf{C}}$ in formamide-water mixtures Cochran, Verhoek, J. Am. Chem. Soc. 69, 2987-2988 (1947)

3:1212 Phenacyl chloride

(9) The reaction of C with phenylhydrazine van Alphen, Rec. trav. chim. 65, 112-116 (1946); C.A. 41, 409 (1947)

3:1370 Chloroacetic acid

(10) New method for the detection and determination of C (using pyridine) Ramsey, Patterson, J. Assoc. Offic. Agr. Chemists 29, 100-111 (1946); C.A. 40, 3369

(11) Effect of pH on rate of hydrolysis of C Berhenke, Britton, Ind. Eng. Chem. 38, 544-546 (1946)

3:1420 1,1,1-Trichloro-2,2-diphenylethane

(12) Derivatives of C

Haskelberg, Lavie, J. Am. Chem. Soc. 69, 2267-2268 (1947)

(13) Symmetrical analogues of DDT Stephenson, Waters, J. Chem. Soc. 1946, 339-343; C.A. 40, 5040 (1946)

3:3298 1,1,1-Trichloro-2,2-bis-(p-chlorophenyl)ethane ("DDT")

(14) Methods of preparation of C

Bailes, J. Chem. Education 22, 122 (1945); C.A. 41, 3085 (1947)

(15) Preparation of technical C

Mosher, Cannon, Conroy, Van Strien, Spalding, Ind. Eng. Chem. 38, 916-923 (1946) (16) Preparation of C using HF as condensing agent Simons, Bacon, Bradley, Cassaday, Heegberg, Tarrant, J. Am. Chem. Soc. 68, 1613-

1615 (1946) (17) Production of C

Castonguay, Ferm, Trans. Kansas Acad. Sci. 49, 167-174 (1946); C.A. 41, 2409 (1947)

(18) Synthesis of C with chlorosulfonic acid as condensing agent W. A. Cook, K. H. Cook, W. H. C. Rueggeberg, Ind. Eng. Chem. 39, 868-870, 1683 (1947)

(19) A colorimetric method for microdetermination of C (xanthydrol/KOH/pyridine method) Stiff, Castillo, Science 101, 440-443 (1945); C.A. 39, 2830 (1945)

Determination of C in organs and body fluids after oral administration (xanthydrol/-(20) KOH/pyridine method) Stiff, Castillo, J. Biol. Chem. 159, 545-548 (1945); C.A. 39, 4695 (1945)

(21) Application of xanthydrol/KOH/pyridine method to the determination of C in water Castillo, Stiff, Military Surgeon 97, 500-502 (1945); C.A. 40, 2561 (1946)

(22) Field test for surface C

Stiff, Castillo, Ind. Eng. Chem., Anal. Ed. 18, 316-317 (1946)

(23) Chemical methods for analysis of C

Ginsberg, J. Econ. Entomol. 39, 174-177 (1946); C.A. 40, 4842 (1946)

(24) Colorimetric determination of p,p'-isomer in technical C Charkin, Ind. Eng. Chem., Anal. Ed. 18, 272-273 (1946)

(25) Determination of p,p'-isomer in technical C

Cristol, Hayes, Haller, Ind. Eng. Chem., Anal. Ed. 18, 339 (1946)

(26) Determination of p,p'-isomer in technical C

Balaban, Calvert, Ind. Eng. Chem., Anal. Ed. 18, 339 (1946)

(27) Determination of p,p'-isomer in technical \bar{C} by a microscopical method McCrone, Smedal, Gilpin, Ind. Eng. Chem., Anal. Ed. 18, 578-582 (1946)

(28) Determination of C in dusts and oil solutions La Clair, Ind. Eng. Chem., Anal. Ed. 18, 763-766 (1946) (29) Determination of C as spray residue on fresh fruit by three independent methods Wichmann, Patterson, Clifford, Klein, Claborn, J. Assoc. Offic. Agr. Chemists 29, 188-190 (1946); C.A. 40, 6705 (1946)

Method 1. Organic chlorine determinations

Klein, Wichmann, ibid. 29, 191-195 (1946); C.A. 40, 6705 (1946)

Method 2. The Shechter-Haller colorimetric procedure Clifford, *ibid.* 29, 195-206 (1946); C.A. 40, 6705 (1946)

Method 3. 2,4-Dinitrophenylhydrazine method

Claborn, Patterson, ibid. 29, 206-218 (1946); C.A. 40, 6705 (1946)

(30) Decomposition and volatility of \(\bar{C}\) and some of its derivatives Wichmann, Patterson, Clifford, Klein, Claborn, J. Assoc. Offic. Agr. Chemists 29, 218-233 (1946); C.A. 40, 6740 (1946)

(31) Colorimetric determination of \(\bar{C}\) in milk and fatty materials Shechter, Pogorelskin, Haller, Ind. Eng. Chem., Anal. Ed. 19, 51-53 (1947)

(32) Estimation of \bar{C} in milk by determination of organic chlorine Carter, Ind. Eng. Chem., Anal. Ed. 19, 54 (1947)

(33) Determination of C by Shechter procedure, particularly in milk and fats Clifford, J. Assoc. Offic. Agr. Chemists 30, 337-349 (1947); C.A. 41, 6839 (1947)

(34) Nature of the by-products in technical C
Gätzi, Stammbach, Helv. Chim. Acta. 29, 563-572 (1946); Experientia 1, 276 (1945);
C.A. 40, 5040-5041 (1946)

(35) Simple purification procedure for C K. H. Cook, W. A. Cook, J. Am. Chem. Soc. 68, 1663-1664 (1946)

(36) Applications of infrared spectroscopy to C

Downing, Freed, Walker, Patterson, Ind. Eng. Chem., Anal. Ed. 18, 461-467 (1946) (37) Some derivatives of \overline{C}

Backeberg, Marais, J. Chem. Soc. 1945, 803-805; C.A. 40, 1156, 5717 (1946) (38) Bromine analogs of C

Cristol, Haller, J. Am. Chem. Soc. 68, 140-141 (1946)

(39) Crystal structure of C and relatives Wild, Brandenberger, Helv. Chim. Acta 29, 1024-1040 (1946); C.A. 41, 428 (1947)

(40) Synthesis of some analogs of C Kirkwood, Dacey, Can. J. Research 24-B, 69-72 (1946); C.A. 49, 5717 (1946)

(41) Catalytic decomposition of C Flenner, J. Am. Chem. Soc. 68, 2399 (1946)

(42) Inhibition of catalyzed thermal decomposition of C Gunther, Tow, J. Soc. Chem. Ind. 66, 57-59 (1947); C.A. 41, 5675 (1947)

(43) Dehydrohalogenation of C

Wain, Martin, Nature 159, 68-69 (1947); C.A. 41, 2715 (1947)

(44) Estimation of \overline{C} by methods depending upon dehydrohalogenation Wain, Martin, Analyst 72, 1-6 (1947); C.A. 41, 2198 (1947)

(45) Preparation of di-(p-chlorophenyl)acetic acid from C Grummitt. Buck. Egan. Org. Syntheses 26, 21-23 (1946)

(46) Reactions of C and associated compounds

Forrest, Stephenson, Waters, J. Chem. Soc. 1946, 333-339; C.A. 49, 5038-5040 (1946)

(47) Crystallization of C from binary melts Gilpin, McCrone, Smedal, Grant, J. Am. Chem. Soc. 70, 208-211 (1947)

3:3320 1.1-Dichloro-2.2-bis-(p-chlorophenyl)ethane ("DDD")

(48) Anhydrous FeCl₃ as rearrangement catalyst for some chlorinated diphenylethanes Fleck, J. Org. Chem. 12, 708-712 (1947)

8:3380 4,6-Dichlororesorcinol

(49) For preparation of isomeric 2,4-dichlororesorcinol see Pectynin, Kuchina, J. Gen. Chem. (U.S.S.R.) 17, 278-282 (1947); C.A. 42, 534-535 (1948)

3:3934 p-Phenylphenacyl chloride

(50) Conversion of C to p-phenylphenacyl iodide Rheinboldt, Perrier, J. Am. Chem. Soc. 69, 3148-3149 (1947)

3:4695 2,4-Dichlorophenoxyacetic acid

(51) Preparation of C from phenol and chloroacetic acid Ebel, Bell, Fries, Kasey, Berkebile, J. Chem. Education 24, 449 (1947)

- (52) Determination of C and its compounds in commercial herbicides Rooney, Ind. Eng. Chem., Anal. Ed. 19, 475-476 (1947)
- (53) The halogenation of aryloxyacetic acids and their homologs Haskelberg, J. Org. Chem. 12, 426-433 (1947)

(54) Preparation of 2,4-dichlorophenoxyacetyl chloride Freed, J. Am. Chem. Soc. 68, 2112 (1946)

3:4375 p-Chlorophenoxyacetic acid

(-) See reference (53) under 3:4095 (above).

3:4410 cis-1,2,3,4,5,6-Hexachlorocyclohexane

(55) Preparation of the benzene hexachlorides

Gunther, Chemistry & Industry 1946, 399; C.A. 41, 1625 (1947)

(56) Infrared spectroscopic analysis of five isomers of C Dassch, Ind. Eng. Chem., Anal. Ed. 19, 779-785 (1947)

(57) Kinetics of the alkaline dehydrochlorination of the benzene hexachloride isomers Cristol, J. Am. Chem. Soc. 69, 338-342 (1947)

(58) Alkaline degradation of benzene hexachlorides Gunther, Blinn, J. Am. Chem. Soc. 69, 1215-1216 (1947)

(59) The gamma isomer of hexachlorocyclohexane

Slade, Chemistry & Industry 1945, 314-319; C.A. 40, 2257-2259 (1946)

(60) The epsilon isomer of hexachlorocyclohexane

Kauer, DuVall, Alquist, Ind. Eng. Chem. 39, 1334-1338 (1947)

(61) Determination of hexachlorocyclohexane is impregnated cloth Goldenson, Sass, Ind. Eng. Chem., Anal. Ed. 19, 320-322 (1947)

3:4612 Di-(p-chlorophenyl)acetic acid

(--) Preparation from "DDT"; see reference (45) under 3:3298 (above)

3:4835 Hexachloroethane

(62) Preparation of C by chlorination of liquid 1,1,2,2-tetrachloroethane and pentachloroethane Pearce, Can. J. Research 24-F, 369-379 (1946); C.A. 40, 7151 (1940)

3:4947 Tetrachlorophthalic anhydride

(63) Reactions and uses of C

Lawlor, Ind. Eng. Chem. 39, 1419-1423 (1947)

(64) Tetrachlorophthalic anhydride, acid and salts Lawlor, Ind. Eng. Chem. 39, 1424-1426 (1947)

(65) The esterification of C Nordlander, Cass, J. Am. Chem. Soc. 69, 2679-2682 (1947)

3:4990 trans-1,2,3,4,5,6-Hexachlorocyclohexane

(-) See references (55)-(61), inclusive, under cis-isomer (3:4410) (above)

3:5000 Carbonyl chloride (Phosgene)

(66) Heat capacity, entropy, vapor pressure, and heats of fusion and vaporization of C Giaque, Jones, J. Am. Chem. Soc. 70, 120-124 (1948)

(67) Preparation of benzoic acid from C with benzene Rueggeberg, Frantz, Ginsburg, Ind. Eng. Chem. 38, 624-626 (1946)

(68) Reaction of C with tertiary amines under conditions for formation of tetrasubstituted ureas

Lastovskii, J. Applied Chem. (U.S.S.R.) 19, 440-444 (1946); C.A. 41, 1214 (1947)

(69) Reaction of C with o-aminobenzoic acid (to give 72-75% yield isatoic anhydride) Wagner, Fegley, Org. Syntheses 27, 45-47 (1947)

3:5028 trans-1,2-Dichloroethylene

(70) Condensation of alkyl chlorides with polychloro-olefins Schmerling, J. Am. Chem. Soc. 68, 1655-1657 (1946)

(71) Reaction of C with isobutane Schmerling, J. Am. Chem. Soc. 70, 379-381 (1948)

3:5042 cis-1,2-Dichloroethylene

(-) See references (70) and (71) under trans-isomer (3:5028) (above)

3:5050 Chloroform

(72) The addition of polyhalomethanes to olefins

Kharasch, Jensen, Urry, J. Am. Chem. Soc. 69, 1100-1105 (1947)

(73) Compound formation of C with pyridine Davidson, Van der Werf, Boatright, J. Am. Chem. Soc. 69, 3045-3047 (1947)

3:5100 Carbon tetrachloride

- See references (72) and (73) under chloroform (3:5050) (above)
- (74) Analysis of the system benzene/ethanol/carbon tetrachloride (by refractive indices and densities) Campbell, Miller, Can. J. Research 25-B, No. 3, 228-242 (1947); C.A. 41, 6839 (1947)

3:5110 1,2-Dichloropropene-1 (low-boiling stereoisomer)

(-) See reference (70) under 3:5028 (above)

3:5130 1.2-Dichloroethane

(75) Reaction of C with benzene

Korshak, Kolesnikov, Kharchevnikova, Compt. rend. acad. sci. U.R.S.S. 56, 169-172 (1947); C.A. 42, 545 (1948)

3:5150 1,2-Dichloropropene-1 (high-boiling stereoisomer)

(—) See reference (70) under 3:5028 (above)

3:5170 1,1,2-Trichloroethylene

See reference (70) under 3:5028 (above) (---)

(76)Dimerization of C

Henne, Ruh, J. Am. Chem. Soc. 69, 279-281 (1947)

3:5190 2.3-Dichloropropene-1

(—) See reference (70) under 3:5028 (above)

3:5210 Trichloroacetaldehyde

(77) Determination of C in technical chloral

Harrington, Boyd, Cherry, Analyst 71, 97-107 (1946); C.A. 40, 3368 (1946)

(78)Determination of small amounts of water in C

Shaw, Bruce, Ind. Eng. Chem., Anal. Ed. 19, 884-885 (1947) (79) Hydrolysis of C in heavy hydrogen water

Lander, Wright, Nature 158, 381 (1946); C.A. 41, 1998 (1947)

3:5220 2,3-Dichlorobutadiene-1,3

(80) Preparation of C from tri-, tetra-, and pentachlorobutanes Klebanskii, Belen'kaya, Chevychalova, J. Applied Chem. (U.S.S.R.) 19, 200-206 (1946); C.A. 41, 685 (1947)

(—) See reference (85) under 3:5350 (below)

3:5280 1.3-Dichloropropene-1

(81) The cis- and trans-isomers of C

Andrews, Kepner, J. Am. Chem. Soc. 69, 2230-2231 (1947)

(82)The catalytic hydrolysis and characterization of C

Hatch, Roberts, J. Am. Chem. Soc. 68, 1196-1198 (1946)

(—) See reference (70) under 3:5028 (above)

3:5330 1,1,2-Trichloroethane

Ternary liquid and binary vapor equilibrium of the system: acetone/water/C (83)Treybal, Weber, Daley, Ind. Eng. Chem. 38, 817-821 (1946)

3:5350 3,4-Dichlorobutene-1

Preparation of C from butadiene-1,3 with chlorine (84)

Taylor, Morey, Ind. Eng. Chem. 40, 432-435 (1948)

Dehydrochlorination of C to 2-chlorobutadiene-1,3 (85) Klebanskii, Sorokina, Khavin, J. Gen. Chem. (U.S.S.R.) 17, 235-252 (1947); C.A. 42, 514-516 (1948)

3-Chloro-1,2-epoxypropane ("Epichlorohydrin") 3:5358

Condensation of C with phenols in presence of BF3

E. Levas, H. LeFebvre, Compt. rend. 222, 555-557 (1946); C.A. 40, 3737 (1946) H. LeFebvre, E. Levas, Mme. E. Levas, Compt. rend. 222, 1439-1440 (1946); C.A. 40, 5712 (1946)

3:5425 Chloroacetone

Condensation of C with formaldehyde (87)Hurd, McPhee, Morey, J. Am. Chem. Soc. 70, 329-331 (1948)

3:5430 a,a-Dichloroacetone

(-) See reference (87) under 3:5425 (above)

3:5550 1.3-Dichlorobutene-2

(88) Oxidation of C with aqueous HNO₂ or Ca(NO₂)₂ Isagulyants, Mkryan, Bull. Armenian Branch Acad. Sci. U.S.S.R., 1944, No. 5/6, 17-21; C.A. 40, 3402 (1946)

[69] Preparation of bis-(3-chlorocrotyl)barbituric acid from C Tatevosyan, Tuteryan, Bull. Armenian Branch Acad. Sci. U.S.S.R., 1944, No. 5/6, 29-35; C.A. 40, 3404 (1946)

(90) Gaseous products of action of zinc dust on C Tatevosyan, Vardanyan, Bull. Armenian Branch Acad. Sci. U.S.S.R., 1941, No. 8, 75-78; C.A. 49, 3394 (1946)

(91) Reaction of C with aromatic hydrocarbons Isagulyants, Muscheghian, Compt. rend. acad. sci. U.R.S.S. 56, 165-168 (1947); C.A. 42, 530 (1948)

3:5552 2-Chloroethanol-1 (ethylene chlorohydrin)

(92) Determination of C (by hydrolysis and determination of chloride ion) Uhrig, Ind. Eng. Chem., Anal. Ed. 18, 469 (1946)

(93) Preparation and properties of β-chloroethyl esters of boric, silicic, and phosphoric acids Jones, Thomas, Pritchard, Bowden, J. Chem. Soc. 1946, 824-827; C.A. 41, 390-391 (1947)

(94) Analysis of water-soluble chlorohydrins Trafelet. Analytical Chemistry 20, 68-69 (1948)

3:5590 1.3-Dichloro-2-methylpropene-1

(95) Preparation of cis and trans isomers of C Hatch, Russ, Gordon, J. Am. Chem. Soc. 69, 2614-2616 (1947)

3:5633 3-Chloro-2-(chloromethyl)propene-1

(-) See reference (95) under 3:5590 (above)

3:5725 1,4-Dichlorobutene-2

(—) Preparation of C from butadiene-1,3 with chlorine See reference (84) under 3:5350 (above)

(—) Dehydrochlorination of C to 2-chlorobutadiene-1,3 See reference (85) under 3:5350 (above)

3:5750 1.1.2.2-Tetrachloroethane (acetylene tetrachloride)

(96) Liquid-vapor and liquid-liquid equilibrium of systems containing isobutyl alcohol and C Fritzsche, Stockton, Ind. Eng. Chem. 38, 737-740 (1946)

(97) Determination of \(\overline{\overline{C}}\) in air Goldenson, Thomas, J. Ind. Hyg. Toxicol. 29, 14-22 (1947); C.A. 41, 1578 (1947)

(—) Chlorination of C as source of hexachloroethane See reference (62) under 3:4835 (above)

3:5880 Pentachloroethane

(—) Chlorination of \overline{C} as source of hexachloroethane See reference (62) under 3:4835 (above)

3:5885 1,2,3-Trichloro-2-methylpropane

(-) See reference (95) under 3:5590 (above)

3:5900 1.3-Dichlorobutanone-2

(98) Formation of C̄ from ethyl methyl ketone by vapor-phase chlorination Rabjohn, Rogier, J. Org. Chem. 11, 781-787 (1946)

3:5910 α,α,β -Trichloro-n-butyraldehyde ("Butyrchloral")

(99) Reaction of C with Grignard reagents Floutz, J. Am. Chem. Soc. 68, 2490-2491 (1946)

3:5960 m-Dichlorobenzene

(100) Synthesis of 2,4-dichloropropiophenone Sheehan, J. Am. Chem. Soc. 68, 1672 (1946)

3:5985 1,3-Dichloropropanol-2 ("\alpha-dichlorohydrin")

(101) Activated C; a new colorimetric reagent for vitamin A Sobel, Werbin, Ind. Eng. Chem., Anal. Ed. 18, 570-573 (1946)

(102) Determination of vitamin A with activated C: a comparison with spectrophotometric and SbCl₃ methods Sobel, Werbin, Ind. Eng. Chem., Anal. Ed. 19, 107-112 (1947)

```
xxiii
```

3:6297 Ethyl α -chloroacetate

(103) Behavior of C with arythydrazines

van Alphen, Rec. trav. chim. 64, 305-308 (1945); C.A. 41, 407 (1947)

3:6550 p-Chlorobenzoyl chloride

(104) Conversion of C with pyridine to p-chlorobenzoic acid Allen, Kibler, McLachlin, Wilson, Org. Syntheses 26, 1-3 (1946)

3:6878 1-Chloronaphthalene

(105) 1-Halonaphthalenes in the Friedel-Crafts reaction Jacobs, Winstein, Ralls, Robson, J. Org. Chem. 11, 27-33 (1946)

3:7005 Methyl chloride

(106) Determination of C in air

Franklin, Gunn, Martin, Ind. Eng. Chem., Anal. Ed. 18, 314-316 (1946)

(107) Preparation of C (free from dimethyl ether) Pieck, Courtoy, Bull. soc. chim. Belg. 56, 65-71 (1947); C.A. 41, 6524 (1947)

3:7010 Vinyl chloride

(108) Condensation of alkyl halides with monohalo-olefins Schmerling, J. Am. Chem. Soc. 68, 1650-1654 (1946)

3:7015 Ethyl chloride

(-) See reference (70) under 3:5028 (above)

3:7020 2-Chloropropene-1

(-) See reference (108) under 3:7010 (above)

3:7025 2-Chloropropane (isopropyl chloride)

-) See reference (70) under 3:5028 (above)

(—) See reference (108) under 3:7010 (above)

3:7035 3-Chloropropene-1 (allyl chloride)

(109) Commercial-scale manufacture of \(\overline{\overline{C}}\) and of allyl alcohol from propylene Fairbairn, Cheney, Cherniavsky, Chem. Eng. Progress 43, No. 6; Trans. Am. Inst. Chem. Engrs. 280-290 (1947); C.A. 41, 5090 (1947)

(110) Conversion of C with Mg to hexadiene-1,5 (biallyl) in 55-65% yield Turk, Chanan, Org. Syntheses 27, 7-9 (1947)

(111) Condensation of C with aromatic hydrocarbons or aryl halides to give 1-aryl-2-chloro-propanes

Patrick, McBee, Hass, J. Am. Chem. Soc. 68, 1009-1011 (1946)

(—) See reference (108) under 3:7010 (above)

3:7040 1-Chloropropane (n-propyl chloride)

(-) See reference (70) under 3:5028 (above)

3:7045 2-Chloro-2-methylpropane (ter-butyl chloride)

(--) See reference (70) under 3:5028 (above)

(—) See reference (108) under 3:7010 (above)

(112) The AlCl₃-catalyzed addition of C to propylene Miller, J. Am. Chem. Soc. 69, 1764-1768 (1947)

(113) The condensation of \(\bar{C}\) with cyclohexene Schmerling, J. Am. Chem. Soc. 69, 1121-1125 (1947)

(114) Formation of C by addition of hydrogen chloride to isobutylene Mayo, Katz, J. Am. Chem. Soc. 69, 1339-1348 (1947)

(115) The hydrolysis of C in 95% water/5% acetone solution Swain, Ross, J. Am. Chem. Soc. 68, 658-661 (1946)

3:7065 Acetyl chloride

(116) Ketene dimers from acid halides Sauer, J. Am. Chem. Soc. 69, 2444-2448 (1947)

3:7080 2-Chlorobutadiene-1,3 (Chloroprene)

(—) See reference (85) under 3:5350 (above)

(117) Composition and structure of dimers of C Klebanskii, Denisova, J. Gen. Chem. (U.S.S.R.) 17, 703-716 (1947); C.A. 42, 1215 (1948)

3:7085 Chloromethyl methyl ether

(118) Reaction of C with terpenes

Allard, Bull. soc. chim. France 1947, 731-735; C.A. 42, 890 (1948)

3:7170 Propionyl chloride See reference (100) under 3:5960 (above) (-) See reference (116) under 3:7065 (above) 3:7210 1-Chlorobutadiene-1.3 (119) Synthesis and properties of C Petrov, Sopov, J. Gen. Chem. (U.S.S.R.) 15, 981-987 (1945); C.A. 40, 6406 (1945) (-) See reference (85) under 3:5350 (above) 3:7220 2-Chloro-2-methylbutane (ter-amyl chloride) (—) See reference (108) under 3:7010 (above) 3:7370 n-Butvrvl chloride (—) See reference (116) under 3:7065 (above) 3:7465 4-Chloro-2-methylbutene-2 (120) Formation of C from isoprene by addition of HCl Jones, Chorley, J. Chem. Soc. 1946, 832-833; C.A. 41, 386 (1947) 3:7560 Isovaleryl chloride (--) See reference (116) under 3:7065 (above) 3:7598 3-Chlorobutanone-2 (—) See reference (98) under 3:5900 (above) 3: 7650 1.3-Dichlorobutene-1 The dichlorobutene prepared from crotonaldehyde (121)Andrews, J. Am. Chem. Soc. 68, 2584-2587 (1946) 3:7865 1.1-Dichlorobutene-2 (--) See reference (121) under 3:7650 (above) 3:7740 n-Valeryl chloride (—) See reference (116) under 3:7065 (above) 3:7747 1-Chloropropanol-2 (propylene chlorohydrin) (—) See reference (94) under 3:5552 (above) 3:7925 1.3-Dichlorobutane Preparation of C and its Friedel-Crafts reaction with benzene (122)Sisido, Nozaki, J. Am. Chem. Soc. 69, 961-964 (1947) 3:8012 1-Chlorobutanone-2 (--) See reference (98) under 3:5900 (above) 3:8110 d.l-1-Chlorobuten-3-ol-2 Some reactions of C (123)Bissinger, Fredenburg, Kadesch, Kung, Langston, Stevens, Strain, J. Am. Chem. Soc. **69.** 2955-2961 (1947) 3:8168 n-Caproyl chloride (—) See reference (116) under 3:7065 (above) 3:8520 n-Heptanoyl chloride Conversion of \bar{C} to n-heptanoic anhydride with pyridine (124)Allen, Kibler, McLachlin, Wilson, Org. Syntheses 26, 1-3 (1946) 3:8535 Benzyl chloride (125)Use of C in production of henzyl benzoate Tharp, Nottorf, Herr, Hoover, Wagner, Weissgerber, Wilkins, Whitmore, Ind. Eng. Chem. 39, 1300-1302 (1947) (126) Reaction of \overline{C} with hexamethylenetetramine in preparation of benzylamines Graymore, J. Chem. Soc. 1947, 1116-1118 (127) Rearrangement in the reaction between benzyl magnesium chloride and diethyl sulfate Burtle, Shriner, J. Am. Chem. Soc. 69, 2059-2060 (1947) 3:8680 n-Octanoyl chloride (-) See reference (116) under 3:7065 (above) 3:9132 8-Chloroisobutyric acid

 $-\beta$ -Chloro-isobutyramide: cryst. from pet. ether/EtOAc, m.p. 102-104°. [From β -chloroisobutyronitrile by partial hydrolysis with H₂SO₄: see reference (3) under

3:0235 (above),]

1946-1947 REFERENCES NOT INCORPORATED IN TEXT

3:9295 5-Chloropentanol-1

xxv

(128) The preparation of 5-diethylaminopentanol-1

— 5-Chloro-n-amyl benzoate: b.p. $141-143^{\circ}$ at 2 mm., $D_{20}^{20}=1.109$, $n_{D}^{20}=1.5169$; [from tetrahydropyran with benzoyl chloride + ZnCl₂ (85% yield)]

Synerholm, J. Am. Chem. Soc. **69**, 2581 (1947)

3:9395 6-Chlorohexanol-1

(129) Preparation of C and its reactions with amines K. N. Campbell, A. H. Sommers, J. F. Kerwin, B. K. Campbell, J. Am. Chem. Soc. 68, 1557 (1946)

3:9567 Phenylacetyl chloride

(130) Friedel-Crafts reactions of \overline{C} with anthracene, phenanthrene, or pyrene Hoi, Royer, Bull. soc. chim. 1946, 659-661; C.A. 41, 3453 (1947)

3:9858 n-Dodecanoyl chloride (lauroyl chloride)

(131) Preparation of C

Ackley, Tesoro, Ind. Eng. Chem. 18, 444-445 (1946)

(—) See reference (116) under 3:7065 (above)

3:9865 1,1,1-Trichloro-2,2-bis-(o-chlorophenyl)ethane ("o,o'-DDT")

(132) Preparation of C

Gätzi, Helv. Chim. Acta 29, 1159-1163 (1946); C.A. 41, 114-115 (1947)

(133) Isolation of C from technical DDT

Cristol, Soloway, Haller, J. Am. Chem. Soc. 69, 510-515 (1947)

3:9885 n-Tetradecanoyl chloride (n-myristoyl chloride)

(—) See reference (116) under 3:7065 (above)

3:9960 n-Octadecanoyl chloride (n-stearoyl chloride)

(—) See reference (116) under 3:7065 (above)



CHAPTER I

INTRODUCTION

1.	The scope of this book	1
2.	The matter of suborders	2
3.	The arrangement of compounds of Order 3 into divisions	2
4.	The sequence of compounds within the three divisions Division A Division B	
	Division C	3
5.	The arrangement of data on individual compounds	4
	A. The heading	4
	B. The fundamental physical constants	7
	C. General data on other constants, preparation and properties	
	D. Preliminary tests	
	E. Derivatives	
	F. Literature references	
6.	Abbreviations	
	Indexes	
•	A. The empirical formula index	
	B. Index of empirical formulas by percentage chlorine content	
	C. Index of empirical formulas by molecular weights	
	D. Index of compounds by chemical types	
	E. Alphabetical name index	19

1. The scope of this book

Systematic classification of organic compounds may be effected in many different ways, each having certain advantages and disadvantages. Although the scope of this present book, by including the aspects of preparation, physical properties, and general chemical behavior as well as identification, is very much broader than that of its precursor, yet the advantages inherent in the general form of classification there employed have led to its extension to the present book.

According to this arrangement, all organic chemical compounds are first classified by orders. The order of a compound is established by its qualitative elementary composition; compounds containing the same elements belong to the same order. Thus, Order 1 is defined as comprising compounds of carbon with hydrogen, or of carbon with both hydrogen and oxygen; this order was treated in the above-mentioned volume. When other elements

¹Identification of Organic Compounds; Tables of Data on Selected Compounds of Order 1, by Ernest Hamlin Huntress and Samuel Parsons Mulliken, John Wiley & Sons, New York, xvii + 691 pages, 1941.

are also present, a compound is said to belong to a higher order: e.g., compounds of carbon with both hydrogen and nitrogen, with oxygen and nitrogen, or with hydrogen, oxygen, and nitrogen comprise Order 2. A systematic arrangement of still higher orders has been developed but need not be fully amplified here.

The substance of the present volume is concerned primarily with compounds of Order 3, i.e., with compounds containing carbon and chlorine; carbon, oxygen, and chlorine; carbon, hydrogen, and chlorine; carbon, hydrogen, and chlorine. To all such compounds deemed of sufficiently general interest to warrant detailed treatment in this book, serial numbers have been assigned as later explained. Although such serial numbers are thus restricted to species of Order 3, a vast number of compounds belonging to other orders inevitably occurs in the course of the individual texts so that this volume has far wider utility than might at first glance be supposed. At the same time not all substances belonging to Order 3 are given numbers since many are not of sufficient value to warrant such extensive treatment.

2. The matter of suborders

In the general plan of ordinal classification, it is sometimes (but not always) useful to effect subdivision of orders into two suborders according to whether or not the pure compounds are colored. For both Orders 1 and 2, such subordering has special merit. For the present Order 3 compounds, however, the proportion of colored individuals is almost negligible, and employment of suborders has been avoided.

3. The arrangement of compounds of Order 3 into divisons

Just as the individual compounds of Order 1 were ultimately further subclassified into various *genera*, each characterized by a common behavior in certain prescribed and carefully defined *generic tests*, so it would of course be perfectly possible to set up an analogous series of genera for any or all of the higher orders. After considerable reflection and experimentation, however, such extension of the method of generic subclassification has seemed an extravagant formality whose added value for the higher orders does not warrant its establishment. Consequently, the individuals comprising the present Order 3 are not arranged by genera, and there are no standardized generic tests to be systematically applied.

Instead of arrangement by genera, therefore, the compounds assigned serial numbers in this book are arranged in three divisions. The first of these divisions comprises members of Order 3 which, when pure, are normally solids with at least reasonably definite melting points. The second comprises members of Order 3 which, when pure, are liquids with boiling points attainable and recorded at ordinary pressure. The third division comprises

members of Order 3 which, even when pure, are liquids which either cannot be distilled at atmospheric pressure without serious decomposition or for which such data are available only under reduced pressure. Ample cross-references connecting the solid and liquid divisions facilitate recognition of appropriate cases.

4. The sequence of compounds within the three divisions

DIVISION A. The individual solids constituting Division A are arranged in the order of increasing magnitude of their respective melting points. For compounds on which there is poor agreement regarding the true melting point, the value determining the position of the compound relative to its neighbors is not necessarily the highest listed. Values printed within square brackets have been regarded by the author on the collateral evidence as possibly doubtful, and such constants have been discounted in assigning positional sequence to the compound.

Division B. This division, comprising liquids of Order 3 with boiling points at ordinary pressure, is (unlike either its predecessor or successor) further subdivided into two sections according to the specific gravity at 20° C. referred to water at 4° C. Section 1 contains such liquids with values of D_4^{20} greater than 1.15; Section 2 contains correspondingly those liquids for which the value of D_4^{20} is less than 1.15. Within each of the sections of Division B the individual species are arranged in the order of increasing magnitude of their respective boiling points, preferably at 760 mm. pressure. For compounds whose boiling points at this standard pressure are unreported, no attempt has been made to calculate over since to do so seems likely to introduce serious uncertainties.

Division C. This division contains all serially numbered compounds of Order 3 which have not been allocated to either of the preceding divisions, such cases usually comprising liquids for which boiling points are reported only at reduced pressures. Within this division an entirely different method of establishing the listing sequence is employed; viz., the compounds are listed in ascending sequence according to the composition of their empirical formulas. For any given number of carbon atoms, compounds containing carbon and chlorine, or carbon, oxygen, and chlorine, or carbon, hydrogen, and chlorine fall in that sequence. Within any one of these four subgroups the sequence is determined by increasing magnitude of the number of component atoms in the sequence (as above) of carbon, hydrogen, oxygen, and chlorine. Although expressed in words this sounds formidable, even casual inspection of the Tables or of the Empirical Formula Index quickly supplies convincing evidence of its complete simplicity in actual practice.

5. The arrangement of data on individual compounds

Whether the amount of data for the compounds comprising this volume is large or small, and irrespective of numerous variations of details, a certain standard form may be recognized as common to all. This form may be construed as made up of the following five elements:

- A. The heading.
- B. Fundamental physical constants.
- C. General data on other constants, preparation and properties.
- D. Designation of special or preliminary tests.
- E. Derivatives.
- F. References to the original literature.

The relative amount of space devoted to these five aspects varies according to circumstances. Each is discussed below in much further detail.

A. The heading

The heading of each numbered compound comprises (in its most general form) five components which always occur in the following sequence from left to right, viz.,

- 1. Location number 2. Name 3. Structural 4. Empirical 5. Beilstein of compound in (or formula formula reference this book (Order 3) names)
- (1) The location number. Each compound on which detailed treatment is given in this book has been assigned an arbitrary number to facilitate frequent cross reference in indexes and other parts of the text. This number consists of a digit representing the order of the compound (thus all species of this volume have location numbers beginning with 3), followed by a colon and then a four-digit arbitrary number. The system is, therefore, entirely comparable to a telephone number, the initial digit preceding the colon corresponding to an exchange, the four following digits corresponding to an individual line.

In assigning serial location numbers to the various individuals treated in this book, a principle has been maintained whose recognition greatly facilitates recognition of the physical nature of the corresponding substances. All members of Division 1 (solids) carry numbers between 1 and 4999; all members of Division 2, Section 1, are between 5000 and 6999; all members of Division 2, Section 2, are between 7000 and 8999; all members of Division 3 are between 9000 and 9999.

For a given compound, the full descriptive data are recorded only in one place, i.e., in that corresponding to the location number. When occasion

arises to be reminded in some other portion of the book of certain properties of a given compound, the *heading only* is repeated followed by a cross reference to the place of detailed description, the section usually occupied by the location number being indicated merely by a dash. The most frequent occasion for this type of cross reference is to indicate the boiling point of a compound normally met with as a solid, or alternatively the melting point of a substance normally met as a liquid.

(2) The name (or names) of the compound. The second element of the heading is devoted to the name (or names) of the compound. Out of all possible names, one (regarded for the purposes of this book as the "principal name") has been printed in bold-face capitals.

In many instances, however, this principal name is followed in ordinary type by one or more other names which are in common use and which might occur alternatively to users of this volume. All these names are appropriately entered in the alphabetical name index so that the location number is readily obtained irrespective of which name may be sought by the user.

(3) The structural formula of the compound. Since it is frequently easier to interpret the chemical reactions of a compound by contemplation of its structural formula rather than its name, such structural pictures are given for all compounds in this volume.

If a particular compound reacts as if it had two different structures, both are pictured.

Although such structural formulations are construed as the third element of the heading of each compound, it may happen that, owing to practical space considerations, the picture is not actually printed as part of the top line but depressed somewhat below it.

- (4) The empirical formula. The fourth element of the heading is the empirical formula. This will be found useful in many ways, particularly in suggesting (especially with the amplification afforded by the empirical formula index) isomeric compounds from which distinction must be made, and in searching the abstract periodicals for data reported after the publication of this volume.
- (5) The Beilstein reference. Each compound listed in these Tables carries in the upper right-hand corner as the fifth element of the heading reference to Beilstein's Handbuch der organischen Chemie. All such references designate the fourth edition of this important tool.

At the time of preparation of these Tables, all twenty-seven volumes of the primary series (covering the literature up to 1910) together with the corresponding twenty-seven volumes of the first supplementary series (1910–1919, inclusive) of Beilstein's Handbuch were available. For every numbered compound of these Tables which appears in either the main or first supple-

mentary series, the Beilstein reference will comprise two parts, the first giving the volume and page in the main series, the second giving corresponding reference to the first supplementary series. To distinguish the latter, the volume reference carries the subscript 1, and the page reference is placed between parentheses to indicate that the regular pagination of such supplementary volume is designated.

In addition to the main and first supplementary series of Beilstein mentioned above, there were also available during the preparation of these *Tables* the first five volumes of the second supplementary series (1920–1929) of Beilstein's *Handbuch*. For such of the present numbered compounds as were treated in this available fragment, the Beilstein reference will, therefore, contain a third element representing the volume and page involved. For this kind of case the volume reference bears the subscript 2 (to indicate second supplementary series) together with the page reference in parentheses as before.

In accordance with the above explanation, a given compound will have either two or three Beilstein references. It is, of course, possible for a compound to have citation to only one or two out of the three maximum possibilities; absence of any data for a particular Beilstein unit is indicated by short dashes after the volume number.

The remaining possible case is that in which the compound in question is of such recent origin that Beilstein contains no reference to it either in the main section or either supplementary series. Many such compounds occur in this Order 3. Under these circumstances the usual Beilstein citation is replaced by the Beilstein System Number of the compound, e.g., Beil. S.N. 644. Such type of reference immediately indicates that no reference to the substance is contained in any Beilstein issues through Vol. V of the second supplementary series. Whenever third, fourth, or later supplementary series become available, however, this system number will indicate the position of the compound within narrow limits, even though volume and page cannot now be predicted.

The practice of giving all three Beilstein citations wherever possible serves as a continual reminder that to look merely in the main series volume of Beilstein yields material only up to 1910; for the next two decades the corresponding first and second supplements must also be examined. In this respect these *Tables of Order 3* extend the practice of those of Order 1, where only the main series citation was made, extension to the first supplement being left to the user.

That these references to Beilstein's *Handbuch* are here included only as an additional convenience to users of these *Tables* should be clearly understood. This book is wholly independent of Beilstein, and those users to whom Beilstein may be inaccessible are reassured that the value of these *Tables* to them is in no way impaired.

B. Fundamental physical constants

The five components of the standard heading having been discussed, some comment upon the next element of each description is required. element comprises what are here designated as "fundamental physical constants" and which in the most general cases consist of data on (1) the melting point, (2) boiling point, (3) density, and (4) refractive index. In the sequence named, these are arranged in four vertical columns from left to right of a given page. For substances which are solids under ordinary conditions, the melting-point column is the first at the left of the page with the boiling-point column next following in the left central section. For such solids only rarely will density or refractive index data appear. For liquids, however, the first left-hand column is devoted to boiling-point data, the melting points being displaced to the next right-hand column because of their subordinate value in such instances.

(1) The melting point. Whereas in the earlier Tables of Order 1 the general practice was to express only a single figure for this constant, the individual descriptions of this book include substantially all values that have been reported. However, values which in the light of collective subsequent results are certainly too low, or those which because of their wide range make no claim to accuracy, are omitted. The survey of values thus set forth, together with the fact that the source of each value is also given, permits the user to form his own opinion concerning the magnitude, degree of concordance. and precision of the available data.

For each individual compound the several values are arranged in the order of diminishing numerical magnitude. In general the value of highest magnitude is employed to determine the place of the individual solid relative to its fellows (i.e., to determine its serial location number). However, values enclosed by square brackets are regarded by the author on collateral evidence as being abnormally high, and such constants are ignored in establishing the serial number of the individual.

The several melting points are recorded here just as they are reported in the original literature; whenever the designations corrected or uncorrected were included in the original source, they are repeated here; most of the values. however, fail to specify whether they are corrected or not. This careless usage of much journal literature is to be deplored.

No attempt has been made in this book generally to maintain a distinction between melting point and freezing point. Undoubtedly, most of the values reported represent conventional capillary-tube melting points; frequently. however, the values are expressed to a degree of precision suggesting that a cooling-curve method was employed. Whenever the distinction is of importance, the user can readily ascertain full details from the cited references.

(2) The boiling point. In complete analogy with its treatment of melting points, the individual descriptions of this book include substantially all recorded values of the boiling point. These are tabulated in the order of diminishing numerical magnitude of the prevailing pressures. Wherever the data can be found, the value at 760 mm. pressure is cited; however, if this is not directly reported, no attempt has been made to convert the available figures over to that pressure, as to do so would introduce unwarranted assumptions. Values of the boiling point at various pressures are meticulously included in the Tables. However, when a careful physicochemical study has been made of the vapor pressure of an individual, selected values are printed and reference made to the original for further detail.

Even a casual examination of the boiling point data reported in this book leads at once to the conviction that there has been a great variation in the precision of measurement of the prevailing pressure over the boiling liquid. In fact an incredible proportion of workers has not reported any pressure figures at all or complacently referred to the "prevailing atmospheric pressure." Even when pressure measurements are reported, the evident general lack of concordance becomes distressing evidence of the inadequacy and inaccuracy of many of the data in the literature.

(3) Densities. Unlike the extensive treatment accorded for melting points and boiling points, this book does not attempt to tabulate all possible published values for the densities of liquid compounds. However, all available data for density at 20°C. referred to water at 4°C. are given; and, whenever possible, the same procedure is extended to values for D_4^{25} and D_4^{15} . Note that, when values are given for various temperatures, those for the highest temperature are printed at the top of the density column, followed in diminishing magnitude of temperature by the other values. This simple and obvious device is intended to assist users of these Tables, but they should be reminded that this plan was not (unfortunately) employed with the Tables of Order 1.

Density data are given for all liquids for which they can be found; for compounds normally solid, the density is occasionally given for some temperature above the melting point, especially if refractive index values at the same temperature are also available.

Whenever in an original paper there exists any uncertainty as to the temperature of the water with which comparison is made, the lower subscript is replaced by a short dash to indicate that the omission of this figure is not accidental but is because of inadequate expression in the original. In many or even most such cases it is possible that the author intended to convey that the density was expressed with respect to water at the same temperature. This author, however, declines to make any such assumption and ventures to express the view that research workers and journal editors should insist upon unambiguous expression of such data.

(4) Refractive indices. These are usually given in the form $n_{\rm D}^{20}$, i.e., the refractive index determined at 20°C. with the D line of sodium light. In some instances data for other lines of the spectrum have been reported here when no data on the D line were available. As with the densities above, refractive index data are frequently printed for other temperatures, and the same typographical convention of placing the higher-temperature values above the lower-temperature ones is continued.

C. General data on other constants, preparation, and properties

The preceding details of the five components of the heading and the four so-called fundamental constants having been discussed, it is now desirable to comment upon the third element of the text of each compound. material comprising this third section actually comprises most of the space of this book. Although sometimes consisting of only a few paragraphs, there are many members of Order 3 for which the general exposition of behavior requires many pages. Such extended treatments are frequently (although not invariably) subdivided by major and minor headings intended to facilitate quick recognition of the probable location of particular types of desired information. Careful examination of the text of any typical individual compound will quickly disclose that it has in general been dealt with in At the same time it is obvious that a line must be drawn generous fashion. somewhere. For example, in connection with the discussion of an alkyl halide such as n-butyl chloride, it is certainly of highest relevance to indicate the mode and extent of its ability to form n-butyl magnesium chloride. Furthermore, the value of the simpler reactions of the RMgCl compounds. particularly with reference to their utility in the identification of the initial halide itself, is evident, but on the other hand no attempt has been made to cover all the known reactions of butyl magnesium chloride since that would involve an undertaking of disproportionate magnitude.

Although details of the texts of individual compounds naturally differ in nature and magnitude and are influenced by the literature content corresponding to the direction of published research, certain aspects occur with sufficient frequency to warrant comment.

The text of each compound invariably comprises its methods of preparation and its chemical behavior. For many of the more common or especially important species, these two aspects are often preceded by an introductory section containing certain physical data (in addition to that of the heading) likely to be of particular interest or utility to organic chemists. Examples of such entries include binary and ternary systems with other compounds, especially with reference to freezing-point composition data, azeotropes, densities and/or refractive indices, etc. In this introductory section also attention is frequently directed to methods of quantitative determination

of the compound, examples of industrial or other utilization, biochemical behavior especially with regard to studies on toxicity, antiseptic character, etc. The selection of entries for this introductory section is admittedly arbitrary, and users are reminded that this book makes no claim to include all known data even on the compounds to which serial numbers are assigned. Indeed, in an effort to keep the volume within reasonable bounds, certain types of data of value to organic chemists have been deliberately (though regretfully) excluded, such as references to absorption or Raman spectra, dipole moments, and viscosities, although many instances of the four fundamental physical constants of the heading are drawn from original publications primarily concerned with these aspects.

Within the text of each individual numbered compound (immediately following the above-mentioned introductory section, if any), there occurs a section on its methods of preparation. This treatment has purposely been made as complete as possible. To a limited degree distinction has been made between preparation and formation; but, because even in contemporary publications many authors fail to report yields, adequate recognition of the appropriate category is not always possible. Original results reported only in terms of weight have been calculated over to percentage yields. Variations in yields by a single method of preparation are contrasted by massing them in the text, the uniform practice of following each statement with its corresponding citation serving conveniently to associate each yield with a particular modification. With compounds for which there are many modes of preparation, the most generally practicable methods are often singled out for particular mention at the beginning of the preparative section, followed by a systematic presentation of all the recorded methods under various subheadings appropriate to the circumstances.

Users of this book will find these sections on preparation not only extremely useful from the viewpoint of comparison of various alternatives but also very stimulating and suggestive in the formulation of unconventional approaches to their particular problems.

Within the text of each numbered compound of this book, following the introductory section (if any) and the preparative section, is next set forth the significant aspects of its chemical behavior. The length of this part of the treatment varies widely from a few phrases to many pages. Very long treatments are appropriately subdivided for practical convenience, the particular sequence of arrangement being dictated by various circumstances. For example, the earlier subdivisions often deal with pyrolysis, reduction, oxidation, and substitution reactions, followed by the behavior with inorganic and organic reactants. With bifunctional compounds the initial group is frequently followed by the behavior of each function with inorganic and organic reactants in that order. Users will experience no difficulty in recognizing

the systematic organization of each compound. Emphasis has been placed upon a systematic and logical presentation of each case, and the above general outline has served the construction of this book only as a general guide rather than a rigid frame.

Two matters continually arising within the descriptive text deserve a further word of comment. The first relates to the fact that, in the course of reporting the chemical behavior of each numbered compound, there is necessarily involved reference to many other substances. Such of these as appear in either this volume (Order 3) or its predecessor (Order 1) are immediately followed by their serial numbers. A great many other compounds belonging to orders not yet written up in this series are inevitably involved; for such compounds reference to Beilstein is usually made for the convenience of the user who may have occasion to follow the matter further.

The second matter involves the practice of this book with respect to citations. Many instances appear which at first glance might appear to involve unnecessary repetition of the citation number, but which really comprise signals to the reader. As a simple illustration, consider the following extract from the text of p-chlorophenol, referring to the method of preparation of its N-(m-nitrophenyl)carbamate, viz.: "From $\bar{\mathbb{C}}$ with m-nitrophenzazide (283) or m-nitrophenyl isocyanate (283) in lgr. (283)." This usage designates the fact that the preparation of both the m-nitrophenyl isocyanate is given in reference (283) together with their utilization as reagents in the conversion of p-chlorophenol to the corresponding N-(m-nitrophenyl)carbamate. Of course, with commonly available reagents such extra citations need not be included.

In view of the nature and magnitude of the text of this book, there may be a tendency to regard it as a specialized Beilstein within its field. Such a characterization would carry the implication that the text comprises all known chemical information with respect to each component compound, whereas only the more important representatives of such data are offered. In this connection one common misunderstanding with respect to Beilstein's Handbuch has significance. The Beilstein classification employs the principle of "latest position in the system." This means that, when a given fact could logically be placed in several different places, it is in general associated with the last of such places in the systematic plan. For example, as the methyl ether of phenol, anisole could conceivably be discussed either under methyl alcohol or under phenol. Following the above principle, however, Beilstein discusses it under phenol with no mention whatever under methyl alcohol. For Beilstein's purpose this principle is extremely well founded. results in an orderly, systematic, and uniform procedure, and, if properly understood, causes no trouble to the user. Its employment does have the unfortunate result, however, that for compounds occurring early in the

systematic sequence the impression is often given to the uninitiated that nothing is known about reactions involving components themselves listed later in the classification scheme. In contrast to the above Beilstein usage, the present *Tables* are unrestricted by any such arbitrary rule. Inasmuch as a large proportion of the compounds with which it deals are those which in the Beilstein classification appear to be inadequately described because of their earlier position in the sequence, users will quickly appreciate the added convenience of a generous treatment of the chemistry involved.

D. Preliminary tests

For certain of the more common compounds included in these *Tables*, there exist specific or semi-specific color tests. These are generally simple to execute, may often be applied satisfactorily to minute amounts of material, and, when positive, are so significant that their trial, if indicated, should invariably precede the derivatization of the sample. Such tests are indicated by the symbol Φ but should be regarded as merely preliminary in character and not always carrying the same conviction as the derivatives.

E. Derivatives

The text section of each numbered compound is usually concluded by a group of derivatives. Those which for one reason or another have special importance are designated by the symbol O placed at the left-hand side of the page. Interspersed with such cases will frequently be found others not bearing this symbol but instead merely designated by a dash. Relatives of the original parent compound so designated comprise materials, knowledge of whose existence (or less commonly nonexistence) or properties may be needed for comparison with related cases for the particular parent or other isomers thereof. Wherever possible, specific data on each relative included in this derivative section are given; in many cases, however, where careful systematic search has failed to uncover any published record of the compound. it is characterized in these tables as "unreported." All chemists recognize that reliable information that a particular compound has not yet been reported is more to be desired than its complete omission; and this feature of this volume will effect substantial economies of time for its users. Naturally, as time goes by the constant publication of new data will enable some of these informational gaps to be filled.

More than one value for the melting point of a particular product derived from a numbered parent or, conversely, several citations for the same value will often be noted through all parts of this book. These practices serve, respectively, to suggest caution because of lack of agreement and to attract attention to the concordance of results of several different workers.

The sequence in which these derivatives are listed has no relation to their

respective merits as means of identification of the particular parent. For each class of compounds, the particular sequence is arbitrary but standard in form and sequence in order to facilitate intercomparison and easy reference. For any particular class, however, the sequence is similar to that employed in Order 1 for the corresponding nonchlorinated parent.

F. Literature references

The fifth and final section of the descriptive material comprising each serially numbered compound comprises the corresponding references to the chemical literature. These are associated with the corresponding portions of the descriptive text by arbitrary numbers set in bold-face carets, e.g. (5), the journal names being uniformly represented by the standard abbreviations employed by Chemical Abstracts. The single exception to the use of Chemical Abstracts abbreviations for literature references is that the German journal recently known as Chemisches Zentralblatt (but formerly as Chemisches Centralblatt) is here designated as Cent. This convention adequately suggests the name of the periodical in less space and improves the corresponding Beilstein abbreviation (C.) by avoiding confusion with Centigrade temperature.

The total number of such literature references in this book is very large, owing in part to the greatly increased scope of this Order 3 as compared with the restricted treatment of compounds of Order 1. It will be observed that, in addition to a much fuller record of the four fundamental physical constants, and a more generous regard for a diversified array of derivatives, this book (unlike its predecessor) deals extensively with the preparation and chemical behavior of its component species. Furthermore, whereas the earlier book arbitrarily excluded references to the patent literature, the present volume not only permits their inclusion but draws rather heavily upon it. The rapid growth of industrial organic chemistry, the fact that numerous chloro compounds of Order 3 represent individuals of great industrial significance, and the circumstances that for many such cases a large proportion of the available information is of such recent origin that little of it can be found in conventional monographs or other compendia have combined to necessitate considerable emphasis on the technical literature.

For a given individual numbered compound, a particular published article or patent is listed *only once*. The citation number representing the reference may be given many times in the descriptive text, but in the literature reference section the reference itself is not repeated. On the other hand, a given original article covering several individual compounds included in this book will be cited under each of the materials to which the article is relevant.

The order in which the literature references are arranged is determined, by the sequence in which necessity for their mention arises in the text. This

results, of course, in what may appear to be a random sequence. The author is well aware that rearrangement of these references into a sequence comprising an alphabetical author index is possible. Such an operation, however, has been regarded as impracticable since it would multiply severalfold the opportunity for error and would be unlikely to confer advantages commensurate with the labor involved.

Literature references to journals considered to be generally accessible are given directly; but those to articles in journals with limited circulation or to articles in languages other than English, German, French, or Italian are usually accompanied by the location of the corresponding abstract in both the Chemisches Centralblatt and the Chemical Abstracts. This leads to the suggestion that users of this book, to whom a particular primary publication may be inaccessible, may themselves locate the corresponding abstracts by means of the usual Author Indexes to these works. Consultation of the abstract must never be regarded as equivalent to examination of the original publication but is generally better than no information at all.

Citations to original articles in scientific journals often refer to individual pages but sometimes also to a spread of pages, depending upon the nature of the article. The practice so frequently employed by others of citing an article merely by giving its initial page and leaving to the reader the often laborious job of locating the individual page germane to the aspect in question is deplored by the present author and has been avoided in this book. a page spread (occasionally extending to the whole of a particular article) is cited, the reason is usually that the construction of the original paper is such that relevant material is scattered throughout the paper and individual page citation might be not only inadequate but even misleading. Since a given article appears (in general) but once in the group of literature references associated with each numbered compound, however, and since therefore the single number representing it may be used many times during the various aspects of the corresponding text, users finding that one of several individual pages so cited is inapplicable will recognize it is to be associated with some other aspect elsewhere in the text.

Attention is called to certain advantageous and unique practices followed by this book in connection with its citations of patents. The first element of patent citation is the name of the inventor (or of all, if more than one) if this information is known. The second element comprises the name of the company to which the patent has been assigned. All American patents are required by law to be issued to the inventors but are commonly assigned to the sponsor of the work. Foreign patents, however, do not always carry the names of individual inventors; in that event the company name has to serve both purposes. The third element is the nationality and number of the patent accompanied by its date of *issue* (not application). The fourth

15 INDEXES

element comprises reference to abstracts of the patent both in the *Chemisches Centralblatt* and in *Chemical Abstracts*. There are three reasons for this multiple form of abstract reference.

The first is that few chemists have immediate access to the corresponding original patents themselves and appreciate the convenience of the abstract. The second is the plain fact that the patent abstracts published by the Chemisches Centralblatt are usually so much more descriptive and more nearly complete than those of Chemical Abstracts that many chemists prefer to use the former. Doubters of this difference of quality between the two abstract journals are invited to convince themselves by direct comparison. Finally, the Chemical Abstracts reference is also included, however, because there may be some users of this book to whom the Centralblatt may not be available or who are timid about their ability to read even technical German. If in a particular case the patent has not been abstracted at all, this fact is also noted. Furthermore, because of the present inaccessibility of more recent issues of the Centralblatt, it has been necessary in some of the more recent references to cite only Chemical Abstracts.

In connection with the citation of patents, many instances will be noted in which the reference includes also the equivalent patents of other countries, each of these being accompanied by its dates, abstract references, etc., as for an individual patent.

The reader's attention is directed to the obvious fact that many patents are expressed in general terms so that, even though the protection sought may frequently cover one or more of the component compounds of this book, the specific individuals are not mentioned by name. No attempt has been made to interpret such general patents. For this reason systematic searchers will often consult higher or lower homologs of the compound comprising their initial interest.

6. Abbreviations

Necessity for economy of space has required in this book a continuation of the extensive set of abbreviations used with the earlier Tables of Order 1 together with certain additions required by new circumstances. All these abbreviations have been selected so as to suggest the full word, particularly when assisted by the context. No attempt has been made to enslave the text to the abbreviations, however, and the full word is sometimes employed even though a mnemonic for it is given in the Table of Abbreviations.

7. Indexes

This book contains five different types of indexes; three of these are distinctly novel and two are conventional, as explained below.

A. The empirical formula index

The index of empirical formulas lists each of the compounds in this book in the conventional familiar form under one or another of four parts according to whether the particular compound contains (1) only carbon and chlorine; (2) carbon, oxygen, and chlorine; (3) carbon, hydrogen, and chlorine; (4) carbon, hydrogen, oxygen, and chlorine. Within each of these parts the individual empirical formulas are arranged in groups according to increasing numbers of carbon atoms, and for a given number of carbon atoms according to increasing numbers of the other component atoms. Within each group of isomeric compounds the order of listing follows the sequence of the eight units comprising the Chemical Type Index (see below).

This empirical formula index contains also for each group of isomers both the molecular weight and the percentage chlorine content, each computed to one place of decimal units. This index not only serves as a convenient record of these constants but also suggests to the user isomers of the particular individual. The formula index may also be employed occasionally as a final verification of the presence or absence of a particular compound from the *Tables*, in possible instances where the names which occur to the worker do not appear in the alphabetical index.

A brief statistical analysis of this index may be of interest. The 1320 individual compounds comprising this book are distributed among 366 groups of isomers as follows:

		Groups of Isomers	Individuals
Part A	C/Cl compounds	11	11
Part B	C/O/Cl compounds	18	21
Part C	C/H/Cl compounds	135	566
Part D	C/H/O/Cl compounds	202	722
	Total	366	1320

The minimum number of isomers for a given empirical formula is obviously one; 28 of the above 366 groups represent such minimum cases. The maximum possible number of individual compounds within a particular empirical formula is, of course, indeterminately large; however, it is of interest to note that, of the 366 groups of isomers in this book, the largest number of individual compounds (21) occurs for the empirical formula $C_8H_7O_2Cl$. Other formulas with substantial numbers of individuals comprise $C_5H_9O_2Cl$ with 20, $C_7H_{15}Cl$ and $C_8H_{17}Cl$ each with 18, $C_5H_{10}Cl_2$ with 17, and $C_6H_{11}Cl$, $C_6H_{18}Cl$, and C_8H_9OCl each with 16, corresponding to a particular molecular weight.

B. Index of empirical formulas by percentage chlorine content

This index lists the 366 empirical formulas of the numbered compounds contained in this book in order of diminishing percentage of chlorine. This

17 INDEXES

type of index is unique; nothing of this sort exists in any other publication so far as is known. Many uses of such an index will suggest themselves, the most obvious example being to suggest various empirical formulas corresponding to a particular chlorine content.

Within this index will be observed many examples of identical chlorine contents for several different formulas; e.g., a percentage chlorine of 37.5 is common to the four different formulas C₂H₃O₂Cl, C₃H₇OCl, C₈H₆OCl₂, and C₁₄H₉Cl₃, despite the fact (as seen from the Empirical Formula Index) that the molecular weights of the last two are quite different from the others.

C. Index of empirical formulas by molecular weights

This index lists the 366 empirical formulas of the numbered compounds contained in this book in order of increasing magnitude of molecular weight. This index (like the preceding one) is unique, and nothing of the sort exists in any other publication so far as is known. Many uses of this index will suggest themselves, the most obvious example being to suggest various empirical formulas having the same molecular magnitude.

Within this index will also be observed many examples of identical molecular weights for several different formulas; e.g., the molecular weight of 136.6 is common to the three different formulas C₅H₉O₂Cl, C₆H₁₃OCl, and C₈H₅Cl.

D. Index of compounds according to chemical types

Since, as more fully explained earlier in this chapter, the component individuals of this book are not arranged in arbitrary genera and no standardized generic tests comparable to those of Order 1 have as yet been developed, the inclusion in this volume of an index in which the compounds are arranged according to the chemical classes to which they belong is of special value and utility.

In this chemical-type index, each compound is listed in at least one of eight chemical classes (units) as follows:

- Unit 1. Chloro substitution products of saturated acyclic hydrocarbons.
- Unit 2. Chloro substitution products of unsaturated acyclic hydrocarbons.
- Unit 3. Chloro substitution products of cyclic hydrocarbons.
- Unit 4. Chloro substitution products of hydroxy compounds (alcohols or phenols).
- Unit 5. Chloro substitution products (and their relatives) of carbonyl compounds (aldehydes, ketones, quinones, aldehyde polymers, acetals, alcoholates, etc.).
- Unit 6. Chloro substitution products of carboxylic acids and anhydrides.
- Unit 7. Acyl chlorides.
- Unit 8. Chlorine substitution products of ethers and of esters.

Compounds of the last five units containing more than one functional group are also listed under such of the others as may be appropriate. For example, 2,5-dichloro-3,6-dihydroxybenzoquinone-1,4 is listed both as a

carbonyl compound (Unit 6) and as a phenol (Unit 4); diethylene glycol mono(chloroacetate) is listed not only as an ester (Unit 8) but also as an alcohol (Unit 4) and an ether (Unit 8).

It may be of interest to summarize briefly the distribution of the compounds in this book among the several classes as shown in the following summary:

Unit 1	221	Unit 5	146
Unit 2	182	Unit 6	137
Unit 3	174	Unit 7	142
Unit 4	211	Unit 8	182

The total number of such unit listings (1395) thus exceeds the number of individual compounds (1320) by an amount representing the cases of multiple functions.

E. Alphabetical Index

This conventional type of index includes not only the "principal" name, but also all the subsidiary names given in the Tables for every numbered compound in this book. It cannot, of course, guarantee to contain every name which might conceivably be applied since, for the field of chemistry, such names are legion. However, with every name that is listed is associated the corresponding location (or serial) number, so that use of this index is perfectly straightforward and the index requires no cross referencing within itself. The first letter of the first syllable of the name proper establishes its position in the alphabetical sequence irrespective of any literal or numerical prefixes such as o-, m-, p-, sec-, ter-, cis-, trans-, α -, β -, γ -, δ -, d-, l-, meso-. Within a particular group of isomers with the same name, however, the sequence is o-, m-, p-; sec-, ter-; or α -, β , γ -, δ , etc. Iso is not construed as a prefix but as part of the main root. Further details of this sort are given in the introduction to the index itself.

CHAPTER II

DIVISION A. SOLIDS

(3:0000-3:0499)

PENTACHLOROACETONE Cl₂CH—C—CCl₃ CaHOCla Beil. I -656 I1---I2--- $M.P. +2.1^{\circ}$ B.P. 192° See 3:6205. Division B: Liquids, Section 1, $D_4^{20} > 1.15$. — 2.5-DICHLOROTOLUENE C7H6Cl2 Beil. V - 296 V1--V₂-(231) M.P. 5° B.P. 199° at 761 mm. $D_{20}^{20} = 1.2535$ See 3:6245. Division B: Liquids, Section 1, $D_4^{20} > 1.15$. p-CHLOROTOLUENE C7H7Cl Beil. V - 292 V₁-(150) V_{2} -(226) $M.P. + 7.8^{\circ}$ B.P. 162° See 3:8287. Division B: Liquids, Section 2, $D_A^{20} < 1.15$. — 1,1-DICHLORO-2-METHYLPROPANOL-2 CH₃ C₄H₈OCl₂ Beil. I -382 (unsym.-Dichloro-ter-butyl alcohol; I_1 — CH3-C-CHCl2 dichloromethyl-methyl-carbinol) ÓН $n_{\rm D}^{19} = 1.4598$ $D_4^{19} = 1.2363$ M.P. $+8^{\circ}$ B.P. 151° See 3:5772. Division B: Liquids, Section 1, $D_4^{20} > 1.15$. o-CHLOROPHENOL OH C₆H₅OCl Beil. VI - 183 VI₁-(98) VI₂-(170) $D_4^{25} = 1.2456$ M.P. 8.0° B.P. 175-176° $n_{\rm D}^{25} = 1.5573$ Sec 3:5980. Division B: Liquids, Section 1, $D_4^{20} > 1.15$. — DI-(β-CHLOROETHYL) CARBONATE C₅H₈O₃Cl₂ Beil. III — ClCH₂CH₂O Ш1-- III_{2} -(5) ClCH₂CH₂O B.P. 240-241° $D_4^{20} = 1.3506$ $n_{\rm D}^{20} = 1.4610$ M.P. 8.5° See 3:6790. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

20

3:0010 CINNAMYL CHLORIDE (3-Chloro-1-phenylpropene-1) CH=CH=CH₂
$$V_1$$
-(232) V_2 -(372)

M.P. B.P. 8-9° (1) 140° at 37 mm., sl. dec. (5) D_-^{25} = 1.08815 (9) n_D^{25} = 1.58065(9) 8° (2) 125-126° at 22 mm. (6) D_+^{15} = 1.101 (6) n_D^{12} = 1.587 (8) 7-8° (3) 120° at 18 mm. (6) D_+^{12} = 1.090 (8) 4-9° (4) 117-119° at 17 mm. (7) 118° at 15 mm. (8) 115° at 13 mm., sl. dec. (5) 119.5-120.5° at 12 mm. (9) 116-117° at 12 mm. (10) 106° at 10 mm. (11) 109-110° at 6 mm. (3) 102-103° at 5 mm. (3) 101.5-103.4° at 5 mm. (12) 94° at 5 mm. (13) 86-87° at 2 mm. (3)

Care should be taken to avoid confusion of \bar{C} with the acid chloride of cinnamic acid; the acid chloride is properly designated as cinnamoyl chloride (3:0330); furthermore note that some of the older publications designate \bar{C} as "styryl chloride," which is now incorrect since in current usage the name styryl is reserved for the radical $C_6H_5.CH$ —CH— derived from styrene (14).

Attention is also drawn to the fact (not fully recognized in the older work) that in some (but not all) reactions of \bar{C} the prods. obtained may in part be derived from the synionic mesomer of \bar{C} , viz., phenyl-vinyl-carbinyl chloride (3-chloro-3-phenylpropene-1); for examples see below.

 \tilde{C} when pure is colorless oil with no odor of HCl; if HCl is present \tilde{C} soon darkens on stdg. — \tilde{C} should leave no residue on distillation, and best yields of RMgCl (see below) are obtainable only with freshly distilled \tilde{C} (3).

[For prepn. of \bar{C} from cinnamyl alc. (1:5920) with HCl gas at 0° (yields: 92–93% (1), 78% (7), 60% (12)) (5) (6) (15), with HCl gas in CCl₄ soln. at room temp. (85% yield (7)), with 6-7 wt. pts. 6 N HCl on distn. (79% yield (4)), or with conc. HCl + ZnCl₂ in C₆H₆ (54% yield (16) see indic. refs.; from cinnamyl alc. (1:5920) with PCl₃ in C₆H₆ (62.5% yield (1)), or PCl₃ + ZnCl₂ in C₆H₆ (65% (16)) (note that PCl₅ + ZnCl₂ in C₆H₆ gave only tar (16)); from cinnamyl alc. (1:5920) with SOCl₂ + pyridine in CHCl₃ (yields: 83% (3), 69–75% (12)), with SOCl₂ + diethylaniline (18) or other tertiary bases (18), or with excess SOCl₂ in C₆H₆ (72% yield (16)) see indic. refs.; from cinnamyl ethers by cleavage with HCl (22° B6) on htg. under press. see (8); from cinnamyl acctate (see below) by passing in dry HCl see (18).]

[For prepn. of Č from phenyl-vinyl-carbinol [Beil. VI-572, VI₁-(283)] (7) with HCl gas (7) (10) or with p-nitrobenzoyl chloride in ether on htg. in s.t. (10); from phenyl-vinyl-carbinyl acetate with HCl gas see (19).]

Č with Br₂ (1 mole) adds 2 atoms halogen yielding (20) (6) (10) α,β -dibromo- γ -chloro-n-propylbenzene, tbls. from ether, m.p. 104- 105° (6) (10).

C with conc. HI (D = 1.7) (3 wt. pts.) in AcOH (7) or C with KI in dry acctone (11) gives in good yield (7) cinnamyl iodide, pale yel. lfts., which after very careful recrystn. from AcOH have m.p. 57° (7); note, however, that the substance is very unstable, cf. (7) (11).

[\bar{C} on htg. with salts of acids yields a mixt. of the corresp. esters of cinnamyl alcohol (1:5920) and phenyl-vinyl-carbinol, the proportions of which vary with the nature of the acid radical, the metal, solvent, etc.; for extensive study of the reaction see (19) (7).] — [For behavior of \bar{C} with ethyl sodioacetoacetate (21), Ag salt of 3-hydroxynaphthoquinone-1,4 (2), or with 1,5-dichloroanthrone + aq. KOH (22) see indic. refs.]

 \bar{C} readily hydrolyzes to the corresp. alc. (1:5920): e.g., \bar{C} with aq. on boilg. for 1 hr. is 75% saponified (7); \bar{C} with boilg. aq. 1 N NaOH is 95% hydrolyzed in 1 hr. (7); note, however, that \bar{C} is remarkably stable toward strong aq. alk. in cold (e.g., with 3.5 vols. 53% aq. NaOH only trace of hydrolysis even after 8 hrs. shaking (7)); note also that the cinnamyl alc. (1:5920) obtd. by hydrol. is contaminated with di-cinnamyl ether, b.p. 231–232°, and probably also by the ether from phenyl-vinyl-carbinol. — \bar{C} (10 g.) with excess cold dil. aq. Na₂CO₃ on shaking 85 hrs. gives phenyl-vinyl-carbinol (1.3 g.) + cinnamyl alc. (1:5920) (0.7 g.), di-cinnamyl ether (2.6 g.) + unhydrolyzed chlorides (4.1 g.) (7).

[C with abs. alc. KOH yields only (7) cinnamyl ethyl ether; note, however, that the course of the reaction is modified by pres. of aq. and that C with NaOH in 70% aq. alc. the cinnamyl ethyl ether is accompanied by 25-30% of ethyl phenyl-vinyl-carbinyl ether (7); furthermore C with silver oxide in abs. alc. (thus even in absence of aq.) gives both ethers (7) (for numerous details see (7)).]

[The behavior of \bar{C} with NH₃ (or amines) is doubtless similarly influenced by the environment but has been less thoroughly studied. — \bar{C} in ether with large excess conc. aq. NH₄OK on stdg. gives (77% yield (23)) tetracinnamylammonium chloride, ndls. from alc., m.p. 199° (23); \bar{C} with abs. alc. NH₃ gives (24) (25) (5) mono-, di- and tri-cinnamylamines.]

Č with tertiary amines forms quaternary salts: e.g., Č with Me₃N in abs. EtOH 24 hrs. at room temp. gives (26) (25) cinnamyl-trimethyl-ammonium chloride, very hygroscopic solid (for derivatives see (25) (26)); for quaternary salt formn. of C with dimethylaniline (15) or pyridine (6) (5) see indic. refs.

[\bar{C} (1 mole) with aniline (4 moles) in ether as directed gives (50% yield (27)) N-(cinnamyl)-aniline, m.p. 21°, b.p. 200–202° at 12 mm., 178° at 3 mm. (27); \bar{C} (1 mole) with hexamethylenetetramine (1 mole) in aq. alc. as directed gives (20–30% yield (8)) cinnamaldehyde (1:0245).]

 \bar{C} (freshly distilled) with Mg in dry ether under special conditions gives (83% yield (3)) (12) RMgCl: note carefully, however, that this Grignard is (or behaves as) a mixture consisting of 27% cinnamyl MgCl, C_6H_5 —CH=CH.CH₂MgCl, accompanied by 73% phenyl-vinyl-carbinyl MgCl, C_6H_5 —C(MgCl).CH=CH₂ (12).

[The reactns. of the Grignard mixture thus obtd. from C therefore generally yield prods. corresponding to both the components sometimes accompanied by material originating from coupling reactns. of RMgCl (either or both types) with itself:e.g., RMgCl (designating the above mixture) on acid hydrolysis with 3 N H₂SO₄ gives not only both propenylbenzene [Beil. V-481, V₁-(231), V₂-(371)], b.p. 176°, and allylbenzene [Beil. V-484, V₁-(233), V₂-(373)], b.p. 156° (from the two RMgCl types) (combined yield 47% (12)), but also a high-boilg. residue (81% yield (12)) (from coupling of RMgCl, see below).]

[Č (2 moles) with Mg (1 atom wt.) in dry ether subsequently hydrolyzed gives a highboilg. fractn. consisting of a solid and a liquid hydrocarbon: the solid hydrocarbon (8-9% yield (28)) (1) is 1,6-diphenylhexadiene-1,5 (dicinnamyl) [Beil. V_1 -(338), V_2 -(597)], lfts. from alc. or AcOH, m.p. 82° (1), 81-82° (29), b.p. 211° at 11 mm. (1), 180° at 5 mm. (29); the liquid hydrocarbon (42.9% yield (28)) has now been recognized (28) (contrary to earlier views (1)) as 1,4-diphenylhexadiene-1,5, b.p. 157-160° at 2 mm., $D_{20}^{20} = 0.9919$, $n_{D}^{20} = 1.5890$ (28). — For mode of formation of these prods. see (28).]

[\bar{C} converted to RMgCl (see above) and reacted with NH₂Cl at -20° gives (14% yield (33)) cinnamylamine.]

- Φ Phenyl-vinyl-acetic acid: cryst. from pet. ether at -10° , m.p. $23-24^{\circ}$ (30). [From RMgCl with CO₂ (note that ord. method gives low yields (38% (3) cf. (17)) but simple modification of carbonation technique raises yield to 62-66% (3)).]—This acid on htg. or on warming with either alk. or acid isomerizes (by change in position of double bond) to α -phenylcrotonic acid (methylatropic acid) [Beil. IX-615)] (see also next paragraph).
- α-Phenylcrotonic acid (methylatropic acid): pr. from alc., ndls. or lfts. from aq., m.p. 135-136° (17) (p-nitrobenzyl ester, m.p. 80-81° (31)) (see also preceding paragraph). [From RMgCl (above) with ethyl chloroformate (3:7295) followed by hydrolysis of the intermediate ethyl phenyl-vinyl-acetate by htg. with 20% HCl or by shaking for 2 days with alkali (the hydrolysis being accompanied by simultaneous rearr. of the unsatd. linkage) (30).]
- **D** Phenyl-vinyl-acetic anilide: cryst. from C_6H_6 , alc., or CHCl₃, m.p. 97-98° (30). [From RMgCl (above) with phenyl isocyanate in dry ether (30); this prod. may be accompanied by a small amt. of α -phenylcrotonanilide, m.p. 192°, from partial somerization during the reactn. (30).]
- N-(Cinnamyl)phthalimide: cryst. from 90% alc. or 90% AcOH (24) or from n-PrOH (32), m.p. 156° (32), 153° (24). [From C with K phthalimide by htg. at 160° for several hrs. (24); note that the structure of this prod. has been confirmed as the cinnamyl (and not the phenyl-vinyl-carbinyl) type (32).]
- 3:0010 (1) Rupe, Bürgin, Ber. 43, 172-178 (1910). (2) Fieser, J. Am. Chem. Soc. 48, 3213 (1926). (3) Gilman, Harris, Rec. trav. chim. 50, 1052-1055 (1931). (4) Norris, Watt, Thomas, J. Am. Chem. Soc. 38, 1078 (1916). (5) Emde, Franke, Arch. Pharm. 247, 333-334 (1909). (6) Klages, Klenk, Ber. 39, 2552-2555 (1906). (7) Meisenheimer, Link, Ann. 479, 211-277 (1930). (8) Bert, Dorier, Compt. rend. 191, 332-333 (1930); Cent. 1930, II 2376; C.A. 24, 5739 (1930). (9) Goebel, Wenzke, J. Am. Chem. Soc. 60, 698 (1938). (10) Meisenheimer, Schmidt, Ann. 475, 178-179 (1929).
- (11) Murray, J. Am. Chem. Soc. **60**, 2663 (1938). (12) Young, Ballou, Nozaki, J. Am. Chem. Soc. **61**, 12-15 (1939). (13) Murray, Cleveland, J. Am. Chem. Soc. **60**, 2665 (1938). (14) C.A. **31**, 9489 (1937). (15) Emde, Ber. **42**, 2593 (1909). (16) Clark, Streight, Trans. Roy. Soc. Canada (3) **23**, III, 77-89 (1929). (17) Gilman, Harris, J. Am. Chem. Soc. **49**, 1825-1828 (1927). (18) Darzens, Compt. rend. **152**, 1316, 1601 (1911). (19) Meisenheimer, Beutter, Ann. **508**, 58-80 (1934). (20) Grimaux, Bull. soc. chim. (2) **20**, 122-123 (1873).
- (21) Bergmann, Corte, J. Chem. Soc. 1935, 1364. (22) Barnett, Goodway, Weekes, J. Chem. Soc. 1935, 1104. (23) Emde, Arch. Pharm. 249, 93-103 (1911). (24) Posner, Ber. 26, 1857-1865 (1893). (25) Emde, Arch. Pharm. 244, 271-277 (1906). (26) Schmidt, Flaccher, Arch. Pharm. 243, 75-78 (1905). (27) von Braun, Tauber, Ann. 458, 107 (1927). (28) Gilman, Harris, J. Am. Chem. Soc. 54, 2072-2075 (1932). (29) von Braun, Köhler, Ber. 51, 84 (1918). (30) Gilman, Harris, J. Am. Chem. Soc. 53, 3541-3546 (1931).
- (31) Knowles, Cloke, J. Am. Chem. Soc. 54, 2037 (1932).
 (32) Bergmann, J. Chem. Soc. 1935,
 1362.
 (33) Coleman, Forrester, J. Am. Chem. Soc. 58, 28 (1936).

--- HEXACHLOROBUTENE-Y

C₄H₂Cl₆ Beil. S.N. 11

M.P. 9.5-11° B.P. 125.5° at 25 mm.

See 3:9050. Division C: Liquids with b.p. only at reduced pressure.

3:0013 7-CHLOROHEPTANOL-1 CH₂.(CH₂)₅.CH₂OH C₇H₁₅OCl Beil. S.N. 24 (ω-Chloro-n-heptyl alcohol)

M.P. B.P. $10-11^{\circ}$ (1) (2) 150° at 20 mm. (1) $D_4^{15} = 0.9998$ (1) $n_D^{25} = 1.45367$ (1) 120° at 13.5 mm. (3)

Cryst. from lt. pet.

[For prepn. of \bar{C} from α , ω -heptamethylene glycol (m.p. 20.2° (3), 18° (1), b.p. 151° at 14 mm. (1), 146° at 9 mm. (3)) with conc. HCl as directed (yields: 65% (4), 46.2% (3), 43% (1)) see indic. refs.]

[C with thiophenol in aq. NaOH htd. 3 hrs. gives (1) 7-hydroxy-n-heptyl phenyl sulfide, ndls. from pet., m.p. 49°; this prod. with SOCl₂ gives (1) 7-chloro-n-heptyl phenyl sulfide,

brown oil (no consts. reported).]

[$\ddot{\mathbf{C}}$ (1 mole) with Et₂NH (3-4 moles) in s.t. at 120-160° for 12-15 hrs. gives (86% yield (3)) 7-(diethylamino)heptanol-1, b.p. 132° at 9.5 mm., $D_4^{20} = 0.8681$, $n_D^{19} = 1.4561$, cf. (6); this prod. with SOCl₂ in C₆H₆ yields (3) (6) 7-(diethylamino)-n-heptyl chloride, b.p. 126° at 15 mm., $n_D^{18} = 1.4528$ (3) (corresp. $\ddot{\mathbf{B}}$.HCl, m p. 82-84° (6)).]

 $\bar{\mathbf{C}}$ with morpholine gives (5) alm. quant. 7-(4-morpholinyl)heptanol-1, b.p. 155.5-155.8° at 5 mm., $D_4^{25}=0.9783$, $u_1^{25}=1$ 4747 (corresp. N-phenylcarbamate, m.p. 71.0-72.0° cor.) (5). — $\bar{\mathbf{C}}$ (1 mole) with N-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (4) in alm. 100% yield (as salt) N-(7-hydroxy-n-heptyl)-N'-phenylpiperazine, m.p. 75.5-76.5° cor. (corresp. N-phenylcarbamate, m.p. 96.5-97.5° cor.).

T-Chloro-n-heptyl N-phenylcarbamate: ndls. from pet. or dil. alc., m.p. 76-77° (3), 76° (1).

3:0013 (1) Bennett, Mosses, J. Chem. Soc. 1931, 1689-1700. (2) Bennett, Reynolds, J. Chem. Soc. 1935, 139. (3) Altman, Rec. trav. chim. 57, 951-952 (1938). (4) Anderson, Pollard, J. Am. Chem. Soc. 61, 3439-3440 (1939). (5) Anderson, Pollard, J. Am. Chem. Soc. 61, 3440-3441 (1939). (6) Pyman, Levene (to Boot's Pure Drug Co.), Brit. 402,159, Dec 21, 1933; Cent. 1934, I 2005; C.A. 28, 3081 (1934).

3:0014 10-CHLORODECANOL-1 CH₂·(CH₂)₈·CH₂OH C₁₀H₂₁OCl Beil. I - 426 (ω-Chloro-n-decyl alcohol) I₁-(213)

M.P. B.P. $10-11^{\circ}$ (1) $164-165^{\circ}$ at 20 mm. (2) $D_4^{25} = 0.9630$ (1) $n_D^{25} = 1.45796$ (1) $147.5-149^{\circ}$ at 9 mm. (3)

Cryst. from pet. eth. (1). — Almost insol. aq.; eas. sol. alc., ether, C6H6, pet. ether.

[For prepn. of \tilde{C} from α,ω -decamethylene glycol [Beil. I-494, I₁-(256), I₂-(560)] (m.p. 74.5° (1)) with conc. HCl (10 vols.) on boilg. 4 hrs. (2) (3) (for improvements of this method see (1)) (yields: 65% (4), 50% (2)) see indic. refs.]

[C on distn. with fused NaOH loses HCl giving two products regarded (2) as decamethylene oxide and decen-1-ol, but their structures have been questioned (3).]

Č with thiophenol in aq. NaOH, heated 3 hrs., yields (1) 10-hydroxy-n-decyl phenyl sulfide, ndls. from lt. pet., m.p. 66.5° (1); this prod. with SOCl₂ gives 10-chloro-n-decyl phenyl sulfide, cryst. from alc., m.p. 27.5° (1).

 \bar{C} with morpholine gives (5) alm. quant. 10-(4-morpholinyl)decanol-1, m.p. 39.5-40.5°, b.p. 164.0-165.0° at 2 mm. (corresp. N-(α -naphthyl)carbamate, m.p. 66.5-67.5° cor. (5)). $-\bar{C}$ (1 mole) with N-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (5) in alm. 100%

24

yield (as salt) N-(10-hydroxy-n-decyl)-N'-phenylpiperazine, m.p. 67.0-68.0° cor. (corresp. N-phenylcarbamate, m.p. 95.0-96.0° cor.).

- 10-Chlorodecyl N-phenylcarbamate: ndls. from alc., m.p. 72° (1).
- 10-Chlorodecyl N-(α -naphthyl)carbamate: m.p. 63-64° (4).

3:0014 (1) Bennett, Mosses, J. Chem. Soc. 1931, 1698-1701. (2) Alberti, Smiecuszewski, Monatsh. 27, 411-419 (1906). (3) Franke, Kienberger, Monatsh. 33, 1191-1196 (1912). (4) Anderson, Pollard, J. Am. Chem. Soc. 61, 3439-3440 (1939). (5) Anderson, Pollard, J. Am. Chem. Soc. 61, 3440-3441 (1939).

o-CHLOROBENZALDEHYDE

C₇H₅OCl Beil. VII - 233 VII₁-(132)

M.P. 11°

B.P. 213-214°

 $D_4^{20} = 1.2512$

 $n_{\rm D}^{20} = 1.56708$

See 3:6410. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

1,1,1,2,3,3,3-HEPTACHLOROPROPANE Cl Cl C3HCl7 Beil. I- I_{1} -(35)

M.P. 11°

B.P. 249°

 $D_A^{34} = 1.7921$

See 3:6860. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

7-PHENOXY-n-PROPYL CHLORIDE

C₉H₁₁OCl

Beil. VI - 142

 $(\gamma$ -Chloro-n-propyl phenyl ether) VI₁--O.CH₂.CH₂.CH₂.Cl VI₂-(145)

M.P. 11.8-12°

B.P. 245-255°

 $D^{20} = 1.1167$

See 3:8820. Division B: Liquids, Section 2, $D_4^{20} < 1.15$.

n-HEXADECANOYL CHLORIDE CH_3 . $(CH_2)_{14}$ —C=O $C_{16}H_{31}OCl$ Beil. II - 374 (Palmitoyl chloride) II_{1} -(167)

M.P. 12° B.P. 199-200° at 20 mm.

See 3:9912. Division C: Liquids with b.p. reported only at reduced pressure.

CHLOROMALEYL (DI)CHLORIDE Beil. XVII ---

M.P. 12.7

B.P. 189°

 $D_4^{20} = 1.602$

 $n_{\rm D}^{20} = 1.5126$

XVII₁-(138)

See 3:6158. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

DICHLOROACETIC ACID Beil. II - 202 C₂H₂O₂Cl₂ II₁-(90) II₂-(194)

M.P. 13° B.P. 194-195° $D_4^{20} = 1.5642$

 $n_{\rm D}^{20} = 1.46582$

Division B: Liquids, Section 1, $D_4^{20} > 1.15$. See 3:6208.

β-METHOXYETHYL TRICHLOROACETATE C₅H₇O₈Cl₃ Beil. S.N. 160 (Methyl "cellosolve" trichloro-CH₂OCH₃ acetate) CH2OCOCCl3

M.P. 14.6-14.8° B.P. 98.0-99.5° at 17 mm.

See 3:9250. Division C: Liquids with b.p. reported only at reduced pressure.

 b-CHLOROBENZOYL CHLORIDE C7H4OCl2 Beil. IX - 341 IX_{1} -(140)

M.P. 15° B.P. 221° $D_4^{20} = 1.3621$

 $n_{\rm D}^{20} = 1.5790$

See 3:6550. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

3:0015 1-CHLOROHEXADECANE CH₃.(CH₂)₁₄.CH₂Cl C₁₆H₃₃Cl Beil. I - 172 (n-Hexadecyl chloride; I_1 cetyl chloride) I₂-(138)

B.P.

(6) $D_4^{20} = 0.8520$ (10) $n_D^{20} = 1.45477$ (2) M.P. 15° (1) 289° dec. 13° (2) 193-197° at 10 mm. (est.) (7) 1.4458 (10) (3) (4) 176-180° at 6 mm. $(2) \ D_{20}^{20} = 0.8384 \ (2)$ β-form 12.1° (5) 150° at 5 mm. (8)

150° at 3 mm. (see text) (9)

α-form 7.4° (5) 149-153° at 2 mm. (4)

 $73-90^{\circ}$ at 1×10^{-4} mm. (10) (see text)

Note that \bar{C} shows dimorphism: the transparent α -variety, f.p. 7.4° (no supercooling), when seeded with cryst. which had been cooled to 0°, changes to a white (opaque) βmodification, m.p. 12.1° (5).

PREPARATION OF C

[For prepn. of C from hexadecanol-1 (cetyl alc.) (1:5945) with dry HCl gas + 1% ZnCl₂ at 160-170° for 6 hrs. (94% yield (11)) or in EtOH with dry HCl gas 6 hrs. at 100° (yield unreported (1)) see indic. refs.; note that using 1% ZnCl₂ yield in 6 hrs. at 130° is 86.8%, rises to a max. of 94.6% at 160° , then falls off again to 89% at 200° (11); note also that in absence of any cat, yield at 160° is only 59% even after 20 hrs. and that with other cat. yields are low (11).]

[For prepn. of \bar{C} from hexadecanol-1 (cetyl alc.) (1:5945) with conc. $HCl + ZnCl_2$ (yields: 65% (4), 62% (2)), with PCl₅ (1 mole) at 135° for 5 hrs. (yield unreported (7)) cf. (6), with SOCl₂ (excess but without pyridine) (87-89% yield (2)) see indic. ref. — For form. of \bar{C} from cetyl alc. + PCl₅ (in pres. of mesityl oxide + Ac₂O) (61.5% yield) see (10). — For form. of \bar{C} from cetyl alc. with PCl₃ see (5), but note that prod. always conts. unchanged cetyl alc. (1:5945) and cetene-1 (1:7000) (12) cf. (2).

[For prepn. of C from cetyl stearate (1:2193) with dry HCl gas (97% yield (11)), from

cetyl acetate (1:2038) with dry HCl gas + ZnCl₂ at 180° (13) see indic. refs.]

[For formn. of C from a mixt. of K palmitate + K chloroacetate by electrolysis see (8).]

PHYSICAL BEHAVIOR OF C

[For study of electrophoretic mobility of emulsions of C see (14).]

CHEMICAL BEHAVIOR OF C

WITH INORGANIC REACTANTS

With metals. [\bar{C} with Li in dry ether under N₂ gives (100% yield (15)) C₁₆H₃₃Li; on carbonation of mixt. with CO₂ this is converted (51% yield (15)) to n-heptadecanoic acid (margaric acid) (1:0635): note, however, that \bar{C} with Li in pet. eth. (b.p. 30-35°) gives (15) only 63% yield C₁₆H₃₃Li and this on carbonation only 27% overall yield of margaric acid accompanied by other prods. — For analogous reacts. of \bar{C} with Na see (15) (16); for react. of \bar{C} with Ca in dry ether under N₂ see (15).]

 \bar{C} with Mg in dry ether + trace I₂ gives in 6 hrs. (96% yield (1)) C₁₆H₃₃MgCl.

With NH₃. [C with liq. NH₃ in alc. in s.t. at 170° for 24 hrs. gives (70% yield (17)) di-n-hexadecylamine, cryst. from alc., m.p. 65°, b.p. 220° at 3 mm. (17), accompanied by (24% yield (17))n-hexadecylamine, m.p. 45°, b.p. 146-148° at 3 mm. (B.HCl, lfts. from abs. alc., m.p. 178° (17)).]

With misc. inorg. reactants. [C over spec. prepd. Al₂O₃ at 250° loses HCl giving (94% yield (18)) of a mixt. of hexadecenes together with other prods.]

[C with KOH at 200-300° gives (19) palmitte acid (1:0050); C with alc. KSH gives (21) n-hexadecyl mercaptan; C with alc. K₂S gives (21) di-n-hexadecyl sulfide.

 $[\bar{C} \text{ with Na}_2SO_3.7H_2O \text{ (6 moles) at 190-200}^{\circ} \text{ for 8 hrs. under press. gives (98% yield (20))}$ sodium cetanesulfonate-1.]

[For study of rate of reactn. of \bar{C} with KI in acctone at 50° and 60° see (3).]

WITH ORGANIC REACTANTS

[\tilde{C} with alc. KOH gives (5) ethyl *n*-hexadecyl ether, f.p. 19.9° (5); \tilde{C} with sodium allyl oxide refluxed 30 hrs. gives (70% yield (22)) allyl *n*-hexadecyl ether, pl. from aq. alc., m.p. 25° (22).]

[\bar{C} (1 mole) with 33% alc. MeNH₂ (1 mole) in s.t. at 140-150° for 18 hrs. gives (68% yield (17)) N-methyl-di-n-hexadecylamine, ndls. from alc., m.p. 36-37°, b.p. 269-271° at 1 mm. (17) accompanied by (15% yield (17)) N-methyl-n-hexadecylamine, b.p. 147-150° at 1 mm. (\bar{B} .HCl, m.p. 169-170° (17)). — \bar{C} (1 mole) with Mc₂NH (2 moles) in alc. in s.t. at 140° for 14 hrs. gives (82.5% yield (17)) N,N-dimethyl-n-hexadecylamine, b.p. 158° at 3 mm. (\bar{B} .HCl, lfts. from AcOEt/dioxane 5/1, m.p. 198° (17)).]

Č with tertiary amines gives by addn. the corresp. quaternary ammonium salts [e.g., C with Me₃N (2 moles) in alc. in s.t. at 100-105° for 12-16 hrs. (17), or C with Me₃N (1 mole) in closed bottle at 110° for 5 hrs. (7), gives (100% yield (17)) trimethyl-n-hexadecyl-ammonium chloride, hygroscopic lfts. from AcOEt/alc., m.p. abt. 70° (17); for study of surface tension of aq. solns. of this salt see (7)].

 \tilde{C} with pyridine (1 mole) in s.t. at 110° for 15 hrs. (23) or at 120° for 8 hrs. (7) gives *n*-hexadecyl-pyridinium chloride, cryst. with 1 H₂O from alc./ether or C₆H₆, m.p. 83° (23), 82° (24) [for study of surface tension (7), conductivity (24), and elec. potential (24) of aq.

solns. of this salt see indic. refs.; for cat. hydrogenation of this salt to N-(n-hexadecyl) piperidine.HCl, m.p. 180° see (23); for study of favorable effect of press. on reactn. of $\tilde{\mathbf{C}}$ with pyridine see (12).

[For analogous reactn. of \bar{C} with N,N-dimethyl-benzylamine (17) or with isoquinoline (23) see indic. refs.]

[For reactn. of \bar{C} with α -picoline + NaNH₂ yielding α -(n-heptadecyl)pyridine, m.p. 23.5°, b.p. 206° at 2.5 mm., \bar{B} .PkOH, m.p. 87°, or of \bar{C} with γ -picoline + NaNH₂ yielding γ -(n-heptadecyl)pyridine, m.p. 33°, b.p. 207–210° at 2.5 mm., \bar{B} .PkOH, m.p. 115°, see (9).]

- --- n-Hexadecyl p-nitrobenzoate: m.p. 58.4° cor. (25). [Prepd. indirectly.]
- --- n-Hexadecyl 3,5-dinitrobenzoate: m.p. 66°. [Prepd. indirectly.]
- --- N-(n-Hexadecyl)phthalimide: unreported.
- ---- S-(n-Hexadecyl)isothiourea hydrochloride: m.p. 126-128° (26). [From C with thiourea in alc. on refluxing 3-4 days (26).]
- —— n-Hexadecyl mercuric chloride: cryst. from pet. eth. or AcOEt, m.p. 114-115° (15). [Prepd. indirectly; note that m.p. of mixts. of this prod. with either n-C₁₂H₂₅HgCl (m.p. 114-114.5°) or C₁₈H₃₇HgCl (m.p. 115-116°) is depressed (15).]

3:0015 (1) Houben, Boedler, Fischer, Ber. 69, 1768-1769; 1779-1780 (1936).
(2) Clark, Streight, Trans. Roy. Soc. Canada (3) 23, 111 77-89 (1929).
(3) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925).
(4) Norris, Taylor, J. Am. Chem. Soc. 46, 756 (1924).
(5) Phillips, Mumford, J. Chem. Soc. 1931, 1732-1735.
(6) Tüttscheff, Jahresber. 1860, 406.
(7) Hauser, Niles, J. Phys. Chem. 45, 954-959 (1940).
(8) Matsui, Arakawa, Mem. Coll. Sci. Kyoto Imp. Univ. A-15, 189-194 (1932); Cent. 1932, II 2167; C.A. 26, 5264 (1932).
(9) Tschttschibabin, Bull. soc. chim. (5) 5, 431-432 (1938).
(10) Drake, Marvel, J. Ory. Chem. 2, 394 (1937).

Guyer, Bieler, Hardmeier, Helv. Chim. Acta 20, 1462-1467 (1937).
 Fawcett, Gibson, J. Chem. Soc. 1934, 396-400.
 Jaya, G. Ger. 567,014, Dec. 24, 1932;
 Cent. 1933, I 1015; C.A. 27, 1361 (1933).
 Dickinson, Trans. Faraday Soc. 37, 140-148 (1941).
 Meals, J. Org. Chem. 9, 211-218 (1944).
 Morton, LeFevre, Hechenbleikner, J. Am. Chem. Soc. 58, 757 (1936).
 Westphal, Jerchel, Ber. 73, 1006-1011 (1940).
 Schrauth, Ger. 327,048, Oct. 4, 1920; C.A. 15, 2009 (1921).
 Turkiewicz, St. Pilat, Ber. 71, 285 (1938).

(21) Fridau, Ann. 83, 16-20 (1852). (22) Davies, Heilbron, Givens, J. Chem. Soc. 1930, 2545. (23) Karrer, Kahnt, Epstein, Jaffe, Ishii, Helv. Chim. Acta 21, 233-236 (1938). (24) Lottermoser, Frotscher, Kolloid-Beihefte 45, 305-307, 316, 320, 324, 340, 343 (1937). (25) Armstrong, Copenhaver, J. Am. Chem. Soc. 65, 2252-2253 (1943). (26) Sprague, Johnson, J. Am. Chem. Soc. 59, 1838-1839 (1937).

- sum.-o-PHTHALYL DICHLORIDE

M.P. 16°

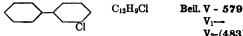
B.P. 276.7° at 760 mm.

 $D_4^{20} = 1.4089$

 $n_{\rm D}^{20} = 1.5692$

See 3:6900. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

--- 3-CHLOROBIPHENYL



M.P. 16°

B.P. 284-285°

See 3:8940. Division B: Liquids, Section 2, $D_4^{20} < 1.15$.

```
3:0020 \gamma-CHLORO-n-BUTYRIC ACID C_4H_7O_2Cl Beil. II - 278 II_1-(124) II_2-(253)
```

```
M.P.
                  B.P.
                                                  D_4^{20} = 1.2236 (5) \quad n_D^{20} = 1.4512 (5)
                                 at 22 mm. (3)
16°
                   196°
         (1)
                  115.0-115.5° at 13 mm. (1)
15-16°
         (2)
13-14° (10)
                  114°
                                 at 11.5 mm. (4)
12°
                   111°
                                 at 8 mm. (10)
         (3)
                                 at 6 mm.
                                           (10)
10.4°
        (11) (8)
                  107-108°
                  93.5-94°
                                 at 3 mm.
                                             (2)
```

Cryst, from ether + pet. ether; spar. sol. aq.

[For prepn. of \bar{C} from γ -chloro-n-butyronitrile (itself prepd. (60-70% yield (6)) from trimethylene chlorobromide) or from methyl γ -chloro-n-butyrate (3:8517) (10) by hydrolysis with conc. HCl (4) (5) (1) (2) see indic. refs.: from γ -butyrolactone (1:5070) with dry HCl see (1); from cyclopropanecarboxylic acid [Beil IX-4, IX₁-(3)] in ether with dry HCl at 0° see (3); from n-butyric acid (1:1035) with SO₂Cl₂ + dibenzoyl peroxide in CCl₄ (45% \bar{C} + 10% α - and 45% β -isomers) see (7).]

 \bar{C} on htg. above 180° loses HCl yielding (8) γ -butyrolactone (1:5070), b.p. 206°.

 $\ddot{\mathbf{C}}$ with alcs. yields corresp. esters (for study of rate of esterification of $\ddot{\mathbf{C}}$ with EtOH see (9)). — $\ddot{\mathbf{C}}$ with SOCl₂ yields γ -chloro-n-butyryl chloride (3:5970) q.v.

- ---- Methyl γ -chloro-n-butyrate: b.p. 175° (see 3:8517).
- Ethyl γ -chloro-n-butyrate: b.p. 186° (see 3:8597).
- \bigcirc γ -Chloro-n-butyramide: m.p. 88-90° (8). [From Me γ -chloro-n-butyrate (3:8517) with NH₄OH (8).]
- \mathfrak{D} γ -Chloro-n-butyr-anilide: lfts. from C_6H_6 + pet. eth., m.p. 69-70° cor. (2) (10). [From γ -chloro-n-butyryl chloride (3:5970) with aniline in ether (2) or C_6H_6 (10).] [This prod. on fusion with 3 pts. KOH yields (2) (by ring closure) N-phenyl- α -pyrrolidone [Beil. XXI-237], m.p. 68-69° cor. (2).]
- 3:0020 (1) Cloves, Ann. 319, 360-363 (1901). (2) Lipp, Caspers, Ber. 58, 1012-1014 (1925). (3) de Barr, Am. Chem. J. 22, 335-336 (1899). (4) Wohlgemuth, Compt. rend. 158, 1578 (1914); Ann. chim. (9) 2, 305-307 (1914). (5) Schjanberg, Z. physik. Chem. A-172, 226, 233 (1935). (6) Allen, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 156-157 (1941), 8, 52-53 (1928). (7) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940). (8) Henry, Bull. soc. chim. (2) 45, 341-342 (1886). (9) Lichty, Ann. 319, 374 (1901). (10) Blicke, Wright, Zienty, J. Am. Chem. Soc. 63, 2489-2490 (1941).
 - (11) Conant, Kirner, J. Am. Chem. Soc. 46, 244 (1924).

3: 0035 d,l-
$$\beta$$
-CHLORO- n -BUTYRIC ACID C₄H₇O₂Cl Beil. II - 277 CH₃.CH.CH₂.COOH II₁-(123) II₂-(253) M.P. B.P. 16-16.5° (1) (2) 116° at 22 mm. (1) $D_4^{20.2} = 1.1861$ (3)

16-16.5° (1) (2) 116° at 22 mm. (1)
$$D_4^{20.2} = 1.1861$$
 (3) 110-113° at 20 mm. (3) 108.5-109.5° at 17 mm. (4) $D_4^{20} = 1.1898$ (6) $n_D^{20} = 1.4421$ (6) 108° at 16 mm. (5) 98.5-99.5° at 12 mm. (2) $n_D^{19.85} = 1.4421$ (3)

White cryst. from dry ether, melting to colorless liq.

[For prepn. of $\bar{\mathbb{C}}$ from α -crotonic acid (1:0425) by satn. of ether soln. with dry HCl (1) (7) (8), or with aq. HCl at 80–100° in s.t. (5), or by boilg. with 20% HCl (9) see indic. refs.; from allyl cyanide with fumg. HCl at 50–60° see (10); from 3-chlorobutanol-1 (3:9165) by oxidn. with alk. KMnO₄ see (11); from β -chloro-n-butyraldehyde (3:9110) by oxidn. with conc. HNO₃ see (12); for formn. of $\bar{\mathbb{C}}$ from n-butyric acid (1:1035) with SO₂Cl₂ + dibenzoyl peroxide in CCl₄ (45% $\bar{\mathbb{C}}$ together with 10% α -chloro and 45% γ -chloro isomers) see (13); for formn. of $\bar{\mathbb{C}}$ from β -amino-n-butyric acid in 25% aq. HCl with NOCl under press. see (14).]

 \bar{C} on htg. with theoret. quant. dil. aq. alk. loses HCl giving quant. yield (2) (11) α -crotonic acid (1:0425), m.p. 72°. [For study of velocity of reactn. of \bar{C} with H₂O at 150°C see (1), of rate of loss of HCl from Na \bar{A} by aq. at 70° see (15).]

 \tilde{C} with EtOH yields ethyl β -chloro-n-butyrate (3:8373) [for study of rate of esterification see (4)]; \tilde{C} with SOCl₂ yields (2) β -chloro-n-butyryl chloride (3:9100) q.v. [for study of behavior of \tilde{C} on cat. hydrogenation see (16)].

 \bar{C} with NH₃ gives (17) β -hydroxy-n-butyramide [Beil. III₁-(116)].

C on conversion to NaA, dislvd. in 2½ pts. aq. and stood 1 day with NaOAc + phenylhydrazine yields (18) (21) β-phenylhydrazino-n-butyric acid [Beil. XV-324], lfts. from alc., m.p. 111° (18) (21). [This prod. on warming with conc. H₂SO₄ ring-closes to 1-phenyl-5-methylpyrazolidone-(3), m.p. 127° (18) (21).]

- Methyl β -chloro-n-butyrate: b.p. 156° (see 3:8224).
- Ethyl β -chloro-n-butyrate: b.p. 169° (see 3:8373).
- --- \beta-Chlorobutyramide: unreported.
- β-Chloro-n-butyranilide: cryst. from dil. alc., m.p. 89-90° (18), 90° (19). [From β-chloro-n-butyryl chloride (3:9100) with aniline (18) in acetone soln. (19).] [This prod. on htg. with AlCl₃ gives (55% yield (19)) 4-methyl-2-keto-tetrahydroquinoline, m.p. 98° (19).]
- β-Chloro-n-butyro-p-toluidide: cryst. from dil. alc., m.p. 124° (19), 115° (20). [From β-chloro-n-butyryl chloride (3:9100) with p-toluidine (20) in acetone soln. (19).]
 [This prod. on htg. with AlCl₃ gives (57% yield (19)) 4,6-dimethyltetrahydroquinoline, m.p. 131° (19).]

3:0035 (1) de Barr, Am. Chem. J. 22, 335, 342-343 (1899). (2) Cloves, Ann. 319, 358-360 (1901). (3) von Auwers, Ann. 421, 37 (1921). (4) Lichty, Ann. 319, 370, 373 (1901). (5) Lovén, Johansson, Ber. 48, 1256 (1915). (6) Schjanberg, Z. physik. Chem. A-172, 232 (1935). (7) Scheibler, Ber. 48, 1443 (1915). (8) von Auwers, Müller, J. prakt. Chem. (2) 137, 128 (1933). (9) Kaufler, Monatsh. 53/54, 124 (1929). (10) Pinner, Ber. 12, 2056 (1879).

(11) I. G., Brit. 479, 690, Feb. 10, 1938; Cent. 1938, I 3833; C.A. 32, 5003 (1938). (12) Karetnikow, J. Russ. Phys.-Chem. Soc. 11, 252 (1879). (13) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940). (14) Fischer, Scheibler, Cent. 1911, II 442; Ann. 383, 354-356 (1911). (15) Simpson, J. Am. Chem. Soc. 40, 680 (1918). (16) Paal, Schiedewitz, Ber. 62, 1937, 1939 (1929). (17) Scheibler, Magasanik, Ber. 48, 1812 (1915). (18) Michael, Ber. 34, 4052-4053 (1901). (19) Mayer, van Zütphen, Phillips, Ber. 60, 860-861 (1927). (20) Wolffenstein, Rolle, Ber. 41, 736 (1908).

(21) Lederer, J. prakt. Chem. (2) 45, 87-89 (1892).

3: 0050
$$d$$
, l - α -CHLORO-ISOVALERIC ACID $C_5H_9O_2Cl$ Beil. II -316 $(\alpha$ -Chloro- β -methyl- n -butyric acid) CH₃—CH—CH—COOH II₁— II₂—

M.P. 16° (1) B.P. 210-212° at 756 mm. (1)
$$D_{-}^{13.2} = 1.135$$
 (1) $n_{-}^{11} = 1.44496$ (1)

30 DIVISION A

C is insol. aq.; sol. in alc. or ether.

[For prepn. from α -chloroisovaleronitrile with conc. HCl at 100° see (1); from sodium isovalerate with aq. HOCl see (2).

 \bar{C} with PCl₃ yields (1) α -chloroisovaleryl chloride (3:8144).

- ---- Methyl α-chloro-isovalerate: unreported.
- ---- Ethyl α-chloro-isovalerate: unreported.
- ---- α-Chloro-isovaleramide: unreported.
- ---- α-Chloro-isovaler-anilide: unreported.
- ---- α-Chloro-isovalero-p-toluidide: unreported.

3:0050 (1) Servais, Rec. trav. chim. 20, 51-53 (1901). (2) Schlebusch, Ann. 141, 323 (1867).

1,2,4-TRICHLOROBENZENE

$$\bigcup_{C_1}^{C_1}$$

C₆H₃Cl₃

Beil. V - 204 V_{1} -(112)

 V_{2} -(156)

M.P. 17°

B.P. 213° cor.

See 3:6420. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

m-CHLOROBENZALDEHYDE



C7H5OCl

Beil. VII - 234 VII₁-(133)

M.P. 17°

B.P. 216°

 $D_4^{20} = 1.2410$

 $n_{\rm D}^{20} = 1.5591$

See 3:6475. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

2,2,2-TRICHLOROETHANOL-1 $(\beta,\beta,\beta$ -Trichloroethyl alcohol)

Cl₃C.CH₂OH C₂H₃OCl₃

Beil. I - 338

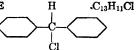
I₁-(170) I_{2} -(337)

M.P. 17-18° B.P. 151°

See 3:5775. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

3: 0060 BENZOHYDRYL CHLORIDE

(Diphenylmethyl chloride, diphenylcarbinyl chloride, diphenyl-chloromethane,



Beil. V - 590

 V_{1} -(278) V_{2} -(500)

a-chlorodiphenylmethane)

M.P. B.P.

at 247 mm. (12) $D_4^{19.5} = 1.1398$ (10) $n_D^{19.5} = 1.5959$ (10) 190-191° [20.5° (1)]

at 19 mm. (13) (14) 18° (2) 173°

17.6 $\langle 3 \rangle$ 169-170° at 17 mm. (10) 17-18° (4) 165° at 17 mm. (15)

17° 167° at 16 mm. (4) (5)

165.5° 13-15° (6) at 15 mm. (1)

14.5° (7) 161-162° at 13 mm. (3) 14°

(8) 158.0-159.5° at 12 mm. (1) (9) (24) 155-157° at 12 mm. (16)

13-14° (10) 156° at 10 mm. (7)

```
12-14° (11)
                148-150°
                               at 6 mm.
                                             (6)
                146.5-147.6° at 6 mm.
                                           (17)
                141°
                               at 4 mm.
                                           (18)
                135-145°
                               at 4 mm.
                                            (8)
                119-120°
                               at 2.5 mm.
                                           (19)
                113-114°
                               at 1.5 mm.
                                            (5)
                115-116°
                               at 1 mm.
                                           (19)
                115°
                               at 1 mm.
                                            \langle 3 \rangle
```

 \bar{C} rapidly becomes turbid in contact with atmosphere and should be kept in sealed tubes (1). — \bar{C} on attempted distn. at ord. press. loses HCl and gives 1,1,2,2-tetraphenylethane [Beil. V-739, V₁-(371)] (20), m.p. 211°, and 1,1,2,2-tetraphenylethylene [Beil. V-743, V₁-(376)] (9), m.p. 227°.

[For prepn. of \bar{C} from diphenylcarbinol (1:5960) with dry HCl gas alone (9) (21), or in C_6H_6 (92% yield (14)), or in C_6H_6 + $CaCl_2$ (yield: 90% (1), 85% (3)) (11) (17), with SOCl₂ in toluene (93.3% yield (2)), with PCl₅ in POCl₃ (92% yield (14)), or with BeCl₂ (77% yield (8)) see indic. refs.; from diphenylmethane (1:7120) with PCl₅ at 170° (together with other products) (22) or with NOCl (together with other products) (23) see indic. refs.: for formn. of \bar{C} from diphenylcarbinyl MgBr with ClCN (42% yield + 8% diphenylacetonitrile + 5% 1,1,2,2-tetraphenylethane) see (10); from bis-(diphenylcarbinyl) ether in C_6H_6 with HCl gas (77% yield) see (11); from diphenylcarbinylhydrazine with boilg. dil. HCl see (24); from diphenyldiazomethane with HCl gas in ether at -80° see (25).]

[\bar{C} with molecular Ag in C_6H_6 in absence of O_2 gives 100% yield (19) of 1,1,2,2-tetraphenylethane (see first paragraph); in pres. of pure O_2 yield drops to 2-8% and other products are formed (19); \bar{C} in C_6H_6 refluxed some hours with Na gives (80-90% yield (14)) (9) (21) 1,1,2,2-tetraphenylethane (see first paragraph); \bar{C} with Na in liq. NH₃ gives (26) 1,1,2,2-tetraphenylethane (65% yield) + diphenylmethane (1:7120) (27% yield).]

 \bar{C} in dry ether treated with Mg + trace of I₂ immediately ppts. 1,1,2,2-tetraphenylethane whose yield may reach 95.5% (2); however, under special conditions (6) \bar{C} in ether with Mg + trace of I₂ gives (51-71%) corresp. RMgCl epd.; this prod. upon treatment with CO₂ gives (yield: 84% (6), 32.5% (2)) diphenylacetic acid (1:0765), m.p. 148°; the RMgCl epd. does not react (2), however, with phenyl isocyanate.

[Č with pure AlCl₃ immediately resinifies $\{11\}$; however, Č in C₆H₆ with AlCl₃ gives $\{11\}$ triphenyl-chloromethane (3:3410) + diphenylmethane (1:7120) with a very little triphenylmethane (1:7220).]

[C htd. with 20% aq. Na₂SO₃ soln. for 3 hrs. at 120° gives (100% yield (28)) (27) bis-(diphenylmethyl) ether [Beil. VI-679, VI₁-(326)], cryst. from alc., m.p. 109° (27), 110° (17); note that this reaction probably results from intermediate diphenylcarbinol and that none of the expected sulfonate can be isolated.]

[For reactn. of \bar{C} with phenols + ZnCl₂ yielding mono-, di- or tri-alkylated phenols according to conditions see (13) (29) cf. (30); for reactn. of \bar{C} with thiophenols see (31); for reactn. of \bar{C} with excess Br.Mg.C=C.MgBr giving (40-50% yield) 1,1,4,4-tetraphenyl-butine see (32); for reactn. of \bar{C} with anthrone + KOH see (33).]

 \bar{C} with aq. hydrolyzes yielding diphenylcarbinol (1:5960) or its reactn. products according to particular conditions; for extensive studies see (34) (12) (35) (18) (40) (35). — \bar{C} with EtOH undergoes alcoholysis yielding ethyl diphenylcarbinyl ether + HCl (for very extensive studies of this and related reactions see (1) (36) (4) (17) (37) (7) (35). — \bar{C} after warming with alc. may then be titrated quant. with stand. alkali using phenolphthalein (1).

^{——} Diphenylcarbinyl acetate [Beil. VI-680, VI₁-(326)]: cryst. from AcOH, m.p. 40-41°. [From C with KOAc in AcOH (22).]

Diphenylcarbinyl benzoate: cryst. from alc., m.p. 88-89° (39), 86-88° (38). [From C in C₆H₆ on shaking with silver benzoate (38); see also text under diphenylcarbinol (1:5960).]

3:0000 (1) Ward, J. Chem. Soc. 1927, 2285-2295. (2) Gilman, Kirby, J. Am. Chem. Soc. 48, 1733-1736 (1926). (3) Weissberger, Sangewald, Z. physik. Chem. B-20, 149 (1933). (4) Norris, Banta, J. Am. Chem. Soc. 50, 1804-1808 (1928). (5) Smith, Andrews, J. Am. Chem. Soc. 53, 3649-3650 (1931). (6) Gilman, Zoellner, J. Am. Chem. Soc. 52, 3984-3988 (1930). (7) Nixon, Branch, J. Am. Chem. Soc. 58, 492-498 (1936). (8) Bredereck, Lehmann, Schönfeld, Fritzsche, Ber. 72, 1424 (1939). (9) Engler, Bethge, Ber. 7, 1128-1129 (1874). (10) Grignard, Ono, Bull. soc. chim. (4) 39, 1594 (1926).

(11) Boeseken, Rec. trav. chim. 22, 312-314 (1903). (12) Taylor, J. Am. Chem. Soc. 86, 2094-2096 (1938). (13) Van Alphen, Rec. trav. chim. 46, 799-800, 803, 811-812 (1927). (14) Montagne, Rec. trav. chim. 25, 403-404, 408 (1906). (15) Straus, Dützmann, J. prakt. Chem. (2) 103, 42 (1921/22). (16) Rule, Bain, J. Chem. Soc. 1930, 1899. (17) Farinacci, Hammett, J. Am. Chem. Soc. 59, 2542-2546 (1937). (18) Church, Hughes, J. Chem. Soc. 1940, 920-925. (19) Nauta,

Mulder, Rec. trav. chim. 58, 1070-1080 (1939). (20) Anschütz, Ann. 235, 220 (1886).

(21) Engler, Ber. 11, 927 (1878). (22) Cono, Robinson, Ber. 40, 2162-2163 (1907). (23) Perrot, Compt. rend. 198, 1425 (1934). (24) Darapsky, J. prakt. Chem. (2) 67, 129 (1903). (25) Staudinger, Anthes, Pfenninger, Ber. 49, 1936-1937 (1916). (26) Dean, Berchet, J. Am. Chem. Soc. 52, 2825 (1930). (27) Wedekind, Schenk, Ber. 44, 201-202 (1911). (28) Schenk, Pharm. Ztg. 54, 725; Cent. 1909, II 1916. (29) Busch, Z. angew. Chem. 38, 1145-1146 (1925). (30) Busch, Knoll, Ber. 60, 2243-2257 (1927).

(31) Finzi, Bellavita, Gazz. chim. ital. 62, 699-709 (1932). (32) Wieland, Kloss, Ann. 470, 215 (1929). (33) Barnett, Goodway, J. Chem. Soc. 1929, 813-814. (34) Straus, Hussey, Ber. 42, 2180-2181 (1909). (35) Bateman, Hughes, Ingold, J. Am. Chem. Soc. 60, 3080-3082 (1938). (36) Norris, Morton, J. Am. Chem. Soc. 50, 1795-1803 (1928). (37) Kny-Jones, Ward, J. Am. Chem. Soc. 57, 2394-2396 (1935). (38) Blicke, Powers, J. Am. Chem. Soc. 51, 3382 (1929). (39) Linnemann, Ann. 133, 22 (1865). (40) Church, Hughes, J. Chem. Soc. 1940, 966-970.

M.P. 18° (1) 4° (2)

Cryst. from ether + pet. ether.

[For prepn. of \bar{C} from δ -phenoxy-n-valeric acid [Beil. VI-165] by htg. with fumg. HCl in s.t. at 180° see (2) (4); from diethyl γ -chloro-n-propylmalonate [Beil. II₁-(278)] with 6 N HCl see (3); from δ -iodo-n-valeric acid [Beil. II-304, II₂-(270)] by susp. in conc. HCl and htg. with AgCl see (1).]

 \bar{C} distils at 141-149° at 12 mm. with sl. decomp. (1). — \bar{C} on htg. between 195-240° at ord. press. evolves HCl and leaves a viscous oil (1). \bar{C} htd. very rapidly at ord. press. over a free flame yields (1) (2) a little δ-valerolactone (1:1139).

C with SOCl₂ yields (5) δ-chloro-n-valeryl chloride (3:9264), b.p. 75-80° at 5-8 mm. (5).

- Methyl δ-chloro-n-valerate: unreported.
- Ethyl δ-chloro-n-valerate: see 3:8727.
- ---- δ-Chloro-n-valeramide: unreported.
- ---- δ-Chloro-n-valeranilide: unreported.
- δ-Chloro-n-valero-p-toluidide: unreported.

3:0075 (1) Cloves, Ann. 319, 363-366 (1901). (2) Funk, Ber. 26, 2574-2576 (1893). (3) Mellor, J. Chem. Soc. 79, 132 (1901). (4) Conant, Kirner, J. Am. Chem. Soc. 46, 244-245 (1924). (5) Child, Pyman, J. Chem. Soc. 1931, 41.

3: 0085 2-HYDROXYBENZOYL CHLORIDE (Salicyloyl chloride)
$$C_7H_5O_2C!$$
 Beil. X—X₁-(43) $C_7H_5O_2C!$ Beil. X—X₁-(43) C_7H

Colorless liq.; contrary to stability originally claimed (3), \bar{C} is now (1) regarded as very unstable, must be used as soon as prepd. since upon keeping (even in sealed tubes) it rapidly decomposes and sometimes explodes.

(6)

at 0.5-1 mm. (2) (1)

at 1 mm.

59°

56°

[For prepn. of \bar{C} from salicylic acid (1:0780) with SOCl₂ in boilg. C_6H_6 (80% yield (1) (7)) (4), with SOCl₂ + trace of AlCl₃ at 45-50° (2) (15), with COCl₂ (3:5000) in C_6H_6 in pres. of tertiary bases such as quinoline (8), or with oxalyl (di)chloride (3:5060) in C_6H_6 (98% yield (9)) see indic. refs.; for prepn. of \bar{C} from sodium (or other) salts of salicylic acid (1:0780) with SOCl₂ (yields: 38% (3), 36% (5)) (10) (11) (12) (13) (6) or with COCl₂ (3:5000) in toluene (14) see indic. refs.]

[\tilde{C} on htg. at 20 mm. begins to lose HCl at 110° yielding (1) polysalicylids; \tilde{C} in C_6H_6 with diethylaniline yields (1) α -disalicylid, cryst. from CHCl₃, m.p. 210-212° (1), c.f. (16) (17); \tilde{C} with PCl₅ yields α -Cl.CO.C₆H₄.OPCl₄ together with other P derivs. (17).

[For reactn. of \bar{C} with Na.C= $C-C_6H_5$ and ring closure of prod. to flavone see (18); for reactn. of \bar{C} with 1,3-dichloropropanol-2 (glycerol α,α' -dichlorohydrin) (3:5985) see (19).]

 \bar{C} with phenol at 50° yields (15) phenyl salicylate ("Salol") (1:1415), m.p. 42°. [For reactn. of \bar{C} with 2-iodoethanol yielding corresp. β -iodoethyl salicylate see (22); for reactn. of \bar{C} with alc. KSH yielding α -thiolsalicylic acid, m.p. 33° see (23).]

 \bar{C} with α -naphthylamine yields (20) salicyl- α -naphthalide [Beil. XII-1248], m.p. 187° (20); \bar{C} with β -naphthylamine yields (20) salicyl- β -naphthalide, m.p. 188-189° (20); \bar{C} (2 moles) with benzidine (1 mole) yields (21) N,N'-disalicyloylbenzidine (use in fixation of basic dyes on cotton (21)).

Č with urea in other yields (24) N-salicyloylurea (salicyl-monoureide) cryst. from AcOH or MeOH, m.p. 192° dec. (24).

[C with McOH presumably yields methyl salicylate (1:1750), b.p. 224°; C with EtOH yields ethyl salicylate (1:1755), b.p. 234°.]

C on hydrolysis presumably yields salicylic acid (1:0780) q.v.

3:0085 (1) Anschütz, Riepenkröger, Ann. 439, 2-4 (1924). (2) Kirpal, Ber. 63, 3190 (1930). (3) Kopetschni, Karczag, Ber. 47, 235-237 (1914). (4) Wolffenstein, Ger. 284,161, May 10, 1915, Cent. 1915, I 1290. (5) McMaster, Ahmann, J. Am. Chem. Soc. 50, 148 (1928). (6) Kahovec, Kohlrausch, Z. physik. Chem. B-38, 137 (1938). (7) Lukasiak, Roczniki Farm. 12, 1-36 (1934); Cent. 1935, I 3005; C.A. 30, 7163 (1936). (8) Soc. Chem. Ind. Basel, Brit. 401,643, Dec. 14, 1933; Cent. 1934, II 2133; French 732,078, Sept. 13, 1932; Cent. 1934, I 287. (9) Adams, Uhlig, J. Am. Chem. Soc. 42, 604 (1920). (10) Anschütz, Ann. 454, 95 (1927).

(11) Higgins (to British Synthetics, Ltd.), U.S. 1,684,273, Sept. 11, 1928; Brit. 278,463, Nov. 11, 1927; French 632,767, Jan. 14, 1928; Swiss 129,881, Jan. 2, 1929; Cent. 1929, I 2471. (12) Kopetschni, Karczag, Ger. 262,883, July 25, 1913, Cent. 1913, II 728. (13) Bogert, McColin, J. Am. Chem. Soc. 49, 2651-2652 (1927). (14) Kopetschni, Karczag, Ger. 266,351, Oct. 21, 1913; Cent. 1913, II 1715. (15) Dvornikoff (to Monsanto Chem. Co.), U.S. 2,007,013, July 2, 1935; Cent. 1936, I 1053; C.A. 29, 5603 (1935). (16) Anschütz, J. prakt. Chem. (2) 105, 158-164 (1923). (17) Anschütz, Ann. 439, 270-272 (1924). (18) Simonis, Z. angew, Chem. 39, 1462 (1926).

(19) Humnicki, Roczniki Chem. 11, 670-673 (1931); Cent. 1931, II 3334. (20) Jusa, Riesz, Monatsh. 58, 143 (1931).

(21) Günther, Haller, Köster (to I.G.), Ger. 441,326, March 1, 1927; Cent. 1927, I 2358. (22) Farbwerke Meister Lucius & Bruning, Ger. 360,491, Oct. 3, 1922; Cent. 1923, II 479. (23) Chem. Fabrik. von Heyden, Ger. 365,212, Dec. 11, 1922; Cent. 1923, II 251. (24) Kaufmann, Arch. Pharm. 265, 235–236 (1927).

--- SUCCINYL (DI)CHLORIDE Cl
$$C_4H_4O_2Cl_2$$
 Beil. II - 613 III-(264) $CH_2-C=0$ $CH_2-C=0$ $CH_2-C=0$

M.P. 20° B.P. 193° at 760 mm.

$$D_4^{20} = 1.3748 \qquad n_D^{20} = 1.4683$$

34

See 3:6200. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

M.P. 20-21° B.P. 231° at 763.5 mm.

See 3:6670. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

$$p$$
-CHLOROACETOPHENONE C_8H_7OCl Beil. VII - 281 VII_{1} -(151)

M.P. 20-21° B.P. 232°

 $D_{-}^{20}=1.188$

See 3:6735. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

$$--- \omega, \omega\text{-DICHLOROACETOPHENONE} \qquad \begin{array}{c} C_8H_6OCl_2 \\ \\ -C-CHCl_2 \end{array} \qquad \begin{array}{c} \text{Beil. VII - 282} \\ \text{VII}_1\text{-(152)} \end{array}$$

M.P. 20° B.P. 247–248°

See 3:6835. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

3: 0090
$$p$$
-CHLOROPHENETOLE Cl OC_2H_5 C_8H_9OCl Beil. VI - 187 VI_1-VI_{2-} (76)

M.P. 21° (1) B.P. 211.6° cor. (3)
$$D_{20.2}^{20.2} = 1.12310$$
 (2) $n_D^{19} = 1.5227$ (5) 20.9° (2) $210-212^{\circ}$ (1)(4) 20° (3)

Colorless oil, volatile with steam (6).

[For prepn. from p-chlorophenol (3:0475) + C_2H_5I in presence of KOH see (1), in presence of K_2CO_3 + acetone (74% yield) see (4).]

Č grad. added to 2 pts. conc. HNO₃ (D=1.485) with cooling, then poured into aq., gives (6) 4-chloro-2-nitrophenetole [Beil VI-238], pale yel. ndls. from alc., m.p. 61° (6). [The mother liquor contains some 4-chloro-2,6-dinitrophenol [Beil, VI-260], m.p. 80° (6).]

 \bar{C} htd. at 100° with abt. 30 pts. of a soln. of const.-boilg. HBr (1 vol.) in AcOH (2 vols.) for 2 hrs. gave (4) 85% yield of p-chlorophenol (3:0475).

- ⑤ 5-Chloro-2-ethoxybenzenesulfonamide: cryst. from dil. alc., m.p. 134-134.5° u.c. (7). [From C̄ by treat. with chlorosulfonic ac. followed by conversion of the intermediate sulfonyl chloride to the sulfonamide by treatment with (NH₄)₂CO₃ (71% yield (7))]. [Note that this prod. depresses the m.p. of the corresponding deriv. (m.p. 132-133° u.c.) from o-chlorophenetole (3:8735) (7).]
- 3:0000 (1) Beilstein, Kurbatow, Ann. 176, 31 (1875). (2) Swarts, J. chim. phys. 20, 76 (1923). (3) Peratoner, Ortoleva, Gazz. chrm. ital. 28, I 226 (1898). (4) Borosel, J. Am. Chem. Soc. 53, 1408-1409 (1931). (5) Cotton, Mouton, Ann. chim. (8) 28, 216 (1913). (6) Reverdin, Düring, Ber. 32, 153 (1899). (7) Huntress, Carten, J. Am. Chem. Soc. 62, 603-604 (1940).
- 3:0095 1-CHLORO-OCTADECANE CH₃.(CH₂)₁₆.CH₂Cl C₁₈H₃₇Cl Beil. S.N. 10 (n-Octadecyl chloride; stearyl chloride)
 - M.P. 21° (1) B.P. 180-190° at 12 mm. (1) (2) 18° (2)

Care must be taken to avoid confusion of \bar{C} with the acid chloride of stearic acid which is often designated as stearoyl chloride (3:9960).

[For prepn. of \bar{C} from octadecanol-1 (stearyl alc.) (1:5953) with excess PCl₅ on htg. (no statement of yields) (1) (10) or with PCl₅ in SOCl₂ (100% yield (10)) see indic. refs.] [For study of heat of adsorption of \bar{C} on steel and its bearing on lubrication see (1); for study of electrophoretic mobility of emulsions of \bar{C} see (3).]

 \bar{C} with Mg in dry ether yields (4) n-C₁₈H₃₇MgCl [this prod. with cyclopentanone (1:5446) gives (4) a tertiary alc. which on dehydration with KHSO₄ yields (4) n-octadecylcyclopentene, b.p. 173-174° at 3 mm., m.p. 19°, $D_4^{20}=0.8462$; similarly C₁₈H₃₇MgCl with cyclohexanone (1:5465) gives (4) a tertiary alc. which with KHSO₄ loses aq. giving (4) n-octadecylcyclohexene, b.p. 179-180° at 3 mm., m.p. 20°, $D_4^{20}=0.8458$].

[\bar{C} with C_6H_6 + AlCl₃ undergoes Friedel-Crafts reactn. yielding (4) n-(?)-octadecylbenzene [Beil. V-473, V₁-(361)], m.p. 25–26°, b.p. 180–181° at 3 mm., $D_4^{20}=0.8566$, $n_D^{20}=1.4826$.]

 \overline{C} (1 mole) with pyridine (1 mole) in s.t. at 110° for 15 hrs. gives (5) the corresp. quaternary salt, N-(n-octadecyl) pyridinium chloride, cryst. from alc./ether or C_6H_6 as monohydrate, m.p. 82° (5), 86° (6); for study of conductivity and electric potential of latter see (6).

- --- n-Octadecyl p-nitrobenzoate: m.p. 64.3° cor. (7). [Prepd. indirectly.]
- ---- n-Octadecyl 3,5-dinitrobenzoate: unreported.
- ---- N-(n-Octadecyl)phthalimide: unreported.
- --- S-(n-Octadecyl)isothiourea: m.p. 83-85° (8). [Prepd. indirectly.]
- —— n-Octadecyl mercuric chloride: m.p. 115-116° (9). [Prepd. indirectly: note that m.p. of this prod. either with C₁₆H₃₃HgCl (m.p. 114-115°) or with C₁₈H₃₇HgBr (m.p. 110-111°) is depressed (9).]
- 3:0095 (1) Frewing, Proc. Roy. Soc. (London) A-182, 270-286 (1944). (2) Meyer, Streuli, Helv. Chim. Acta 20, 1179-1183 (1937). (3) Dickinson, Trans. Faraday Soc. 37, 140-148 (1941). (4) Suida, Gemassner, Ber. 72, 1168-1173 (1939). (5) Karrer, Kahnt, Epstein, Jaffe, Ishii, Helv. Chim. Acta 21, 233-234 (1938). (6) Lottermoser, Frotscher, Kolloid-Beichefte 45, 305-306, 320-321, 325, 341 (1937). (7) Armstrong, Copenhaver, J. Am. Chem. Soc. 65, 2252-2253 (1943). (8) Snell, Weissberger, J. Am. Chem. Soc. 61, 453 (1939). (9) Meals, J. Org. Chem. 9, 213-217 (1944). (10) Davies, Heilbron, Owens, J. Chem. Soc. 1930, 2546.

--- n-OCTADECANOYL CHLORIDE
$$C_{18}H_{35}OCl$$
 Beil. II - 384 (Stearoyl chloride) CH_{3} .(CH₂)₁₆--C=O II_{1} -(176) II_{2} -(360)

M.P. 23-24° B.P. 215° at 15 mm.

See 3:9960. Division C: Liquids with b.p. reported only at reduced pressure.

M.P. 24° (1) B.P. 192-195° at 10 mm. (1)

[For prepn. of \bar{C} from N-benzoylheptadecylamine (N-(n-heptadecyl)benzamide) with PCl₅ on distn. (50% yield) see (1); from silver stearate (or other stearates of metals of 1st, 2nd, or 3rd group) with Cl₂ see (2).]

- ---- n-Heptadecyl p-nitrobenzoate: m.p. 53.8° cor. (3). [Prepd. indirectly.]
- --- n-Heptadecyl 3,5-dinitrobenzoate: unreported.
- --- N-(n-Heptadecyl)phthalimide: unreported.
- --- S-(n-Heptadecyl)isothiourea picrate: unreported.
- ---- n-Heptadecyl mercuric chloride: unreported.

3:0100 (1) von Braun, Sobecki, Ber. **44**, 1473 (1911). (2) C. Hunsdiecker, H. Hunsdiecker, E. Vogt, U.S. 2,176,181, Oct. 17, 1939; C.A. **34**, 1686 (1940): Brit. 456,565, Dec. 10, 1936; Cent. **1937**, I 2258; C.A., **31**, 2233 (1937): French 803,941, Oct. 12, 1936; Cent. **1937**, I 2258; [C.A. **31**, 2616 (1937)]. (3) Armstrong, Copenhaver, J. Am. Chem. Soc. **65**, 2252-2253 (1943).

3:0120 2-CHLOROCYCLOHEXANONE-1

$$\begin{array}{c|c} O & C_{\theta}H_{\theta}OCl & \textbf{Beil. VII - 10} \\ & H & & \textbf{VII_{1^-}(8)} \\ H_2C & CH & & \\ & C_{H_2} & & \\ & &$$

M.P. B.P. 24° (1) 90-91° at 14-15 mm. (19)
$$D_{15}^{20} = 1.161$$
 (6) $n_D^{20} = 1.4825$ (6) 23-24° (2) 88-90° at 16 mm. (5) 23.2° cor. (19) 82-85° at 14 mm. (8) 23° (3) (4) (5) 82° at 13 mm. (4) 22-23° (6) (7) 82-83° at 10 mm. (3) 80.5° at 11 mm. (5) 79° at 7 mm. (6)

Č has very disagreeable physiological effects; breathing of its ether solutions or exposure of skin to its vapor produces violent illness and temporary complete blindness; also produces an eczema on the hands (although sensitivity of individuals varies) (9). — Č dec. slightly on distn. even in vacuo (10).

[For prepn. from cyclohexanone (1:5465) with $Cl_2 + H_2O$ (61-66% yield (19)), by actn. of $Cl_2 + CaCO_3 + H_2O$ (HOCl) (50-60% yield (7) (8)) see (7) (8) (10) (3) (4); by direct

actn. of Cl₂ in AcOH (100% yield (8)) see (8); via N-chlorourea (80% yield (5)) or electrochem. chlorination in HCl (18); for prepn. from cyclohexanol (1:6415) by actn. of Cl₂ + $CaCO_3 + H_2O$ (HOCl) (50-60% yield (6) (9)) (1) see these; for prepn. (57% yield (5)) from 2-chlorocyclohexanol-1 (3:0175) by oxidn, with $K_2Cr_2O_7 + H_2SO_4 + AcOH$ see (5).

C with alc. KOH (11) yields (by ring contraction) cyclopentanecarboxylic acid [Beil. IX-6] or its ethyl ester [Beil. IX₁-(4)]. — \bar{C} with dil. alk. (3) or boilg. conc. K₂CO₃ soln. (3) (12) or shaking with 40% K₂CO₃ (50% yield (13)) gives corresp. alc., viz., cyclohexanol-2-one-1 or adipoin [Beil. VIII₁-(504)], cryst. from alc., m.p. 113° (3) (14) (after fusion remelts at 90° (14), 98° (13), 92-92.5° (12). [Adipoin gives oxime, m.p. 102-103° (13); p-nitrophenylhydrazone, m.p. 146° dec. (14); semicarbazone, m.p. 238° (13); benzoate, m.p. 122-123° (13).]

Č with NaCN (2 moles) in alc. gives (64% yield (6)) 2-cyanocyclohexanone-1, b.p. 140-141° at 15 mm. or 129-131° at 7 mm. (6), which upon alk, hydrolysis gives (84.7% yield (6)) n-pimelic acid (1:0456), m.p. 104-105° (6). [Used in mfg. of pimelic acid (15).]

C with ter-butyl-, cyclohexyl-, or isopropyl MgCl is reduced to cis-2-chlorocyclohexanol (3:9374). [Č with other R.Mg.X cpds, leads to 5-membered ring cpds, which cannot be considered here.l

 $[\bar{C} \text{ with diazomethane gives (7) } (100\% \text{ yield (17)}) \alpha$ -chlorocycloheptanone.]

3:0120 (1) Vavon, Mitchovitch, Bull. soc. chim. (4) 45, 965 Note (a) (1929). (2) Favorskii, Bozhovskii, J. Russ. Phys.-Chem. Soc. 46, 1098 (1914); Cent. 1915, I 984. (3) Bouveault, Chereau, Compt. rend. 142, 1086 (1906). (4) Kotz, Gretho, J. prakt. Chem. (2) 80, 487 (1909). (5) Detoeuf, Bull. soc. chim. (4) 31, 178 (1922). (6) Meyer, Helv. Chim. Acta 16, 1291-1295 (1933). (7) Steadman, J. Am. Chem. Soc. 62, 1608 (1940). (8) Bartlett, Rosenwald, J. Am. Chem. Soc. 56, 1992 (1934). (9) Ebel, Helv. Chim. Acta 12, 9-10 (1929). (10) Osterberg, Kendall, J. Am. Chem. Soc. 42, 2618 (1920).

(11) Favorskii, Bozhovskii, J. Russ. Phys.-Chem. Soc. 50, 582-588 (1917); Cent. 1923, III 1359. (12) Ref. 4, pp. 488-489. (13) Kötz, Blendermann, Rosenbusch, Sirringhaus, Ann. 400, 62-63 (1913). (14) Willstätter, Sonnenfeld, Bcr. 46, 2957-2958 (1913). (15) Meyer, Swiss 164,832, Jan. 2, 1934; Cent. 1934, I 3266; C.A. 28, 5473 (1934). (16) Bartlett, J. Am. Chem. Soc. 57, 224-227 (1935). (17) Giratis, Bullock, J. Am. Chem. Soc. 59, 945 (1937). (18) Szper, Bull. soc. chim. (4) 51, 656 (1932). (19) Newman, Farbman, Hipsher, Org. Syntheses, 25, 22-24 (1945).

4-METHOXYBENZOYL CHLORIDE

C₈H₇O₂Cl

Beil. X - 163 X1-(77)

M.P. 24°

B.P. 262-263°

 $D_4^{20} = 1.2609$

 $n_{\rm D}^{20} = 1.5802$

Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

3:0138 ter-BUTYL TRICHLOROACETATE

C₆H₉O₂Cl₃ Cl₃C.CO.O.C₄H₉

Beil. S.N. 160

 $D_4^{25} = 1.2363 (1) \quad n_-^{25} = 1.4398 (1)$ B.P. 37° at 1 mm. (1) M.P. 25.5° (1)

Cryst, from pentane or MeOH at 0° (1).

[For prepn. of C from trichloroacetyl chloride (3:5420) with ter-butyl alc. (1:6140) in pyridine in cold (95% yield (1)), or from trichloroacetic acid (3:1150) with isobutylene at 60° (80% yield (1)) see indic. refs.]

3:0138 (1) Scovill, Burk, Lankelma, J. Am. Chem. Soc. 66, 1039 (1944).

3.5-DICHLOROTOLUENE

C₇H₆Cl₂ Beil. V -2.96

V₁---V₂---

M.P. 26°

B.P. 201-202° cor. at 760 mm.

See 3:6310. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

---- α-NAPHTHOYL CHLORIDE

M.P. 26°

B.P. 297.5°

See 3:6930. Division B: Liquids, Section 1, $D_4^{20} > 1.15$.

3: 0142 2,4,6-TRICHLOROBENZAL (DI)CHLORIDE C₇H₃Cl₅ Beil. S.N. 466 (2,4,6-Trichlorobenzylidene (di)chloride)

Cl—CHCl₂

M.P. 27° (1)

B.P. 158° at 15 mm. (1)

Cryst. from MeOH

[For prepn. of \bar{C} from 2,4,6-trichlorotoluene (3:0380) with Cl_2 at 200° (82% yield) see (1).]

 \tilde{C} on hydrolysis with fumg. H_2SO_4 gives (94% yield (1)) 2,4,6-trichlorobenzaldehyde (3:1200).

3:0142 (1) Lock, Ber. 66, 1532 (1933).

3: 0150 2,6-DICHLORO-3-METHYLPHENOL OH $C_7H_6OCl_2$ Beil. VI — (2,6-Dichloro-m-cresol) CI CI VI₁—

VI₁— VI₂-(356)

M.P. 27° (1)

B.P. 240.5-242.5°

(1)

(2)

239.5-240.5° at 745 mm. (2)

80-85° at 4 mm.

[For prepn. of \tilde{C} from 4-amino-2,6-dichloro-3-methylphenol (1) via diazotization and treatment with alk. SnCl₂ (very poor yield) see (1); from 3-methylphenol-2,6-disulfonic acid (1) or from 3-methylphenolsulfonic acid-6 in nitrobenzene (2) with Cl₂ see indic. refs.; from 2-chloro-3-methylphenol (3:1055) or from 6-chloro-3-methylphenol (3:0700) in cold CHCl₃ with 1 mole Cl₂ see (1); from *m*-cresol (1:1730) in CHCl₃ at 0° with Cl₂ (other products are also formed) see (1).]

 \tilde{C} in CHCl₃ with 1 mole Cl₂ gives alm. quant. yield (1) 2,4,6-trichloro-m-cresol (3:9618), m.p. 46° (1).

 \bar{C} in CHCl₃ with 1 mole Br₂ yields (2) 2,6-dichloro-4-bromo-3-methylphenol, m.p. 64-65° (2).

② 2,6-Dichloro-3-methylphenyl benzoate: clusters of small prismatic pl. from alc., m.p. 90.5° (1). [From \(\bar{C}\) with benzoyl chloride in pyridine (1).]

- **D 2,6-Dichloro-3-methylphenyl benzenesulfonate:** thin lustrous pl. from alc., m.p. 70° (1). [From \bar{C} with benzenesulfonyl chloride in pyridine (1).] [Note proximity of the m.p. of this deriv. to that of the corresp. deriv. of 2,4-dichloro-3-methylphenol (3:1205).]
- **② 2,6-Dichloro-3-methylphenyl** p-toluenesulfonate: small pr. from alc., m.p. 92-92.5° (1). [From \bar{C} with p-toluenesulfonyl chloride in pyridine (1).]
- 3:0150 (1) Huston, Chen, J. Am. Chem. Soc. 55, 4217-4218 (1933). (2) Huston, Neely, J.Am. Chem. Soc. 57, 2178 (1935).

M.P. 27° (1)

Cryst. from lt. pet.

[For prepn. of \bar{C} from 2-amino-3,4-dimethylphenol (3-amino-o-4-xylenol) (1) via diazotization and use of Cu₂Cl₂ reaction (yield not stated) see (1).]

The nitration of \bar{C} has not been reported, and neither of the two possible mononitroderivs, nor the corresp. dinitro-deriv. is known.

- ---- 2-Chloro-3,4-dimethylphenyl acetate: unreported.
- 2-Chloro-3,4-dimethylphenyl benzoate: m.p. 87° (1).

3:0158 (1) Hinkel, Ayling, Bevan, J. Chem. Soc., 1928, 2531.

3: 0165
$$\beta$$
-PHENOXYETHYL CHLORIDE C_8H_9OCl Beil. VI - 142 $(\beta$ -Chloroethyl phenyl ether; ω -chlorophenetole) $O.CH_2.CH_2Cl$ VI_1 -(81) VI_2 -(144)

Insol. aq., very cas. sol. alc., ether, C6H6, lgr.

[For prepn. from β -phenoxyethyl alcohol (1:6518) + SOCl₂ + pyridine (88% yield (7)) see (7) (1); from sodium phenolate + ethylene dichloride (3:5130) (poor yield) see (5) (3); from ethylene chlorobromide see (6) (1)].

- \bar{C} + AlCl₃ + phthalic anhydride in CS₂ yields (9) o-[4(?)-(β -chloroethyl)-benzoyl]-benzoic ac., cryst. from C_6H_6 , m.p. 145° (9).
 - \bigcirc N-(\$\beta\$-Phenoxyethyl)tetrachlorophthalimide: rods from acetone, m.p. 155–156° (10) [From \bigcirc with K tetrachlorophthalimide (10).]

3:0165 (1) Jones, J. Chem. Soc. 1936, 1861. (2) Henry, Compt. rend. 96, 1233 (1883). (3) Clemo, Perkin, J. Chem. Soc. 121, 644-645 (1922). (4) Butler, Renfrew, Cretcher, Souther, J. Am. Chem. Soc. 59, 229 (1937). (5) Wohl, Berthold, Ber. 43, 2179 (1910). (6) Bentley, Haworth, Perkin, J. Chem. Soc. 69, 165 (1896). (7) Kirner, J. Am. Chem. Soc. 48, 2748 (1926), (8) Földi, Ber. 53, 1845 (1920). (9) Bruson, Eastes, J. Am. Chem. Soc. 60, 2504 (1938). (10) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934).

40

Beil. S.N. 24 3:0170 9-CHLORONONANUL-1 CH₂.(CH₂)₇.CH₂OH C₀H₁₉OCl (ω-Chloro-n-nonyl ĊI alcohol)

M.P. 28° (1) B.P. 140-145° at 20 mm. (1) at 14 mm. (2) 146.5°

Cryst, from lt. pet.

[For prepn. of \bar{C} from α, ω -nonamethylene glycol [Beil. I₂-(558)] (m.p. 46° (1)) with conc. HCl as directed (yields: 90% (1), 86% (2), 65% (3)) see indic. refs.]

C with thiophenol in aq. NaOH htd. 3 hrs. gives (1) 9-hydroxy-n-nonyl phenyl sulfide, cryst. from lt. pet., m.p. 60°. [This prod. with SOCl2 gives (1) 9-chloro-n-nonyl phenyl sulfide, cryst. from aq. alc. at low temp., m.p. 5° (1).

[C (1 mole) with Et₂NH (3-4 moles) in s.t. at 120-160° for 12-15 hrs. gives (90% yield (2)) 9-(diethylamino)nonanol-1, b.p. 161.5° at 12 mm., $D_4^{15.4} = 0.8635$, $n_D^{19} = 1.4574$ (2), cf. (5); this prod. with SOCl2 in C6H6 gives (2) (5) 9-(diethylamino)-n-nonyl chloride, b.p. 145° at 10 mm., $n_{\rm D}^{17.5} = 1.4535$ (2) (corresp. B.HCl, m.p. 85–86° (5)).]

C with morpholine gives (4) alm. quant. 9-(4-morpholinyl)nonanol-1, m.p. 31°, b.p. 173.0-173.5° at 5 mm. (corresp. N-(α -naphthyl)carbamate, m.p. 54.0-56.0° cor.). — \bar{C} (1 mole) with N-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (3) in alm. 100% yield (as salt) N-(9-hydroxy-n-nonyi)-N'-phenylpiperazine, m.p. 80.0-80.5° cor. (corresp. Nphenylcarbamate, m.p. 94.0-95.0° cor.).

- D 9-Chloro-n-nonyl N-phenylcarbamate: cryst. from dil. alc., m.p. 70.0-70.5° (3), 67° (1) (2).
- **D** 9-Chloro-n-nonyl N-(m-nitrophenyl)carbamate: m.p. 57° (2).

3:0170 (1) Bennett, Mosses, J. Chem. Soc. 1931, 1697-1701. (2) Altman, Rec. trav. chim. 57. 951-952 (1938). (3) Anderson, Pollard, J. Am. Chem. Soc. 61, 3439-3440 (1939). (4) Anderson, Pollard, J. Am. Chem. Soc. 61, 3440-3441 (1939). (5) Pyman, Levene (to Boot's Pure Drug Co.), Brit. 402,159, Dec. 21, 1933; Cent. 1934, I 2005; C.A. 28, 3081 (1934).

3:0172 12-CHLORODODECANOL-1 C₁₂H₂₅OCl Beil. S.N. 24 $(\omega\text{-Chloro-}n\text{-dodecyl})$ CH₂.(CH₂)₁₀.CH₂OH alcohol; ω-chlorolauryl alcohol)

M.P. 28° (1) B.P. 134° at 1 mm. (1)

Colorless cryst. from lt. pet.

[For prepn. of \bar{C} from α, ω -dodecamethylene glycol [Beil. I₂-(562)] (m.p. 83.5-84.5° (1)) with conc. HCl on htg. as directed (50% yield crude prod.) see (1).

12-Chlorododecyl N-phenylcarbamate: ndls. from pet., m.p. 66° (1).

3:0172 (1) Bennett, Gudgeon, J. Chem. Soc. 1938, 1679-1681.

3: 0175 trans-2-CHLOROCYCLOHEXANOL-1 C₆H₁₁OCl Beil. VI - 7 (trans-Cyclohexene chlorohydrin) OH VI₂-(12)

M.P. B.P. 29° (1) (2) 104–106° at 45 mm. (4)
$$D_{-}^{35} = 1.1233$$
 (3) $n_{D}^{35} = 1.4832$ (3) 27° (3) 93° at 26 mm. (3) 88–90° at 20 mm. (4) $D_{-}^{16} = 1.146$ (1) $n_{D}^{16} = 1.4850$ (1) 85–86° at 17 mm. (26) 84–85° at 16 mm. (2) (7) 87° at 15 mm. (1) 92° at 10 mm. (5)

[See also cis-2-chlorocyclohexanol-1 (3:9374).]

Both the two theoretically possible geometrical stereoisomers of 2-chlorocyclohexanol-1 are known. The single form obtained from cyclohexene (tetrahydrobenzene) by addn. of HOCl or from cyclohexene oxide by addn. of HCl is now regarded (3) as the *trans* isomer $\bar{\mathbf{C}}$. The *cis* form (3:9374) is obtd. by other methods.

Colorless pr. from mixt. of $C_6H_6+lgr.$ at low temp.; \bar{C} has characteristic odor, is vol. with steam.

[For prepn. of \bar{C} from cyclohexene (tetrahydrobenzene) (1:8070) with HOCl (yields: 70–73% (4), 70% (5)) (6) (7) (8) or with N-chlorourea (yield: 74% (26), 54% (9)) see indic. refs.; from cyclohexene oxide (see below) with conc. HCl or with ZnCl₂ in dry ether see (3); for probable formn. of \bar{C} from cyclohexene (1:8070) with EtOCl (3:7022) see (10); for formn. of a mixt. of both stereoisomeric 2-chlorocyclohexanols contg. 27–28% \bar{C} + 72–73% cis-isomer from 2-chlorocyclohexanone (3:0120) by reductn. with isopropyl MgCl, ter-butyl MgX, or cyclohexyl MgX see (3); for formn. of a mixt. (b.p. 78–80° at 12 mm.) of both isomers by hydrolysis of 2-chlorocyclohexanyl acetate see (11).]

C with aq. NaOH at room temp. gives (yields: 70-73% (12), 70-75% (5), 80% (9), 55% (13)) cyclohexene oxide (1,2-epoxycyclohexane) [Beil. XVII-21], b.p. 131.5° at 760 mm. [Note that reactn. of C with alk. is 300 times as fast as that of the cis isomer (3:9374) (use in detn. of proportion of C in mixts. of isomers), that the latter with alk. gives no epoxy cpd. but instead cyclohexanone, and finally that C can be separated from its isomer by conversion to cyclohexene oxide from which the remaining cis isomer can be sepd. by distn. (3).]

 \bar{C} with alk. or with alc. KCl is not converted to cis isomer (3) but \bar{C} on protracted htg. with HCl rearr. to a small extent to the cis isomer.

[For use of C as seed disinfectant see (15).]

The halogen atom of $\ddot{\mathbf{C}}$ is fairly reactive, but its replacement often involves rearr. of the cyclohexyl ring to a cyclopentyl ring.

[C on boilg, with dil. alc. slowly gives (1) trans-cyclohexanediol-1,2 [Beil VI-740] with cyclopentylformaldehyde (formylcyclopentane), the latter increasing in pres. of dil. H₂SO₄ or of CaCl₂ (1).]

[$\bar{\mathbf{C}}$ with NaOMe in MeOH yields (14) cis-2-methoxycyclohexanol-1 [Beil. VI-740], b.p. 181.5° at 760 mm., $D_{-}^{20}=1.015,\,n_{\mathrm{D}}^{20}=1.4605$ (14); $\bar{\mathbf{C}}$ with NaOEt in EtOH (14) (or $\bar{\mathbf{C}}$ in EtOH treated with Na in attempted reductn. (16) gives (87% yield (16)) cis-2-ethoxycyclohexanol-1 [Beil. VI-740], b.p. 187° at 760 mm., $D_{-}^{20}=0.982,\,n_{\mathrm{D}}^{20}=1.4563$ (14); $\bar{\mathbf{C}}$ with sodium n-propylate yields (14) 2-n-propoxycyclohexanol, b.p. 205° at 760 mm., $D_{-}^{20}=0.970,\,n_{\mathrm{D}}^{20}=1.4580$ (14); $\bar{\mathbf{C}}$ with sodium cyclohexanolate yields (14) 2-cyclohexanoxycyclohexanol, m.p. 50° (14).]

[C with C₆H₅.CH₂MgCl gives (54% yield (17)) benzyl-cyclopentyl-carbinol, b.p. 166-169° at 20 mm., m.p. 30° (3,5-dinitrobenzoate, m.p. 100.5-101.5° (17)). — C with excess MeMgI gives (50% yield (13)) mixt. of both cis and trans 2-methylcyclohexanols (1:6420). — C with cyclohexyl MgCl (cf. 3:8040) yields (18) cyclohexyl-cyclopentyl-carbinol, m.p.

34° (p-nitrobenzoate, m.p. 49-50°, 3,5-dinitrobenzoate, m.p. 102°, acid phthalate, m.p. 92-93°, N-phenylcarbamate, m.p. 122° (18)).]

[\bar{C} with conc. aq. NH₄OH shaken for 24 hrs. (19) or \bar{C} with NH₃ in alc. htd. in s.t. for 1 hr. (6) gives (yields: 71% (19), 61% (6)) cis-2-aminocyclohexanol [Beil. XIII-348], m.p. 65° (19) (6), b.p. 110° at 24 mm. (19). — \bar{C} with diethylamine (2 moles) htd. in s.t. at 150° for several hrs. (20) (or similarly with BuOH as solvent (21)) yields 2-(diethylamino)-cyclohexanol, b.p. 225° at 740 mm. (21), 224° at 730 mm. (20), $D_{25}^{25} = 0.9280$ (21), $n_{25}^{24} = 1.4659$ (21) (hydrochloride, m.p. 170.5–171.5° (21)). — \bar{C} with 5 pts. piperazine hydrate htd. 3 hrs. at 140° gives (22) both N,N'-bis-(2-hydroxycyclohexyl)piperazine, m.p. 205–206° (22), and N-(2-hydroxycyclohexyl)piperazine, m.p. 67–68° (22) (the latter separable by treatment of mixt. with CS₂ pptg. its dithiocarbamate).]

[$\bar{\mathbf{C}}$ also reacts as a secondary alcohol: e.g., $\bar{\mathbf{C}}$ with PCl₅ yields (14) 1,2-dichlorocyclohexane [Beil. V-22, V₁-(8)], b.p. 187–189°, $\bar{\mathbf{C}}$ with PBr₅ yields (14) 1-bromo-2-chlorocyclohexane, b.p. 94° at 17 mm., $D^{20} = 1.514$, $n^{20}_{D} = 1.5481$ (14).

C on oxidn. with K₂Cr₂O₇/H₂SO₄/AcOH gives (57% yield (9)) 2-chlorocyclohexanone (3:0120).

(Note: the following derivatives are listed as cis on the assumption of inversion during formation.)

- —— cis(?) 2-Chlorocyclohexanyl acetate: oil with odor like EtOAc, b.p. 95-96° at 11 mm. (23), 99-101° at 13 mm. (24), $D_{25}^{25} = 1.1182$ (23), $n_D^{25} = 1.46195$ (23). [From \bar{C} with AcCl at 10-20° (23) or in C_6H_6 (espec. in pres. of K_2CO_3 or $BaCO_3$) (70% yield (24)), or from cyclohexene (1:8070) with Ac_2O or with $Ac_2O + SO_2Cl_2$ in CHCl₃ (11). [This ester with MeOH + dry HCl gas yields \bar{C} (11). Cf. (25).]
- cis(?) 2-Chlorocyclohexanyl benzoate: lfts. from dil. alc., m.p. 120-121° (24). [From C with BzCl htd. 10 hrs. (70% yield) (24).]
- —— cis(?) 2-Chlorocyclohexanyl p-nitrobenzoate: cryst. from dil. alc., m.p. 240° dec. (24). [From Č with p-nitrobenzoyl chloride in dry ether or C₆H₆ + Na₂CO₃ refluxed 5 hrs. (70% yield) (24).]
- —— cis(?) 2-Chlorocyclohexanyl N-phenylcarbamate: m.p. 97-98° (2), 94-96° (17). [From C with phenyl isocyanate in lt. pet. (17).]
- —— cis(?) 2-Chlorocyclohexanyl N-(α -naphthyl)carbamate: m.p. 165° (3). [From \bar{C} with α -naphthyl isocyanate at 100° for 4 hrs (3)]
- Godchot, Mousseron, Granger, Compt. rend. 200, 748-749 (1933). (2) Godchot, Compt. rend. 176, 448 (1923). (3) Bartlett, J. Am. Chem. Soc. 57, 224-227 (1935). (4) Coleman, Johnstone, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 158-159 (1941). Coll. Vol. 1 (1st ed.) 151-153 (1932); 5, 31-32 (1925). (5) Kendall, Osterberg, Mackenzie, J. Am. Chem. Soc. 48, 1388-1389 (1926). (6) Osterberg, Kendall, J. Am. Chem. Soc. 42, 2621-2622 (1920). (7) Fortey, J. Chem. Soc. 73, 948 (1898). (8) Levine, Cass (to du Pont Co.), U.S. 2,119,485, May 31, 1938; Cent. 1938, II 952. (9) Detoeuf, Bull. soc. chim. (4) 31, 177-178 (1922). (10) Goldschmidt, Endres, Dirsch, Ber. 58, 574 (1925).
- (11) Friese, Dj'iang, Ber. 71, 667-670 (1938). (12) Osterberg, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 185-186 (1941); Coll. Vol. 1 (1st ed.), 179-180 (1932); 5, 35-36 (1925). (13) Godehot, Bedos, Bull. soc. chim. (4) 37, 1454-1457 (1925). (14) Mousseron, Granger, Compt. rend. 205, 327-328 (1937). (15) Consolidite Alkaliwerke, Ger. 607,010, Dec. 15, 1934; Cent. 1935, I 3835. (16) Kötz, Busch, J. prakt. Chem. (2) 119, 36 (1928). (17) Cook, Hewitt, Lawrence, J. Chem. Soc. 1936, 74-75. (18) Vavon, Mitchovitch, Compt. rend. 186, 703-705 (1928). (19) Wilson, Read, J. Chem. Soc. 1935, 1272. (20) Osterberg, Kendall, J. Am. Chem. Soc. 43, 1370-1371 (1921).
- (21) Heckel, Adams, J. Am. Chem. Soc. 49, 1305-1306 (1927).
 (22) Mousseron, Bull. soc. chim.
 (4) 51, 790-793 (1932).
 (23) Bedos, Compt. rend. 183, 562-565 (1926); Cent. 1926, II 2795.
 (24) Kötz, Merkel, J. prakt. Chem. (2) 113, 64-65 (1926).
 (25) Winstein, Buckles, J. Am. Chem. Soc. 65, 616 (1943).
 (26) Newman, Vander Werf, J. Am. Chem. Soc. 67, 235 (1945).

White ndls. from dil. alc.; eas. sol. alc., ether, C₆H₆.

[For prepn. of \bar{C} from *m*-chloroiodobenzene [Beil. V-220] by htg. with Cu powd. under various conditions (yield: 95% (5), 67% (2), 61% (1)) see indic. refs.; from 3,3'-dinitro-biphenyl with SOCl₂ in s.t. at 200–210° for 10 hrs. see (4); from 3,3'-dichloro-4,4'-diamino-biphenyl (3,3'-diaminobenzidine) [Beil. XIII-234, XIII₁-(67)] via tetrazotization and htg. with alc. see (6); from 3,3'-dichloro-2,4'-diaminobiphenyl via tetrazotization and treatment with H₃PO₂ see (3).]

Č on tetranitration, e.g., with mixt. of 5 pts. abs. HNO₃ + 20 pts. conc. H₂SO₄ for 2 hrs. at 100° {5}, yields {5} (7) 3,3'-dichloro-4,6,4',6'-tetranitrobiphenyl [Beil. V₁-(274)], m.p. 191° {5}, 189° (7), 184° {5}: note that this prod. appears to exist in two forms: when the lower-melting form is dislvd. in boilg. AcOH and pptd. with boilg. aq., or if it is allowed to solidify after fusion, the prod. has m.p. 191°; if the above AcOH soln. is slowly cooled, however, the prod. melts at 184° {5}. [This tetranitro-\bar{C} htd. with NaOMe in MeOH yields 3,3'-dimethoxy-4,6,4',6'-tetranitrobiphenyl, m.p. 244° {5}.] — [Note also that under some conditions {7} some 3,3'-dichloro-6,6'-dinitrobiphenyl [Beil. V-585, V₁-(274)], m.p. 170° {8} {7}, may form during nitration of \bar{C}.]

 \bar{C} on oxidn. with $CrO_3 + V_2O_5$ yields (3) m-chlorobenzoic acid (3:4392).

Weissberger, Sängewald, Z. physik. Chem. B-20, 155 (1933).
 Ullmann, Ann. 332, 54 (1904).
 Bellavita, Gazz. chim. ital. 65, 641 (1935).
 Mascarelli, Gatti, Gazz. chim. ital. 59, 808-809 (1929).
 van Alphen, Rec. trav. chim. 51, 362-363 (1932).
 Cain, J. Chem. Soc. 85, 7 (1904).
 Borsche, Scholten, Ber. 50, 610 (1917).
 Ullmann, Forgan, Ber. 34, 3804 (1901).

M.P. 29° B.P. 62-63° at 15 mm.

See 3:9504. Division C: Liquids with b.p. reported only at reduced pressure.

Hard cryst. with camphoraceous odor (3). [For crystallographic constants see (9).] [For prepn. from tetrachloroethylene (3:5460) (or pentachloroethane (3:5880) (2) (3)) + CHCl₃ (3:5050) by condensation in presence of AlCl₃ (88-93% yield (2), 85% yield (1) (10)) see (1) (2) (5) (7); from pentachloroacetone (3:6205) by htg. with PCl₅ in s.t. at 180° for 6-8 hrs. see (3); from dichloroacetyl chloride (3:5290) with AlCl₃ on warming (CO + CHCl₃ + HCl are also formed) see (11).]

Č has large mol. freezing-point lowering, viz., 120° (6). [For use in detn. of mol. wt. of org. compds. by f.p. lowering see (6).]

C on htg. especially in presence of catalysts such as ZnCl₂ yields HCl + hexachloropropene (3:6370); with CuCl a second reaction also occurs yielding HCl and tetrachloroethylene (3:5460). [For extensive study of these see (7) (8).]

 \bar{C} in alc. on titration with alk. gives (4) (3) an apparent Neut. Eq. of 285.5 because of loss of 1 HCl and formation of hexachloropropene (3:6370).

3:6269 (1) Prins, Rec. trav. chim. 54, 249-252 (1935). (2) Farlow, Org. Syntheses 17, 58-59 (1937). (3) Fritsch, Ann. 297, 314 (1897). (4) Prins, J. prakt. Chem. 89, 415-416 (1914).
 (5) Henne, Ladd, J. Am. Chem. Soc. 60, 2491-2495 (1938). (6) Böeseken, Benedictus, Rec. trav. chim. 37, 121-129 (1918). (7) Böeseken, van der Scheer, de Voogt, Rec. trav. chim. 34, 78-95 (1915). (8) Böeseken, Rec. trav. chim. 45, 467-468 (1926). (9) Gilta, Bull. soc. chim. Belg. 39, 585-587 (1930). (10) Bergmann, Haskelberg, J. Am. Chem. Soc. 63, 1438 (1941). (11) Böeseken, Rec. trav. chim. 29, 108-111 (1910); Böeseken, Prins, Cent. 1911, I 466.

3:0220 p-C	HLOROBEN	ZYL CHLORIDE	$C_7H_6Cl_2$	Beil. V - 297
		Cl	CH ₂ Cl	V_{1} -(152)
		`		V ₂ -(231)
M.P. 30°	(1)	B.P. 217-218°	at 772 mm. (8)	
29°	(2) (3) (4)	214°	at 758 mm. (3)	
(5) (6) (7) (35)	214°	(9) (10)	
28.2-2	28. 4° (12)	213-214°	(11)	
26°	(8)	114-117°	at 30 mm. (35)	
		114°	at 25 mm. (12)	
		113-115°	at 24 mm. (13)	
		106.5-107.5°	at 23 mm. (14)	
		117°	at 20 mm. (3)	•
		94-96°	at 14 mm. (8)	

Cryst. from alc., AcOH or lgr. — Eas. sol. warm but less so cold alc., very eas. sol. ether, AcOH, C_6H_6 , CS_2 . — Sublimes at ord. temp. — At b.p. under ord. press. tends to decompose (7). — \bar{C} has agreeable arom. odor, but strongly attacks mucous membrane (2).

[For prepn. of \bar{C} from benzyl chloride (3:8535) with Cl_2 in pres. of I_2 (11) (8) (15) or $SbCl_5$ (16) see indic. refs.; from p-chlorotoluene (3:8287) with $SO_2Cl_2 + Bz_2O_2$ in dark (70% yield) (35), with Cl_2 in light (2) (17) (11) (5) (4) (18) (19) or with $PbCl_4.2NH_4Cl$ (9) see indic. refs.; from toluene with Cl_2 see (20); for prepn. of \bar{C} from chlorobenzene (3:7903) with $CH_2O + HCl$ (36), with bis-(chloromethyl) ether (3:5245) or chloromethyl methyl ether (3:7085) (formed by use of formaldehyde or paraformaldehyde + chlorosulfonic acid + conc. H_2SO_4 or hexamethylenetetramine + conc. HCl (3)) as directed (50% yield (3)) (1) see indic. refs.]

[Č with phenol in toluene yields (21) 2-(p-chlorobenzyl)phenol, m.p. 60-61°, and p-chlorobenzyl phenyl ether, m.p. 85.5-86.5°; Č with 2,4-dichlorophenol in toluene yields (21) 2-(p-chlorobenzyl)-4,6-dichlorophenol, m.p. 69.5-70.5°, and p-chlorobenzyl 2,4-dichlorophenol at the property of the property

phenyl ether, m.p. 64.5-65.5°.]

[Č with phenol + AlCl₃ yields (21) 4-(p-chlorobenzyl)phenol, m.p. 87-87.5° (benzoate, m.p. 115-116°); Č with 2,6-dichlorophenol + AlCl₃ yields (21) 4-(p-chlorobenzyl)-2,6-dichlorophenol, m.p. 61.5-62.5° (benzoate, m.p. 116-117°).]

[For condens. of \bar{C} with p-chlorophenol (3:0475) and use of prod. as anti-moth prepn. see (22); for condens. of \bar{C} with o-cresol (1:1400) or its Na salt or with 3,5-dimethylphenol (sym-m-xylenol)(1:1455) and use of products as bactericides see (23); for condens. of \bar{C} with sulfonated phenol and use as tanning agent see (24); for condens. of \bar{C} with resorcinol (1:1530) + AlCl₃ in nitrobenzene yielding 55% 4-(p-chlorobenzyl)resorcinol see (25),

Č with Mg in dry ether yields (10) p-Cl.C₆H₄.CH₂.MgCl which with phenyl isocyanate as directed (10) gives p-chlorophenylacetanilide [Beil. XII-275], lfts. from alc., m.p. 168° cor. (26), 165−166° u.c. (10), 164.5° (27).

 \bar{C} on boilg. with aq. (2) (3) hydrolyzes to p-chlorobenzyl alc. [Beil. VI-444], m.p. 70-71° (3) (for rate see (7)); \bar{C} on boilg. with Pb(NO₃)₂ for 2 days (28) or on boilg. in 60% alc. with hexamethylenetetramine (29) yields p-chlorobenzaldehyde (3:0765), m.p. 46-47° (3).

 $\ddot{\mathbf{C}}$ with alc. KOH yields (30) p-chlorobenzyl ethyl ether [Beil. VI-444, VI₁-(222)], oil, b.p. 225° (for study of rate of reactn. see (31)); $\ddot{\mathbf{C}}$ with KOAc in abs. alc. yields (28) p-chlorobenzyl acetate [Beil. VI-445], b.p. 240° (28); $\ddot{\mathbf{C}}$ with boilg. alc. KCN yields (11) (28) (20) p-chlorobenzyl cyanide [Beil. IX-448], m.p. 30° (20), b.p. 265-267° (20), which on hydrolysis yields p-chlorophenylacetic acid (3:3135), m.p. 105° (20).

 \bar{C} with KI in alc. gives alm. quant. yield (17) p-chlorobenzyl iodide, m.p. 64° (17) (for study of rate of reactn. of \bar{C} with NaI (34) or KI (14) (6) in acetone see indic. refs.); \bar{C} with Na₂SO₃ yields (18) (13) sodium p-chlorotoluene- ω -sulfonate (corresp. sulfonamide,

m.p. 157° (18), corresp. sulfonanilide, m.p. 235° (18)).

[\bar{C} with thiourea (1 mole) in alc. refluxed 30 min. gives (37) S-(p-chlorobenzyl)isothiourea hydrochloride (p-chlorobenzyl isothiuronium chloride), cryst. from 1:1 conc. HCl + aq., m.p. 197°; this prod. is useful in identification of organic acids (37).]

 \bar{C} on oxidn. with CrO₃ (11) (3) or with KMnO₄ (1) (12) yields p-chlorobenzoic acid (3:4940), m.p. 236°.

3:0220 (1) Blanc, Bull. soc. chim. (4) 33, 317-318 (1923). (2) Jackson, Field, Ber. 11, 904-905 (1878). (3) Stephen, Short, Gladding, J. Chem. Soc. 117, 522 (1920). (4) Jones, J. Chem. Soc. 1938, 1416. (5) Weissberger, Sängewald, Z. physik. Chem. B-20, 147 (1933). (6) Bennett, Jones, J. Chem. Soc. 1935, 1818-1819. (7) Olivier, Rec. trav. chim. 41, 307-308 (1921). (8) Bergmann, Engel, Z. physik. Chem. B-15, 96 (1931-2). (9) Seyewetz, Travitz, Compt. rend. 136, 241 (1903). (10) Underwood, Gale, J. Am. Chem. Soc. 56, 217-2120 (1934).

Beilstein, Kuhlberg, Neuhoff, Ann. 148, 320-322 (1868).
 de Bruyne, Davis, Gross, J. Am. Chem. Soc. 55, 3938 (1934).
 Sprung, J. Am. Chem. Soc. 52, 1640-1649 (1930).
 Conant, Kirner, Hussey, J. Am. Chem. Soc. 47, 499 (1925).
 Olivier, Rec. trav. chim. 41, 419-421 (1921).
 Wertyporoch, Ann. 493, 162-163 (1932).
 van Raalte, Rec. trav. chim. 18, 388-392 (1899).
 Clutterbuck, Cohen, J. Chem. Soc. 123, 2508-2515 (1923).
 (19)

46 3:0220-3:0235

Zelinsky, Schering-Kahlbaum, Ger. 478,084, June 20, 1929; Cent. 1929, II 1216. (20) von Walther, Wetzlich, J. prakt. Chem. (2) 61, 187-188 (1900).

(21) Huston, Guile, Headley, Warren, Baur, Mate, J. Am. Chem. Soc. 55, 4639-4643 (1933). (22) Weiler, Berres (to I.G.), Ger. 542,069, Jan. 20, 1932; Cent. 1932, I 3014. (23) Klarmann, Gates (to Lehn and Fink, Inc.), U.S. 1,926,873, 1,926,874, Sept. 12, 1933; Cent. 1934, I 83. (24) I.G., Brit. 320,056, Oct. 31, 1929, Cent. 1930, I 590; Brit. 321,190, Nov. 28, 1929; Cent. 1930, I 1259. (25) Klarmann, von Wowern, J. Am. Chem. Soc. 51, 608 (1929). (26) Jenkins, Richardson, J. Am. Chem. Soc. 55, 1619 (1933). (27) Mehner, J. makt. Chem. (2) 62, 562 (1900). (28) Beilstein, Kuhlberg, Ann. 147, 345, 346, 352 (1868). (29) Mayer, English, Ann. 417, 78-79 (1918). (30) Naquet, Ann. Suppl. 2, 250-251 (1862/63).

(31) Franzen, Rosenberg, J. prakt. Chem. (2) 101, 334-335 (1921). (32) Kindler, Ann. 452, 119-120 (1927). (33) von Walther, Hirschberg, J. prakt. Chem. (2) 77, 377-378 (1903). (34) Westheimer, J. Am. Chem. Soc. 62, 1893 (1940). (35) Kharasch, Brown, J. Am. Chem. Soc. 61, 2146 (1939). (36) Tschunkur, Eichler (to I.G.), Ger. 509,149, Oct. 8, 1933; Cent. 1931, I 360

[C.A. 25, 711 (1931)]. (37) Dewey, Sperry, J. Am. Chem. Soc. 61, 3251-3252 (1939).

CHLOROBENZOTRICHLORIDE C7H4Cl4 Beil. V - 302 V_1 -(153) V_{2} -(234)

M.P. 30° **B.P. 260°**

Division B: Liquids, Section 1, $D_4^{20} > 1.15$. See 3:6880.

2,3-DICHLORODIOXANE-1,4 C₄H₆O₂Cl₂ Beil. S.N. 2668

M.P. 30° B.P. 100-101° at 24-25 mm.

See 3:9105. Division C: Liquids with b.p. only at reduced pressure.

3: 0235 α-CHLORO-ISOBUTYRIC ACID C₄H₇O₂Cl Beil. II-294 II1---II₂—

M.P. 31° (1) (2) B.P. 118° at 50 mm. (1) 28-30° (3) 116-118° at 50 mm. (4) 80-82° at 12 mm, (2)

Eas. sol. aq.

[For prepn. of C from isobutyric acid (1:1030) with Cl2 in light (5) (10) or with cat, as specified (6) (7), or with SO₂Cl₂ + dibenzoyl peroxide in CCl₄ (15% C + 85% β-chloro isomer) (3:9132) (3), see indic. refs.; from β,β,β -trichloro-ter-butyl alc. ("Chloretone") (3:2662) with aq. alk. (small yield together with other prods.) see (1) (2); from 2-chloro-2methylpropanol-1 (β-chloro-isobutyl alc.) (3:7305) by oxidn. with conc. HNO₃ see (8); from α -chloro-isobutyryl chloride (3:5385) by hydrolysis with ag. see (9),1

 \bar{C} with aq. alk. yields (5) α -hydroxy-isobutyric acid (1:0431) together with other products. — C with aq. Ca(OCl)₂ yields (4) chloroform (3:5050) + AcOH (1:1010) + CO₂. C with SOCl₂ (11) yields α-chloro-isobutyryl chloride (3:5385), b.p. 117-118°

- Methyl α -chloro-isobutyrate: b.p. 129° (see 3:7918).
- ---- Ethyl α -chloro-isobutyrate: b.p. 148° (see 3:8147).
- ---- α-Chloro-isobutyramide: unreported.
- D α -Chloro-isobutyr-anilide: m.p. 71–71.5° (3), 68° (12), 67–68° (13). [From α -chloro-isobutyryl chloride with aniline (3).] [Note that β -chloro-isobutyr-anilide has m.p. 109.0–109.5° (3).]
- \bigcirc α -Chloro-isobutyro-p-toluidide: unreported.

3:0235 (1) Ostropjatow, J. Russ. Phys.-Chem. Soc. 28, 50 (1896); Ber. 29, Referate, 908-909 (1896). (2) Jacob, Bull. soc. chim. (5) 7, 581-586 (1940); C.A. 36, 3507 (1942). (3) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940). (4) Ssuknewitsch, Tschilingarjan, Ber. 68, 1216 (1935). (5) Balbiano, Ber. 11, 1693 (1878); Gazz. chim utal. 8, 371 (1878). (6) Bass (to Dow Chem. Co.), U.S. 2,010,685; Aug. 6, 1935; Cent. 1936, I 880; C.A. 29, 6608 (1935). (7) Loder, Ries (to du Pont), U.S. 2,043,670; June 9, 1936, Cent. 1936, II 2229; C.A. 30, 5240 (1936). (8) Henry, Bull. soc. chim. (2) 26, 24 (1876). (9) Michael, Ber. 34, 4054 (1901). (10) Zal'kind, Markov, J. Applied Chem. (U.S.S.R.) 10, 1042-1044 (1937); Cent. 1938, II 2421; C.A. 32, 1652 (1938). [Note that C.A. has erroneously rendered isobutyric acid as "isocleic acid" throughout.] (11) Blaise, Montagne, Compt. rend. 174, 1555 (1922). (12) von Braun, Jostes, Munch, Ann. 453, 127-128 (1927). (13) Bischoff, Walden, Ann. 279, 113-114 (1894).

3: 0240 DIMETHYL meso- α , α' -DICHLOROSUCCINATE $C_6H_8O_4Cl_2$ Beil. II -619

COOCH₃

$$H_{-C}$$
 H_{-C}
 H_{-C}
 H_{-C}
 H_{-C}
 H_{-C}

M.P. 31.5-32° (1)

[For prepn. of \check{C} from $meso-\alpha,\alpha'$ -dichlorosuccinic acid (3:4930) in MeOH with HCl gas see (1).]

[For studies on dipole moment see (2).]

3:0240 (1) Kirchhoff, Ann. 280, 215 (1894). (2) Hassel, Naeshagen, Tids. Kemi Bergvesen 10, 126-127 (1930); Cent. 1931, I 893; C.A. 25, 1493 (1931).

M.P. 32°

[For prepn. from p-xylene, chloroacetyl chloride (3:5235) + AlCl₃, see (1) (2).] \bar{C} on oxidn. with alk. KMnO₄ gives (2) trimellitic ac. (1:0551), m.p. 228°.

3:0245 (1) Kunckell, Ber. 30, 579 (1897). (2) Collet, Bull. soc. chim. (3) 17, 509 (1897).

[See also 2-(chloromethyl)naphthalene (3:0747).]

Colorless cryst. from alc. at -15° (9); \tilde{C} on distn. tends to dec. and even in vacuum must be distd. with care (11), since it readily changes to a chlorine-free solid melting around 200° (11). — \tilde{C} is a powerful skin irritant (15).

The prepn. of \bar{C} has been much studied in recent years because of its importance in prepn. of the important plant-growth stimulant α -naphthylacetic acid (1:0728).

[For prepn. of $\bar{\bf C}$ from naphthalene + paraformaldehyde (or trioxymethylene) in AcOH with conc. HCl + H₃PO₄ (yields: 70-72% (15), 56.5% (20), 54% (21), 45% (15) (13)) see indic. refs.; from naphthalene + paraformaldehyde (or trioxymethylene) in AcOH with dry HCl gas (yields: 73-95% (3), denied (15), 51.5% (19), 31.6% (20)) or in AcOH/H₃PO₄/conc. HCl (74-77% yield (44)) cf. (15) see indic. refs.; from naphthalene + paraformaldehyde (or trioxymethylene) + ZnCl₂ in pet. ether (yields: 42% (4), 36% (17), 11% (4)) see indic. refs.: for prepn. of $\bar{\bf C}$ from aq. formaldehyde soln. (formalin) with conc. HCl + HCl gas see (8) (7), or with replacement of the HCl gas by conc. H₂SO₄ (yields: 68-70% (11), 60-70% (24) cf. (46), 60% (22), 33% (23)) (6) (26); for prepn. of $\bar{\bf C}$ from naphthalene + chloromethyl ether (3:7085) (50% yield) see (10); from naphthalene + sym.-dichlorodimethyl ether (3:5245) + H₃PO₄ (or H₂SO₄) see (27); note that in prepn. of $\bar{\bf C}$ by the preceding methods other products are also formed, notably 1,5-bis-(chloromethyl)naphthalene, cf. (2) (13), colorless cryst. from C₆H₆, m.p. 144° (2), b.p. 175-185° at 12 mm. (2), and di-(α -naphthyl)methane [Beil. V-728, V₁-(360)], cryst. from alc., m.p. 108° (13).]

[For prepn. of \bar{C} from α -methylnaphthalene (1:7600) with Cl_2 see (9) (12) (14); from α -naphthylmethylcarbinol [Beil. VI-667, VI₁-(320)] with SOCl₂ in toluene (79% yield (18)) or with conc. HCl on htg. in s.t. (30% yield (1)) see indic. refs.; from N-benzoyl- α -naphthylmethylamine (1) or N-benzoyl- α -naphthylmet

C on oxidn. with Cu(NO₃)₂ or C with hexamethylenetetramine refluxed in alc. gives

(yields: 60% (4), 59-60% (11), 48% (6)) α-naphthaldehyde [Beil. VII-400, 955, VII₁-(212)], b.p. 291-292° (28), 158-159° at 14 mm. (6) (oxime, m.p. 98° (11) (28), phenylhydrazone, m.p. 82° (11), p-nitrophenylhydrazone, m.p. 237° (11), 2,4-dinitrophenylhydrazone, m.p. 254° (11), semicarbazone, m.p. 224° (4), 219° (11)).

[\bar{C} on cat. hydrogenation (10) or on reductn. with Zn in alc. + dry HCl gas at 0° (68% yield (4)) (15), or by hydrolysis of α -C₁₀H₇.CH₂MgCl (see below) (80% yield (15)), gives α -methylnaphthalene (1:7600); note that reductn. of \bar{C} with 4Na + alc. is incomplete (4).]

[Č with Mg in dry ether + trace I₂ + trace MeI under N₂ readily gives (88–92% yield (15)) (18) corresp. α-C₁₀H₇.CH₂MgCl. This RMgCl cpd. shows many of usual reactns.: e.g., with aq. it gives (80% yield (15)) α-methylnaphthalene (1:7600); on carbonation with CO₂ and subsequent acidification it gives (59.4% yield (18)) α-naphthylacetic acid (1:0728); with phenyl isocyanate it gives (36% yield (18)) (15) α-naphthylacetic anilide, m.p. 156–157° (15); with α-naphthyl isocyanate it gives (15) α-naphthylacetic α-naphthalide, cryst. from xylene, m.p. 175–177° (15); with HgCl₂ it gives (15) α-naphthylcarbinyl-mercuric-chloride, cryst. from 80% alc., m.p. 126–128° (15); with Me2SO₄ it gives (55.1% yield (18)) α-ethylnaphthalene; with ClNH₂ it gives (47% yield (45)) α-(aminomethyl)-naphthalene. However, in certain cases, the RMgCl cpd. shows abnormal reactns.: e.g., with formaldehyde gas it gives (18) α-methyl-β-naphthylcarbinol + 1,2-di-(α-naphthyl)-ethane; with ethyl chloroformate it gives (18) ethyl α-methyl-β-naphthoate; with acetyl chloride it gives (poor yield (22)) 1,3-di-α-naphthyl-2-methylpropene-1. (Note also that the closely related α-C₁₀H₇.CH₂.COOMgCl with C₂H₅MgBr or iso-C₃H₇MgCl yields (29) α-naphthylmalonic acid, m.p. 151° dec.)]

[\bar{C} with diethyl malonate + NaOEt in alc. gives (yields: 82% (19), 80% (8)) diethyl α -naphthylmethylmalonate which upon hydrolysis gives (99% yield (19)) α -naphthylmethylmalonic acid, and this on htg. at 175° loses CO₂ giving (92% yield (19)) β -(1-naphthyl)propionic acid, m.p. 156.0–156.6° cor. (19) (methyl ester, m.p. 36° (2)). — \bar{C} with diethyl methyl-malonate + NaOEt in abs. alc. gives similarly (70.5% yield (21)) diethyl methyl-(α -naphthylmethyl)malonate, and ultimately (73% yield (21)) β -(1-naphthyl)isobutyric acid, m.p. 91.8–92.6° (21).]

[\bar{C} with KCN in dil. EtOH (yields: 87% (31), 40% (14) (20) (26) (30) (46) or with NaCN in MeOH (yield 85% (2)) gives α -naphthylacetonitrile, b.p. 183–187° at 13 mm., m.p. 31–32° (31), which on hydrolysis with AcOH/H₂SO₄/aq. (20) (2) (31) cf. (32) (46) gives α -naphthylacetic acid (1:0728).]

[\bar{C} with KOAc in AcOH refluxed for 2 hrs. gives (2) α -naphthylcarbinyl acetate, b.p. 134-136° at 1.5 mm. (2), which on hydrol. with alc. KOH gives α -naphthylcarbinol (see above). — \bar{C} with aq. Na₂SO₃ + NaOH gives (4) sodium 1-naphthylmethanesulfonate. — For study of nitration of \bar{C} see (42) (43).]

[\overline{C} with paraformaldehyde + ZnCl₂ + dry HCl gas in pet. ether gives (57% yield (4)) 1,5-bis-(chloromethyl)naphthalene, m.p. 144° (see above).]

[For reactn. of \tilde{C} with 2-(chloromethyl)naphthalene (3:0747) see (33); for reactn. of \tilde{C} with β -methylnaphthalene (1:7605) + AlCl₃ in CS₂ see (33).]

[For reactn. of \bar{C} with xylene in prepn. of synthetic resins see (34); for reactn. of \bar{C} with 2,2'-dihydroxydiethyl sulfide ("thiodiglyccl") in prepn. of textile assts. see (35); for condens. of \bar{C} with 2-hydroxy-3-naphthoic acid derivs. in prepn. of prods. for animalization of vegetable fibers see (37).]

[\bar{C} with aq. at 100° for 1½ hrs. is 21.5% hydrolyzed (1). — \bar{C} with MeOH gives (87% yield (36)) (2) methyl α -naphthylmethyl ether, b.p. 134° at 11 mm. (36), 101–103° at 1.5 mm. (2); \bar{C} with EtOH + CaCO₃ gives ethyl α -naphthylmethyl ether, b.p. 144.5° at 11 mm. (36); other alcs. behave similarly (36). — For reactn. of \bar{C} with cresol in prepn. of synthetic resins see (38).]

[\bar{C} with liq. NH₃ as directed (39) gives 72% α -naphthylmethylamine (N-benzoyl deriv., lfts. from alc., m.p. 154° (1)) + 20% bis-(α -naphthylmethyl)amine (N-benzoyl deriv., pr. from alc., m.p. 134° (1)). — \bar{C} with alc. NH₃ as directed (39) gives 11% of the above prim. amine + 38% of the above sec. amine + 47% tris-(α -naphthylmethyl)amine, cryst. from alc., m.p. 178° (39). — Note the use of the above bis-(α -naphthylmethyl)amine as useful reagent for quant. pptn. of HNO₃ (6). — For reactn. of \bar{C} with (CH₃)₂NH see (1). — \bar{C} with aniline at 100° gives (77% yield (4)) N-(α -naphthylmethyl)aniline, m.p. 67° (4) (corresp. nitroso cpd., m.p. 57° (4)).]

[\bar{C} with thiourea in alc. as directed (40) yields $S-(\alpha-\text{naphthylmethyl})$ isothiourea hydrochloride, m.p. 238° (40). — \bar{C} with p-toluenesulfonamide + alc. KOH refluxed 12 hrs. gives (57% yield (6)) $N,N-bis-(\alpha-\text{naphthylmethyl})p$ -toluenesulfonamide, cryst. from boilg. alc., m.p. 134° (6).]

[C with various polynitrophenols gives addn. prods.: e.g., that from pieric acid has m.p. 80-82° (41), 84° (4); that from 2,4,6-trinitro-m-cresol has m.p. 81.5-82° (41); that from 2,4,6-trinitroresorcinol (styphnic acid) has m.p. 112.5-113° (41).]

① N-(α -Naphthylmethyl)phthalimide (α -phthalimido- α -methylnaphthalene): white ndls. from hot alc., m.p. 174-175° (6). [From \bar{C} + Na phthalimide refluxed 6 hrs. in alc. in 82% yield (6).] — [Hydrolysis of this prod. with 4 pts. conc. HCl in s.t. 2 hrs. at 100° gives (86% yield (6)) α -naphthylmethylamine (see above).]

3:0250 (1) von Braun, Moldaenke, Ber. 56, 2167-2172 (1923). (2) Manske, Ledingham, Can. J. Research 17-B, 14-20 (1939); Cent. 1939, I 4037; C.A. 33, 5387 (1939). (3) Darzens, Levy, Compt. rend. 202, 73-75 (1936). (4) Anderson, Short, J. Chem. Soc. 1933, 485. (5) de Pommereau, Compt. rend. 175, 105-106 (1922). (6) Rupe, Brentano, Helv. Chem. Acta 19, 581-586 (1936). (7) Reddelien, Lange (to I.G.), Ger. 508,890, Oct. 2, 1930, Brit. 337,289, Nov. 20,1930; Cent. 1931, I 1830. (8) von Braun, Nelles, Ber. 66, 1470 (1933). (9) Davies, Oxford, J. Chem. Soc. 1931, 220-221. (10) Vavon, Bolle, Callin, Bull. soc. chem. (5) 6, 1032-1033 (1939).

Coles, Dodds, J. Am. Chem. Soc. 60, 853-854 (1938).
 Scherler, Ber. 24, 3929-3930 (1891).
 Lock, Walter, Ber. 75, 1158-1161 (1942).
 Wislicenus, Wren, Ber. 38, 506-507 (1905).
 Grummitt, Buck, J. Am. Chem. Soc. 65, 295-296 (1943).
 Ruggli, Burckhardt, Helv. Chim. Acta 23, 443 (1940).
 Blanc, Bull. soc. chim. (4) 33, 319 (1923).
 Gilman, Kirby, J. Am. Chem. Soc. 51, 3475-3478 (1929).
 Fieser, Gates, J. Am. Chem. Soc. 62, 2338 (1940).
 Cambron, Can. J. Research 17-B, 10-13 (1939).

(21) Fieser, Novello, J. Am. Chem. Soc. 62, 1856-1857 (1940). (22) Campbell, Anderson, Gilmore, J. Chem. Soc. 1940, 821. (23) Ruggli, Preuss, Helv. Chim. Acta 24, 1349-1350 (1941). (24) Shmuk, Guseva, Doklady Vsesoyuz Akad. Sci'sko-Khoz. Nauk im. Lenna 1940, No. 14, 3-5; C.A. 37, 2005 (1943). (25) Lange (to I.G.), Ger. 533,132, Sept. 9, 1931; Cent. 1931, II 2659. (26) Roblin, Hechenbleikne (to Arrerican Cyanamide Co.), U.S. 2,166,554, July 18, 1939; Cent. 1939, II 4354. (27) Cambron (to Hon. Advis. Council for Sci. and Ind. Research), U.S. 2,304,537, Dec. 8, 1942; C.A. 37, 2748 (1943). (28) Hinkel, Ayling, Beynon, J. Chem. Soc. 1936, 342. (29) Ivanov, Pchenitchy, Bull. soc. chim. (5) 1, 232 (1934). (30) Higginbottom, Short, Rec. trav. chim. 53, 1141 (1934).

(31) Briggs, Wilson, J. Chem. Soc. 1941, 501. (32) Buu-Hoi, Cagniant, Bull. soc. chim. (5) 9, 725-727 (1942); C.A. 37, 5393 (1943). (33) Clar, Lombardi, Gazz. chim. ital. 62, 542-544 (1932); C.A. 27, 81 (1933). (34) Deutsche Hydrierwerke, Brit. 465, 148, May 27, 1937; Cent. 1937, II 4397. (35) I.G., French 811,273, April 10, 1937; Cent. 1937, II 1083. (36) Reddelien, Lange (to I.G.), Ger. 516,280, Jan. 21, 1931; Cent. 1931, I 2396. (37) I.G., Brit. 462,290, April 1, 1937; Cent. 1937, II 2456. (38) Kränzlein, Voss, Brunner, Ger. 526,391, June 5, 1931; Cent. 1931, II 1203. (39) von Braun, Ber. 70, 979-980, 983-984 (1937). (40) Sprague, Johnson, J. Am. Chem. Soc. 59, 1839 (1937).

(41) Dermer, Proc. Oklahoma Acad. Sci. 22, 160-162 (1941); C.A. 37, 4376 (1943). (42) Izmail'skii, Kozin, Compt. rend. acad. sci. U.R.S.S. 28, 621-624 (1940); C.A. 35, 2882 (1941). (43) Izmail'skii, Compt. rend. acad. sci. U.R.S.S. 29, 98-102 (1940); C.A. 35, 3248 (1941). (44) Grummitt, Buck, Org. Syntheses 24, 30-32 (1944). (45) Coleman, Forrester, J. Am. Chem. Soc. 58, 28 (1936). (46) Shmuk, Guseva, J. Applied Chem. (U.S.S.R.) 14, 1031-1035 (1941); C.A. 39, 4069 (1945).

3:0255 m-CHLOROPHENOL

M.P. 32.8° (1) B.P. 215.5-217.1° (7)
$$D_{-}^{50} = 1.237$$
 (9) $n_{D}^{40} = 1.5565$ (1) 32° (2) 216° (17) $D_{-}^{25} = 1.268$ (9) 31-32° (3) 213-216° (8) 31° (4) 214° (6) cor. (16) 28.5° (5) 211-212° u.c. (5) 28° (6) 98° at 12 mm. (2)

 \bar{C} has odor like phenol (for study of strength of odor in aq. soln. see (10)). — \bar{C} in pres. of aq. has unusual tendency to form supersatd. solns. (11) (for temp./compn. data on soly. of \bar{C} in aq. or in C_6H_6 see (11)). — \bar{C} eas. discolors in air.

[For prepn. of \bar{C} from *m*-chloroaniline [Beil. XII-602, XII₁-(300)] via diazotization and subsequent reaction with aq. (yields: alm. quant. {12} {13}, 67% {1}, 64% {8}, 55% {4}, 50% {14}) {15} {5} {16} see indic. refs. (note that the process is sensitive to conditions and refs. indic. give valuable information on its control); for formn. of \bar{C} from *m*-dichlorobenzene (3:5960) with NaOMe in MeOH in s.t. at 180° for 30 hrs. see (17).

 \bar{C} like its isomers is sol. in conc. Na₂CO₃ soln. at room temp. and is repptd. by CO₂ (18). [For studies of value of ionization const. of \bar{C} in aq. or dil. MeOH or dil. EtOH see (19) (20) (6) (21) (22).]

 $\tilde{\mathbf{C}}$ on fusion with KOH yields (23) resorcinol (1:1530). — [For condens. of $\tilde{\mathbf{C}}$ with phthalic anhydride to yield 3,6-dichlorofluorane ("fluorescein chloride") [Beil. XIX-147] (impt. intermed. in prepn. of rhodamine dyes) see (12) (68).]

[Č conv. to dry Na salt and treated with CO₂ under press. yields after acidifn. (14) 6-carboxy-3-chlorophenol (4-chloro-2-hydroxybenzoic acid) (4-chlorosalicylic acid) (3:4908), ndls. from aq., m.p. 207° (14).]

[\bar{C} in the Reimer-Tiemann reactn. with alk. (or better Ca(OH)₂ + Na₂CO₃ (24)) and chloroform (24) or bromoform (25) yields both 6-aldehydo-3-chlorophenol (4-chlorosalicylaldehyde) (3:0960) and 4-aldehydo-3-chlorophenol (3:4280) in o/p ratio of 0.71 with CHCl₃ (26) (25) and 0.84 with CHBr₃ (25).] — [The 4-aldehydo-3-chlorophenol has also been obtd. (50% yield) from \bar{C} in C₆H₆ with HCl + HCN + ACl₃ (29).]

 $[\bar{C}]$ in aq. Na₂CO₃ soln couples with 1 equiv. of benzenediazonium chloride yielding (27) (18) 3-chloro-4-phenylazophenol, or.-yel. ndls. from 25% AcOH, m.p. 95° (27), or, on expos. to HCl, or.-red, m.p. 114° (27) (18); \bar{C} in aq. NaOH with 2 equivs. of benzenediazonium chloride yields (27) 3-chloro-2,4-bis (phenylazo)phenol, dark red-brn., m.p. 181°; no tris-azo cpds. appear to be formed (27). — For study of coupling of \bar{C} with p-nitrobenzene-diazonium bisulfate see (28).

 $[\bar{C} \text{ is } not \text{ reduced by HI in AcOH (30); for study of replacement of Cl by H with H₂ + Ni cat. at room temp. see (31).]$

[$\bar{\mathbf{C}}$ with p-aminophenol oxidized in alk. soln. with NaOCl yields (32) indochlorophenol; $\bar{\mathbf{C}}$ with p-aminodimethylaniline on oxidn. with NaOCl as directed (8) yields 3-chloro-N,N-dimethylindoaniline.]

[For condensation of \bar{C} with formaldehyde (33) or with benzaldehyde-o-sulfonic acid (34) and use of product as mothproofing agents see indic. refs.; for reactn. of \bar{C} with unsatd. halides in pres. of alk. yielding m-chlorophenyl alkenyl ethers which by rearr. yield corresp. substituted phenols used as bactericides see (35) (36).]

[For condens. of \tilde{C} with malic acid $(1:0450) + \text{conc. } H_2SO_4$ giving small yield of 7-chlorocoumarin [Beil. XVII-331] see (37); with ethyl acetoacetate $(1:1710) + H_2SO_4$

giving small yield of 7-chloro-4-methylcoumarin [Beil. XVII-336] see (37); with ethyl methylacetoacetate $(1:1712) + P_2O_5$ yielding 7-chloro-2,3-dimethylchromone [Beil. XVII₁-(177)] see (38).]

 \bar{C} with 3 moles Br₂ (in aq. KBr) gives 100% yield (39) 2,4,6-tribromo-3-chlorophenol, ndls. from dil. alc., m.p. 105-106° cor. (39) (methyl ether, m.p. 96° (39)); \bar{C} in 10% aq. KOH with 4 moles I₂ (in aq. KI) gives 2,4,6-triiodo-3-chlorophenol, ndls. from boilg. AcOH, m.p. 139-140° (39).

[C in dil. NaOH mixed with aq. NaNO₂ and acidified as directed (40) gives (40% yield (40)) (43) 3-chloro-4-nitrosophenol, m.p. 133° (40), 129.6° (41); on soln. in Na₂CO₃ and subsequent acidification this cpd. yields (40) (43) the isomeric 3-chlorobenzoquinone-4-monoxime, m.p. 184° dec. (40), cf. (42).

[C on mononitration with H₂SO₄ + NaNO₃ as directed (44) or C in AcOH with fumg. HNO₃ at 0° (45) gives (yield: 32% (45), 22% (44)) 3-chloro-6-nitrophenol [Beil. VI-238], volatile with steam, m.p. 41° (44), together with (60% yield (44)) 3-chloro-4-nitrophenol [Beil. VI-240], not volatile with steam, white ndls. from dil. HCl or aq., m.p. 121-122° (44). — Note that the two other position isomers although known have been obtd. indirectly: 3-chloro-2-nitrophenol, anhydrous form, yel. cryst., m.p. 45-47° (46) (47); monohydrate, colorless cryst. from pet. ether, m.p. 37.5-38° (46) (47) (44); 3-chloro-5-nitrophenol [Beil. VI-239] (48), m.p. 147°.]

[C on dinitration as directed (44) (49) gives 3-chloro-4,6-dinitrophenol [Beil. VI-259, VI₁-(128)], colorless cryst. from aq. or lt. pet., m.p. 92-93° (44). — Note that two other position isomers are known but prepd. indirectly: 3-chloro-2,6-dinitrophenol, white cryst. from dil. HCl, m.p. 114.5° (44) (49); 3-chloro-2,4-dinitrophenol, cryst. from aq., m.p. 138-140° (44) (49).]

Č on trinitration by soln. in 1½ pts. fumg. H₂SO₄ (27% SO₃) and treated in cold for 1 hr. with 10 pts. 70% HNO₃ (44) cf. (4) (50) yields 3-chloro-2,4,6-trinitrophenol [Beil. VI-292], cryst. from aq. or dil. H₂SO₄, m.p. 114° (44), 116° (4), 119° (50). — [Note that if \bar{C} is sulfonated prior to trinitration the isomeric 3-chloro-2,5,6-trinitrophenol, m.p. 112.5−113.5° (44), is obtd. (44).]

[For studies on the sulfonation of \bar{C} see (44) (51) (52) (53).]

[\bar{C} in MeOH/KOH with MeI yields (29) m-chlorophenyl methyl ether (m-chloroanisole) (8:6195).] [\bar{C} in EtOH/KOH with EtI gives (18) 3-chlorophenyl ethyl ether (m-chlorophenetole) (3:6323), b.p. 204–205° at 717 mm., $D_4^{20} = 1.1712$ (18) (for rate of formn. from sodium salt of \bar{C} with EtI in alc. soln. see (55)).]

- —— m-Chlorophenyl acetate [Beil. VI-185]: oil, b.p. 116.5° at 21 mm. (18), 108° at 12 mm. (57), $84-86^{\circ}$ at 2 mm. (57), m.p. -1.5° to -0.5° (18), $D_4^{20} = 1.2209$ (18). [From \bar{C} with $Ac_2O + NaOAc$ (18) or indirectly from m-chloroaniline via diazotiazation, etc. (57).] [For rate of reactn. of \bar{C} with AcBr see (58).]
- m-Chlorophenyl benzoate [Beil. IX-117]: pr. from dil. alc. or dil. acetone, m.p. 71-72° (18). [From C in 10% aq. Na₂CO₃ with BzCl (18); for study of rate of benzoylation of C see (59).]
- m-Chlorophenyl m-nitrobenzoate: ndls. from alc. or dil. acetone, m.p. 94-95° (18). [From C in alk. with m-nitrobenzoyl chloride (18).]
- m-Chlorophenyl p-nitrobenzoate: m.p. 99°.
- m-Chlorophenyl 3,5-dinitrobenzoate: m.p. 156°.
- —— m-Chlorophenyl benzenesulfonate: unrecorded.
- ---- m-Chlorophenyl p-toluenesulfonate: unrecorded.
- —— m-Chlorophenyl benzyl ether: m.p. 59°. [From C + benzyl-phenyl-dimethyl-ammonium chloride (60).]
- —— m-Chlorophenyl p-nitrobenzyl ether: unrecorded.

- —— m-Chlorophenyl 2,4-dinitrophenyl ether: pale yel. ndls. from alc., m.p. 75° (61). [From C in alk. with alc. 2,4-dinitrochlorobenzene (61).]
- m-Chlorophenoxyacetic acid: cryst. from aq., m.p. 108-110° u.c. (62), Neut. Equiv. 186.5. [From Č in aq. NaOH with chloracetic acid (62).]
- ---- m-Chlorophenyl N-phenylcarbamate: unrecorded.
- m m-Chlorophenyl N-(p-bromophenyl)carbamate: ndls. from C_6H_6 + EtOAc, m.p. 121-123° cor. (64). [From \ddot{C} + p-bromobenzazide in lgr. (64).]
- 0 m-Chlorophenyl N-(p-iodophenyl)carbamate: m.p. 138-139° (69). [From $\ddot{\textbf{C}}$ with p-iodobenzazide in hot lgr. (69).]
- m-Chlorophenyl N-(m-nitrophenyl)carbamate: m.p. 115-116° u.c., 117-118° cor. (70). [From C with m-nitrophenyl isocyanate in lgr. (70).]
- m m-Chlorophenyl N-(p-nitrophenyl)carbamate: pale yel. pr. from lgr., m.p. 144° cor. (65). [From $\ddot{\mathbf{C}}$ + p-nitrobenzazide in lgr. (65).]
- m-Chlorophenyl N-(3,5-dinitro-4-methylphenyl)carbamate: or.-yel. pr. from lgr., m.p. 170-172° u.c., 174-176° cor. (63). [From C with 3,5-dinitro-4-methylbenzazide in lgr. (63).]
- \bigcirc m-Chlorophenyl N-(α -naphthyl)carbamate: cryst. from lgr., m.p. 157-158° (66). [From $\bar{C} + \alpha$ -naphthyl isocyanate in lgr. (66).]
- m-Chlorophenyl N-(β-naphthyl)carbamate: pr. from igr., m.p. 114-115° u.e., 116-117° cor. (67). [From C + β-naphthyl isocyanate (or azide) in lgr. (67).]
- ---- m-Chlorophenyl N,N-diphenylcarbamate: unreported.
- 3:0255 (1) Holleman, Rinkes, Rec. trav. chim. 30, 81-82, 86 (1911); 42, 1092 (1923). (2) Kuhn, Wassermann, Helv. Chim. Acta 11, 14 (1928). (3) Williams, Fogelberg, J. Am. Chem. Soc. 52, 1358 (1930). (4) Seekles, Rec. trav. chim. 42, 76-77 (1923). (5) Uhlemann, Ber. 11, 1161-1162 (1878). (6) Bennett, Brooks, Glasstone, J. Chem. Soc. 1935, 1523. (7) Kohlrausch, Pongratz, Monatsh. 65, 202 (1935). (8) Fieser, Thompson, J. Am. Chim. Soc. 61, 382-383 (1939). (9) Thole, Mussell, Dunstan, J. Chem. Soc. 101, 1115 (1913). (10) Holleman, Rec. trav. chim. 37, 106 (1918).
- (11) Sidgwick, Turner, J. Chem. Soc. 121, 2256-2263 (1922). (12) Hodgson, J. Soc. Dyers Colourists 42, 175-179 (1926). (13) British Dyestuffs Corp., Ltd., & Hodgson, Brit. 200,714, Aug. 9, 1923; Cent. 1925, II 2297. (14) Varnholt, J. prakt. Chem. (2) 36, 27-28 (1887). (15) Tschunkur, Herdieckhoff (to L.G.), Ger. 497,412, May 9, 1930; Cent. 1930, II 984. (16) Beilstein, Kurbatow, Ann. 176, 45 (1875). (17) Holleman, de Mooy, Rec. trav. chim. 35, 19, 27 (1915). (18) Wohlleben, Ber. 42, 4371-4373 (1909). (19) Murray, Gordon, J. Am. Chem. Soc. 57, 110-111 (1935). (20) Schwarzenbach, Egli, Helv. Chim. Acta 17, 1181 (1934).
- Hodgson, Smith, J. Chem. Soc. 1939, 263-264. (22) Jenkins, J. Chem. Soc. 1939, 1137-1140. (23) Tijmstra, Chem. Weekblad 5, 96-101 (1908), Cent. 1908, I 1051. (24) Hodgson, Jenkinson, J. Chem. Soc. 1927, 1740-1742. (25) Hodgson, Jenkinson, J. Chem. Soc. 1929, 1641-1642. (26) Hodgson, Jenkinson, J. Chem. Soc. 1929, 469-471. (27) Hodgson, Turner, J. Chem. Soc. 1942, 433-435. (28) Richardson, J. Chem. Soc. 1937, 1363-1365. (29) Gattermann, Ann. 357, 334, 349 (1907). (30) Shoesmith, Hetherington, Slater, J. Chem. Soc. 125, 1317-1318 (1924).
- (31) Kelber, Ber. 54, 2255-2260 (1921). (32) Heller, Ann. 418, 270-271 (1918). (33) Weiler, Berres, Wenk, Stötter (to I.G.), Ger. 536,551, Oct. 24, 1931; Cent. 1932, I 3013. (34) I.G., Austrian 124,284, Aug. 25, 1931; Cent. 1933, II 375. (35) Deichsel (to Winthrop Chem. Co.), U.S. 2,002,447, May 21, 1935; Cent. 1935, II 2581; C.A. 29, 4376 (1935). (36) Deichsel (to I.G.), Brit. 443,113, March 19, 1936; Cent. 1937, I 384; C.A. 30, 4873 (1936). (37) Clayton, J. Chem. Soc. 93, 2021-2022 (1908). (38) Simonis, Schuhmann, Ber. 50, 1146 (1917). (39) Kohn, Zandmann, Monatsh. 47, 362, 366 (1926). (40) Hodgson, Kershaw, J. Chem. Soc. 1929, 1553, 1555.
- (41) Hodgson, Moore, J. Chem. Soc. 123, 2502-2503 (1923). (42) Hodgson, Nicholson, J. Chem. Soc. 1940, 1268. (43) British Dyestuffs Corp., Ltd., & Hodgson, Brit. 206,734, Dec. 6, 1924; Cent. 1925, II 2094. (44) Hodgson, Moore, J. Chem. Soc. 127, 1599-1604 (1925). (45) Roberts, Rhys, J. Chem. Soc. 1937, 41. (46) Hodgson, Moore, J. Chem. Soc. 1926, 156, 156, 158. (47) Hodgson, J. Soc. Dyers Colourists, 43, 73 (1927). (48) Hodgson, Wignall, J. Chem. Soc. 1926, 2077. (49) Hodgson, Kershaw, J. Chem. Soc. 1930, 2169-2171. (50) Tijmstra, Rec. trav. chim. 21, 293 (1902).
 - (51) Hodgson, Kershaw, J. Chem. Soc. 1930, 1419-1425; 1929, 2918, 2923. (52) Schoepfle.

Van Natta, Clarkson, J. Am. Chem. Soc. 50, 1174 (1928). (53) Schlubach, Mergenthaler, Ber. 58, 2734 (1925). (54) Ghaswalla, Donnan, J. Chem. Soc. 1936, 1344. (55) Goldsworthy, J. Chem. Soc. 1926, 1254. (56) Réverdin, Eckhard, Ber. 32, 2626 (1899). (57) Haller, Schaffer, J. Am. Chem. Soc. 55, 4954-4955 (1933); U.S. 1,933,975, Nov. 7, 1933; Cent. 1934, I 948. (58) Bassett, J. Chem. Soc. 1931, 2516-2518. (59) Bernoulli, St. Goar, Helv. Chim. Acta 9, 755 (1926). (60) Baw, J. Indian Chem. Soc. 3, 101-104 (1926).

(61) Bost, Nicholson, J. Am. Chem. Soc. 57, 2368-2369 (1935). (62) Koelsch, J. Am. Chem. Soc. 53, 304-305 (1931). (63) Sah, Rec. trav. chim. 58, 587-588 (1939). (64) Sah, Cheng, Rec. trav. chim. 58, 596-599 (1939). (66) French, Wirtel, J. Am. Chem. Soc. 48, 1736-1739 (1926). (67) Sah, Rec. trav. chim. 58, 454-458 (1939). (68) British Dyestuffs Corp., Ltd., & Hodgson, Brit. 205,254, Nov. 8, 1923; Cent. 1924, I 711. (69) Sah, Young, Rec. trav. chim. 59, 357-363 (1940). (70) Sah, Woo, Rec. trav. chim. 58, 1014-1015 (1939).

3: 0270 d,l- β -CHLORO-n-VALERIC ACID $C_5H_9O_2Cl$ Beil. S.N. 162 CH_3 -CH₂-COOH Cl

M.P. 33° (1) B.P. 112° at 10 mm. (1) $D_4^{20} = 1.1484$ (1) $n_D^{20} = 1.4462$ (1)

[For prepn. of C from propylidene-acetic acid (penten-2-oic acid-1) [Beil. II-426, II₁-(191), II₂-(399)] with dry HCl gas at 20° for 2 days (100% yield) see (1).]

- ---- Methyl β-chloro-n-valerate: unreported.
- Ethyl β -chloro-n-valerate: b.p. 189° see (3:8629).
- —— β-Chloro-n-valeramide: unreported.
- ----- β-Chloro-n-valeranilide: unreported.
- ----- β-Chloro-n-valero-p-toluidide: unreported.

3:0270 (1) Schjanberg, Ber. 70, 2385-2391 (1937).

3:0280 CHLOROMALEIC ANHYDRIDE

Cl—C—C

O

H—C—C

O

H—C—C

O

M.P. B.P. 33° (1) 196.3° cor. (2)
$$D_{25}^{25} = 1.5421$$
 (2) $n_{\text{He}}^{16.7} = 1.50594$ (1 34.5° (2) (3) 194° $D_{4}^{15} = 1.5427$ (1) $n_{\text{He}}^{13.9} = 1.50933$ (1 150–151° at 210 mm. (2) 95° at 25 mm. (3A) 87° at 14 mm. (1) 78° at 8 mm. (1)

C usually observed as a colorless oil. On cooling and scratching it solidifies to a cryst. mass fusing about 0° and suddenly changing to a hard cryst. form, m.p. 34.5°, with evoln. of ht. (2) (3).

[For prepn. from chlorofumaric ac. (3:4853) by distn. with P_2O_5 see (1) (4), by distn. with $POCl_3$ see (5) (such products are claimed by (1) to be impure); for prepn. by distn. with AcCl see (2); for still other methods see Beil. XVII-434.]

[For Diels-Alder addn. of \bar{C} to cyclopentadiene-1,3 (1:8030) giving 71% yield of prod. m.p. 161°, or to anthracene (1:7285), giving 56% yield of prod., m.p. 157°, see (7); note, however, that \bar{C} with isoeugenol (1:1785) or with isosafrole (1:7610) not only adds but also loses HCl giving (8) derivs. of 3-methyl-3,4-dihydronaphthalene-1,2-dicarboxylic anhydride.]

 \bar{C} reacts with aq. evolving ht. and upon evapn. yields (3) (3A) (6) chloromaleic ac. (3:3432), cryst. from mixt. of CHCl₃ + AcOH (6), which after drying at 100° have m.p. 114-115° (6).

3:0280 (1) von Auwers, Harres, Bcr. 62, 1686-1687 (1929).
 (2) Perkin, J. Chem. Soc. 53, 703-705 (1888).
 (3) van der Riet, Ann. 280, 227 (1894).
 (3A) Zincke, Fuchs, Ber 26, 508 (1893).
 (4) Walden, Ber. 30, 2885-2886 (1897).
 (5) Thomas-Mamert, Bull. soc. chim. (3) 13, 847 (1895).
 (6) Michael, Tissot, J. prakt. Chem. (2) 52, 331 (1895).
 (7) Synerholm, J. Am. Chem. Soc. 67, 1229-1230 (1945).
 (8) Synerholm, J. Am. Chem. Soc. 67, 345 (1945).

3:0290 TRICHLOROMETHYL TRICHLOROACETATE C₃O₂Cl₆ Beil. III -17 (Perchloromethyl acetate) Cl₃C.O.CO.CCl₃ III₁— III₂—

M.P. 34° (1) B.P. 191-192° (1)
$$D_4^{35} = 1.67331$$
 (1) $73-74$ ° at 10 mm. (1)

Sol. without decompn. in other, CHCl₃, C₆H₆, or pet. eth.

[For prepn. (71% yield (3)) by electrolysis of potassium trichloroacetate (3) or mixt. of Na and Zn trichloroacetates (2) (4) see (2) (3) (4); for formn. from methyl trichloroacetate on chlorination see (1).

 \bar{C} with aq. decomposes to trichloroacetic acid (3:1150) + phosgene (3:5000) + HCl (2) (4).

 \bar{C} with aniline yields N,N'-diphenylurea + aniline trichloroacetate + aniline hydrochloride (2).

 \overline{C} with AlCl₃ yields hexachloroethane (3:4835) + $\overline{CO_2}$ (5).

3:0290 (1) Anschütz, Emery, Ann. 273, 59 (1893). (2) Elbs, Kratz, J. prakt. Chem. (2) 55, 502-505 (1897). (3) Gibson, Proc. Roy. Soc. Edunburgh 44, II 140-152 (1924); C.A. 18, 3041 (1924). (4) Fichter, Fritsch, Müller, Helv. Chim. Acta 6, 506 (1933). (5) Jaeger, Cent. 1912, I 1817.

M.P. 34°	(2) (3) (4) (5)	B.P. 273.7-273.8	° at 738 mm.	(7)
33°	(6)	267-268°		(2)
32.2	3° (7)	210-211°	at 150 mm.	(8)
31°	(15)	165-170°	at 28 mm.	(3)
		154°	at 12.5 mm.	(15)
		150-155°	at 10 mm.	(5)

Cryst. from alc. — Volatile with steam (6). — Sol. alc., CCl_4 (7); very sol. C_6H_6 or pet. eth. (2).

[For prepn. (36.8% yield $\{7\}$) (together with other products) from biphenyl by direct chlorination in presence of Fe or other cat. see $\{7\}$ (2) (8) (9); for prepn. (25-38% yield (5)) from diazotized o-chloroaniline + C₆H₆ see $\{5\}$ (4); for prepn. (60% yield (15)) from diazotized o-aminobiphenyl via Cu₂Cl₂ method see $\{15\}$ (10).]

[\bar{C} with aq. 15-30% NaOH at 300-400° (16) in pres. of Cu (17), or \bar{C} with aq. Na₂ $\bar{C}O_3$ + Cu at 300° (12), or \bar{C} with aq. vapor over cat. at 525-560° (11), gives 2-hydroxybiphenyl (1:1440) (16) (17) (11) or its mixt. with 3-hydroxybiphenyl (1:1475) (12).]

[For reactn. of \tilde{C} with phthalic anhydride + AlCl₃ yielding o-[4-(2'-chlorophenyl)-benzoyl]benzoic acid, short rods from AcOH, m.p. 190° cor., see (13) (14).]

 \tilde{C} (12 g.) on mononitration at 40° with a mixt. of conc. HNO₃ (D=1.43) (10 g.) + conc. H₂SO₄ (15 g.) gives (25% yield (3)) (18) of 2-chloro-4'-nitrobiphenyl, cryst. from pet. ether, m.p. 74-75° (18), 73-74° (3) accompanied by (50% yield (3)) of 2-chloro-4',5'-dinitrobiphenyl (see next paragraph). [Note that only one other nitro-2-chlorobiphenyl isomer is known, viz., 2-chloro-2'-nitrobiphenyl, m.p. 71° (19), and this has been prepd. only by indirect means (19).]

 $\tilde{\mathbb{C}}$ on dinitration (see above) or 2-chloro-4'-nitrobiphenyl on further nitration with fumg. HNO₃ (D=1.5) at 100° for 5 min. gives (18) 2-chloro-4',5'-dinitrobiphenyl, cryst. from AcOH, m.p. 159-160° (18), 158-159° (3) (formerly erroneously regarded (3) as the 2-chloro-3',4'-dinitro isomer). [Note that two other isomeric dinitro-2-chlorobiphenyls are known, viz., 2-chloro-4,4'-dinitrobiphenyl, m.p. 153-154° (18), and 2-chloro-3,5-dinitrobiphenyl, m.p. 115-116° (20), 119° (21), but both have been obtd. only by indirect means.] [$\tilde{\mathbb{C}}$ with Mg in evacuated hard-glass tube at 200-215° for 6 hrs. gives (32% yield (15)) o-xenyl MgCl.]

C on oxidn. with CrO₃ + AcOH yields (2) o-chlorobenzoic acid (3:4150), m.p. 141°.

3:0360 (1) Hale, J. Am. Chem. Soc. 54, 4458-4459 (1932). (2) Kramers, Ann. 189, 142-145 (1877). (3) Mascarelli, Gatti, Gazz. chim. ital. 63, 656-660 (1933). (4) Weissberger, Sangowald, Z. physik. Chem. B-20 155 (1933). (5) Elks, Haworth, Hey, J. Chem. Soc. 1940, 1284-1286. (6) Bell, J. Chem. Soc. 128, 2773. (7) Jenkins, McCullough, Booth, Ind. Eng. Chem. 22, 31-34 (1930). (8) Britton, Stoesser (to Dow Chem. Co.) U.S. 1,835,754, Dec. 8, 1931; Cent. 1932, I 1440; C.A. 26, 995 (1932). (9) Britton, Stoesser (to Dow Chem. Co.), U.S. 1,890,427, Dec. 6, 1932; Cent. 1933, II 2894; C.A. 27, 1642 (1933). (10) Mascarelli, Gatti, Pirona, Atti accad. Lincei (6) 14, 506-511 (1931); Cent. 1932, I 2713 [C.A. 26, 4322 (1932)].

(11) Booth (to Swann Research, Inc.), U.S. 1,925,367, Sept. 5, 1933; Cent. 1934, I 128 [C.A. 27, 5342 (1933)]. (12) Britton (to Dow Chem. Co.), U.S. 1,959,283, May 15, 1934; Cent. 1934, II 1688; C.A. 28, 4433 (1934). (13) Groggins, Ind. Eng. Chem. 22, 622-623 (1930). (14) Groggins, U.S. 1,786,526-1,786,529, Dec. 30, 1930; Cent. 1931, II 3157-3158. (15) Zaheer, Faseeh, J. Indian Chem. Soc. 21, 27-28 (1944); C.A. 39, 291 (1945). (16) du Pont Co., Brit. 496,319, March 22, 1934; Cent. 1934, I 3801 [C.A. 28, 4745 (1934)]. (17) Britton (to Dow Chem. Co.), U.S. 1,996,744, April 9, 1935; Cent. 1935, II 1962 [C.A. 29, 3354 (1935)]. (18) Case, J. Am. Chem. Soc. 65, 2137-2138 (1943). (19) Mascurelli, Gatti, Atti accad. Lincei (6) 13, 887-892 (1931); Cent. 1931, II 2605; not in C.A. (20) Bradsher. Amore, J. Am. Chem. Soc. 66, 1283-1284 (1944). (21) Borsche, Scholten, Ber. 50, 602-603 (1917).

3: 0310 m-XYLYLENE (DI)CHLORIDE $(\omega,\omega'\text{-Dichloro-}m\text{-xylene})$ CH₂Cl $C_8H_8Cl_2$ Beil. V - 373 V₁— V₂—(291) .

M.P. 34.2° (1) B.P. 250-255° (1) 32-34° (4)

Cryst. which show remarkable ability to supercool without solidification. — Č sublimes. — Sol. in alc., ether, CHCl₃, pet. eth.

[From prepn. from m-xylyleneglycol + boilg. conc. HCl see (1); from m-xylene (1:7420) + PCl₅ at 190° see (2); for formn. of \bar{C} (3%) during chloromethylation of benzyl chloride (3:8535) see (4).]

 \bar{C} on htg. with K phthalimide yields (3) N,N'-m-xylylenediphthalimide [Beil. XXI-496], white ndls. from AcOH, m.p. 237° (3).

3:0310 (1) Colson, Ann. chim. (6) 6, 113-114 (1885). (2) Colson, Gauthier, Ann. chim. (6) 11, 23 (1887). (3) Posner, Schreiber, Ber. 57, 1137 (1924). (4) Kulka, Can. J. Research 23-B, 107 (1945).

3: 0320 1,2-DICHLORONAPHTHALENE
$$C_{10}H_6Cl_2$$
 Beil. V - 542 V_{1^-} (262) C_1 C_1 C_2 C_2 C_3 C_4 C_4 C_4 C_5 C_4 C_5 C_6 C_7 C_8 C_8 C_9 C_9

M.P. B.P. 35° (1) 295–298° (5)
$$D_4^{48.5} = 1.3147$$
 (6) $n_D^{48.5} = 1.63375$ (6) (2) (10) 151–153° at 19 mm. (6) 34–35° (3) (4) 34° (7) (8) 33–34° (5)

Colorless cryst. from alc. (4). — Volatile with steam (2).

[For prepn. of \bar{C} from 2-chloronaphthalenesulfonyl chloride-1 on distn. with excess PCl₅ (1) or on htg. with 3 moles PCl₅ at 160–165° for 5 hrs. (36% yield (5)); from 2-amino-1-chloronaphthalene (3) (4) or 2-amino-1-nitronaphthalene (2) via diazotization and use of Cu₂Cl₂ see indic. refs.; from 1-chloronaphthol-2 (3:1700) by htg. with PCl₅ see (8); from potassium 7,8-dichloronaphthalenesulfonate-2 + H₃PO₄ on distn. with superheated steam see (7).]

[\bar{C} on nitration with a mixt. of equal pts. fumg. HNO₃ (D=1.45) + conc. H₂SO₄ gives (9) 1,2-dichloro-x,y-dinitronaphthalene, pale yel. ndls. from hot AcOH, m.p. 169.5° (9).]

[C on monosulfonation with ClSO₃H in CS₂ yields (10) a mixt. of 1,2-dichloronaphthalene-sulfonic acid-5 [Beil. XI-163] (corresp. sulfonyl chloride, m.p. 106°, corresp. sulfonamide, m.p. 217°) and 1,2-dichloronaphthalenesulfonic acid-6 [Beil. XI-182] (corresp. sulfonyl chloride, m.p. 167°, corresp. sulfonamide, m.p. 190°.]

C on oxidn. with CrO₃/AcOH yields (9) 5,6-dichloronaphthoquinone-1,4 [Beil. VII-730], yel. ndls., m.p. 181° (9).

3:0320 (1) Armstrong, Wynne, Chem. News 73, 55 (1896). (2) Clemo, Cockburn, Spence, J. Chem. Soc. 1931, 1272. (3) Cleve, Ber. 20, 1991 (1887). (4) Weissberger, Sängewald, Hampson, Trans. Faraday Soc. 30, 890 (1934). (5) Beattie, Whitmore, J. Am. Chem. Soc. 55, 1546-1548 (1933). (6) von Auwers, Frühling, Ann. 422, 194, 200 (1921). (7) Cleve, Ber. 25, 2489 (1892). (8) Cleve, Ber. 21, 896 (1888). (9) Hellström, Ber. 21, 3268-3269 (1888). (10) Armstrong, Wynne, Chem. News 60, 58 (1889); 61, 274 (1890).

3: 0330 CINNAMOYL CHLORIDE
$$C_9H_7OCl$$
 Beil. IX - 587 IX₁-(233)

M.P. B.P. 36° (1) (2) 257.5° at 760 mm. (2) $D_4^{45.3} = 1.1617$ (15) $n_D^{42.5} = 1.61364$ (15) (5) (6) 170-171° at 58 mm. (9) $D_-^{37.6} = 1.1632$ (7) (9) 154° u.c. at 25 mm. (6) $n_D^{37.6} = 1.6202$ (7) 35° (7) (14) 131° at 20 mm. (15) 34° (8) 147° at 16 mm. (10) 136-137° at 15 mm. (3) (5) 130° at 14 mm. (11) 130° at 12 mm. (4) (12) 136° at 11 mm. (13) 131° at 11 mm. (14) 127.3-127.6° at 8 mm. (15) 101° at 8 mm. (15) 101° at 2 mm. (16)

58

White cryst., sol. in CCl₄ and in pet. eth. — Note that the name cinnamoyl chloride avoids confusion with cinnamyl chloride, C₆H₅.CH=CH.CH₂Cl (3:0010).

[For prepn. of \bar{C} from cinnamic acid (1:0735) with PCl₅ (86% yield (17)) (9) (18), with PCl₃ (19) (15) (6), with PCl₃ + ZnCl₂ (86% yield (17)), with SOCl₂ alone (yields: 98% (17), 90–95% (13), 89% (11)) (62) (1) (2) (16) or in CCl₄ (80% yield (3)), with COCl₂ (3:5000) in pres. of tertiary bases (20), with p-toluenesulfonyl chloride in pyridine or diethylaniline (21), see indic. refs.; from sodium salt of cinnamic acid (1:0735) with oxalyl (di)chloride (3:5060) in C₆H₆ (75–90% yield) see (22).]

[\bar{C} in CCl₄ with Cl₂ in dark gives (5) an oily prod. which with aq. hydrolyzes to a mixt. of cinnamic acid dichloride [Beil. IX-514, IX₁-(200)], m.p. 167°, and allocinnamic acid dichloride [Beil. IX-514], m.p. 84°; \bar{C} in CCl₄ with Cl₂ in direct sunlight, however, yields (5) α,β -dichloro- β -phenylpropionyl chloride (the acid chloride of cinnamic acid dichloride), ndls. from pet. eth., m.p. 54-55° (5), 55° (23).]

[Č is not reduced by copper hydride (24) but on cat. hydrogenation as directed (25) (26) yields cinnamaldehyde (1:0245).] [Č with KCN + quinoline gives (34% yield (57)) 1-cinnamoyl-2-cyano-1,2-dihydroquiroline which on acid hydrolysis yields 30% cinnamaldehyde (1:0245).]

[\bar{C} with 5% H_2O_2 in acetone + pyridine yields (27) di-cinnamoyl peroxide, m.p. 144° (27).]

[C with anhydrous neutral K oxalate (28), or with dil. aq. KOH + methylaniline or dimethylaniline (29) or with pyridine (30), or with excess $K_2S_2O_5$ in pyridine (31), or with Na cinnamate (6), yields cinnamic anhydride [Beil. IX-586, IX₁-(232)], ndls. from C_6H_5 or alc., m.p. 136° (30).] — [\bar{C} with aq. under certain conditions yields cinnamic anhydride + HCl (for use in micro detn. of aq. (2), or indirectly for micro detn. of O_2 (after combustion), see (4) (32)).]

[For reactn. of \bar{C} with diethyl malonate (1 mole) + Na (2 moles) see (33); for reactn. of \bar{C} with ethyl sodio-acetoacetate giving (60% yield (10)) (34) ethyl α -cinnamoylacetoacetate, m.p. 44° (10) (Cu enolate, m.p. 164° (10)), with methyl sodio-acetoacetate giving (35) methyl α -cinnamoylacetoacetate, m.p. 49-50° (35), with ethyl sodio-benzoylacetate giving (10) ethyl cinnamoyl-benzoyl-acetate (Cu enolate, m.p. 202° (10)), or with sodio-benzoylacetone giving (36) benzoyl-cinnamoyl-methane, m.p. 111° u.c. (36), see indic. refs.]

[\bar{C} with $C_6H_6+AlCl_3$ in CS_2 gives (37) (38) (39) (41) (by combined ring closure and addition to the unsatd. linkage or vice versa) 3-phenylhydrindone-1 (3-phenylindanone-1) [Beil. VII-483, VII₁-(265)], cryst. from MeOH, m.p. 78° (37), 77-78° (39) (oxime, m.p. 141° (40), phenylhydrazone, m.p. 130° (40), p-nitrophenylhydrazone, m.p. 220-221° (39), semicarbazone, m.p. 223-225° (39)), accompanied by β , β -diphenyl-propiophenone (1,3,3-triphenylpropanone-1 [Beil. VII-524, VII₁-(293)] (38) and other prods.: note that under similar conds. (41) with toluene or o-xylene neither of the corresp. indanones is formed (see also below); however, \bar{C} + m-xylene + AlCl₃ in CS_2 yields (41) 5,7-dimethyl-3-phenylindanone-1, m.p. 101° (semicarbazone, m.p. 195-197° (41)), and \bar{C} + p-xylene + AlCl₃ in CS_2 yields (41) 4,7-dimethyl-3-phenylindanone-1, m.p. 94-95° (oxime, m.p. 218-219°; phenylhydrazone, m.p. 193-194°; semicarbazone, m.p. 232° (41)).]

[\bar{C} with many arom. cpds. in pres. of AlCl₃ condenses with loss of HCl to yield corresp. benzalacetophenone (chalcone) derivs.: \bar{C} with C_6H_6 + AlCl₃, however, gives no (41) chalcone (see above); \bar{C} with toluene + AlCl₃ yields (41) 4'-methylchalcone, m.p. 76° (41); \bar{C} with o-xylene + AlCl₃ in CS₂ gives (63% yield (41)) 3',4'-dimethylchalcone, m.p. 72-73° (41); \bar{C} with m-xylene + AlCl₃ in CS₂ yields (41) 2',4'-dimethylchalcone, oil, b.p. 218-219° at 11 mm. (41); \bar{C} with biphenyl + AlCl₃ in CS₂ gives (78% yield (45)) (11) 4'-phenylchalcone, m.p. 155-156° (45), 165° (11).]

[Similar chalcone formation occurs with many arom. ethers; e.g., \bar{C} with anisole + AlCl₃ in CS₂ gives (42) 4'-methoxychalcone [Beil. VIII-193, VIII₁-(580)], m.p. 106-107° (42); \bar{C} similarly with phenetole gives (42) 4'-ethoxychalcone [Beil. VIII-193], m.p. 74-75° (42); \bar{C} similarly with methyl p-tolyl ether gives (43) not only 2'-methoxy-5'-methylchalcone, m.p. 55-56°, but also by demethylation 2'-hydroxy-5'-methylchalcone, m.p. 111° (43); \bar{C} similarly with methyl 3,4-dimethylphenyl ether yields (13) 4',5'-dimethyl-2'-methoxychalcone, m.p. 78° (13); \bar{C} similarly with methyl β -naphthyl ether yields (44) β -methoxynaphthochalcone, m.p. 138-140° (44); \bar{C} similarly with diphenyl ether yields (37) 4'-phenoxychalcone, m.p. 85° (37); for extension of this reactn. to ethers of polyhydric phenols such as \bar{C} + AlCl₃ + catechol dimethyl ether (veratrole) (1:7560) (44), resorcinol dimethyl ether (1:7570) (13), resorcinol diethyl ether (1:7585) (13) (43), hydroquinone diethyl ether (1:7185) (43), and pyrogallol trimethyl ether (1:7145) (44) see indic. refs.]

[Similar formation of substituted chalcones occurs with $\bar{C} + AlCl_3 + phenols$; e.g., for cases of \bar{C} with o-cresol (1:1400) (46), resorcinol (1:1530) (47), phloroglucinol (1:1620) (47) cf. (48) see indic. refs.]

[\bar{C} with diazomethane in ether gives (49) (50) (note both replacement of Cl and addn. to unsatd. linkage) 5-(diazoacetyl)-4-phenylpyrazoline, cryst. from C_6H_6 + pet. eth.; m.p. 80-81° (49), 77-78° (50).]

 $[\bar{C} + \text{NaN}_3]$ in ether gives (12% yield (51)) (52) cinnamoyl azide, cryst. from lgr., m.p. 86° dec. (51) (52); this cpd. on htg. above m.p. or preferably in C_6H_6 readily loses N_2 and rearr. giving (77% yield (53)) (51) (52) styryl isocyanate, b.p. 107° at 12 mm.; this isocyanate (or even its azide precursor) with aq. at 50° yields (51) N_iN' -distyrylurea, m.p. 213–214° (51); for its reactn. with MeOH yielding (52) methyl N-styrylcarbamate, m.p. 126°, with EtOH yielding (52) ethyl N-styrylcarbamate, m.p. 87°, with ammonia gas in dry ether yielding (51) N-styrylurea, m.p. 143°, or with aniline yielding (52) N-phenyl-N-styrylurea, m.p. 217°, see indic. refs.]

[\bar{C} with free NH₂OH in C₆H₆ gives (100% yield (16)) cinnamoylhydroxamic acid, cryst. from hot EtOAc by addn. of lgr., m.p. 119.5° (16), 111.5° (54).]

[\bar{C} htd. with urea at 70° gives (44% yield (55)) (56) N-cinnamoylurea, m.p. 208–209° (55), 197° (56).]

[For reactn. of \bar{C} with C_6H_5MgBr see (58); for reactn. of \bar{C} with cellulose see (59); for reactn. with o-aminothiophenol yielding 1-styrylbenzothiazole see (60); for reactn. of \bar{C}

with m-aminobenzoic acid and ring closure of intermediate m-(cinnamoylamino)benzoic acid to 1-(N),9-pyridanthrone-2', m.p. 408°, see (61).]

[C with MeOH yields methyl cinnamate (1:2090), m.p. 36°; C with EtOH yields ethyl cinnamate (1:4206), b.p. 271°; C with phenol (1:1420) gives (63-75% yield (62)) phenyl cinnamate, cryst. from 95% alc., m.p. 75-76° (62).]

 $\bar{\mathbf{C}}$ on hydrolysis yields cinnamic acid (1:0735), m.p. 133°; for the amide, anilide, p-toluidide, and other derivs. corresp. to $\bar{\mathbf{C}}$ see cinnamic acid (1:0735). [For reaction of $\bar{\mathbf{C}}$ with piperidine giving 93% yield cinnamopiperidide, m.p. 122°, or with morpholine giving 99% yield cinnamomorpholide, m.p. 94°, see (63).]

3:0330 (1) Meyer, Monatsh. 22, 428 (1901). (2) van Nieuwenberg, Mikrochim. Acta 1, 71-74 (1937). (3) Bergs, Wittfeld, Frank, Ber. 67, 1621 (1934). (4) LaCourt, Compt. rend. 205, 280-282 (1937). (5) Michael, Smith, Am. Chem. J. 39, 26 (1908). (6) Liebermann, Ber. 21, 3372-3373 (1888). (7) Koehl, Wenzke, J. Am. Chem. Soc. 59, 1418 (1937). (8) Kohlrausch, Pongratz, Monatsh. 64, 383 (1934). (9) Claisen, Autweiler, Ber. 13, 2124 (1880). (10) Borsche, Peter, Ann. 453, 153-156 (1927).

(11) Bergmann, Wolff, J. Am. Chem. Soc. 54, 1646-1647 (1932). (12) Benary, Reiter, Soenderop, Ber. 50, 75, Note 3 (1917). (13) von Auwers, Risse, Ber. 64, 2220-2222 (1931). (14) Rupe, Ann. 369, 318 (1909). (15) von Auwers, Schmidt, Ber. 46, 483 (1913). (16) Jones, Mason, J. Am. Chem. Soc. 49, 2534 2535 (1927). (17) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (18) Rostoski, Ann. 178, 214 (1875). (19) Griffin, Nelson, J. Am. Chem. Soc. 37, 1563 (1915). (20) Soc. Chem. Ind. Basel, Brit. 401,643, Dec. 14, 1933; Cent. 1934, II 2133: French 732,078. Sept. 13, 1932; Cent. 1934, I 287.

(21) Ullmann, Nadai, Ber. 41, 1871 (1908). (22) Adams, Uhlich, J. Am. Chem. Soc. 42, 606 (1920). (23) Clarke, J. Chem. Soc. 97, 892-893 (1910). (24) Neunhoeffer, Nordel, J. prakt. Chem. (2) 144, 63-66 (1935). (25) Rosenmund, Zetsche, Ber. 56, 1483-1484 (1923). (26) Zetsche, Swiss 92,404, Jan. 2, 1922; Cent. 1922, IV 889. (27) Gelissen, Ger. 480,362, Aug. 7. 1929; Dutch 14,663, June 15, 1926; Cent. 1929, II 2831. (28) Gerhardt, Ann. 87, 76 (1853). (29) Edeleanu, Zaharia, Bul. Chim. Soc. Română Stiinte 3, 83 (1900). (30) Wedekind, Ber. 34, 2074-2075 (1901).

(31) Gazopoulos, Praktika 6, 347-353 (1931); Cent. 1932, I 3172; C.A. 27, 3204 (1933). (32) LaCourt, Bull. soc. chim. Belg. 46, 428-433 (1937). (33) Lampe, Milobedzka, Ber. 46, 2237-2238 (1913). (34) Fischer, Kuzel, Ber. 16, 166-167 (1883). (35) Lampe, Blenderowna, Bluman, Roczniki Chem. 17, 216-225 (1937); Cent. 1937, II 2988. (36) Hiemesch, Ber. 47, 116 (1914). (37) Kohler, Heritage, Burnley, Am. Chem. J. 44, 64-66 (1910). (38) McKenzie, Barrow, J. Chem. Soc. 119, 72-73 (1921). (39) von Auwers, Auffenberg, Ber. 52, 110-111 (1919). (40) Liebermann, Hartmann, Ber. 25, 2128-2129 (1892).

(41) von Auwers, Risse, Ann. 502, 290-299 (1933). (42) Stockhausen, Gattermann, Ber. 25, 3535-3537 (1892). (43) Simonis, Lear, Ber. 59, 2911-2912 (1926). (44) Monti, Gazz. chim. ital. 60, 45-48 (1930). (45) Bachmann, Wiselogle, J. Am. Chem. Soc. 56, 1559 (1934). (46) Neurath, Monatsh. 27, 1148-1149 (1906). (47) Shinoda, Sato, J. Pharm. Soc. Japan 48, 109-114 (1928); Cent. 1928, II 1885. (48) K. W. Rosenmund, M. Rosenmund, Ber. 61, 2611 (1928). (49) Grundmann, Ann. 524, 35, 48 (1936). (50) Bradley, Schwarzenbach, J. Chem. Soc. 1928, 2909.

(51) Jones, Mason, J. Am. Chem. Soc. 49, 2531-2532 (1927).
(52) Forster, J. Chem. Soc. 95, 437-438 (1909).
(53) Nelles, Ber. 65, 1347 (1932).
(54) Thiele, Pickard, Ann. 309, 194 (1899).
(55) Jerzmenowska-Sienkiewiczowa, Roczniki Chem. 15, 510-515 (1935); Cent. 1936, I 2554;
C.A. 30, 2933 (1936).
(56) Clark, Moore, MacArthur, Trans. Roy. Soc. Can. (3) 28, III
199 (1934); Cent. 1935, II 45; C.A. 29, 1078 (1935).
(57) Sugasawa, Tsuda, J. Pharm. Soc. Japan
58, 103-105 (1936); Cent. 1938, II 3670; C.A. 32, 5836 (1938).
(58) Kohler, Heritage, Am. Chem. J. 33, 30-31 (1905).
(59) von Frank, Mendrzyk, Ber. 63, 875-887 (1930).
(60) Mills, Whitworth, J. Chem. Soc. 1927, 2748.

(61) Seka, Ber. 58, 1778-1781 (1925). (62) Womack, McWhirter, Org. Syntheses 20, 77-78 (1940). (63) Cromwell, Caughlan, J. Am. Chem. Soc. 67, 904 (1945).

3: 0340 p-CHLOROPHENYL ETHYL KETONE C₉H₉OCl Beil. VII - 301 (4-Chloropropiophenone) Cl CO.CH₂.CH₃

Insol. aq.; sol. alc., ether, CS₂, and most org. solv. — Cryst. from abs. alc. at -15° (1). [For prepn. from propionyl chloride (3:7170) (2) (81% yield (4)) or propionic anhydride (1:1100) (1) + chlorobenzene + AlCl₃ see (1) (2) (4); for prepn. from p-chloro- α -methoxystyrene (68% yield (3)) by htg. in s.t. 2 hrs. at 300° see (3).

 $\bar{\mathbb{C}}$ on treatment with *n*-butyl nitrite + dry HCl gas in ether (1) (4) gives (83% yield (4)) 4-chloro-isonitrosopropiophenone, ndls. from dil. alc., m.p. 122-123° (4); 114° (1). $[\bar{\mathbb{C}} + \text{NaOEt}]$ in abs. alc. + *n*-butyl nitrite yields (1) only *p*-chlorobenzoic acid (3:4940), m.p. 243° (1).]

- D p-Chloropropiophenone oxime: from $\ddot{\textbf{C}}$ + hot alc. NH₂OH soln. (2); lfts., m.p. 62-62.5° (2).
- D p-Chloropropiophenone semicarbazone: ndls., m.p. 175-176° (3).

3:0340 (1) Edkins, Linnell, Quart. J. Pharm. Pharmacol. 9, 203-229 (1936); Cent. 1937, I 4781; C.A. 30, 6724 (1936). (2) Collet, Compt. rend. 126, 1577 (1898). (3) Lauer, Spielman, J. Am. Chem. Soc. 55, 4928 (1933). (4) Hartung, Munch, Crossley, J. Am. Chem. Soc. 57, 1091 (1935).

3: 0350 3,5-DICHLOROBENZYL CHLORIDE $C_7H_5Cl_3$ Beil. S.N. 466 Cl — CH_2Cl

M.P. 36° (1)

Cryst. from MeOH (1); note that $\tilde{\mathbf{C}}$ has same m.p. as 3,5-dichlorobenzal dichloride (3:0370), but the m.p. of a mixture of the two is depressed (1).

[For prepn. of C from 3,5-dichlorobenzyl alc. with PCl₅ (91% yield) see (1).]

3:0350 (1) Asinger, Lock, Monatsh. 62, 347 (1933).

3: 0360 3,5-DICHLOROBIPHENYL Cl $C_{12}H_8Cl_2$ Beil. V $V_1-V_{2^-}$ (484)

M.P. 36° (1) B.P. 180° at 15 mm. (2) 166° at 10 mm. (1)

[For prepn. from 5-phenyl-4,5-dihydroresorcinol [Beil. VII-706] by conversion with PCl_5 in CHCl₃ to 3,5-dichloro-1-phenylcyclohexadiene-2,4, colorless oil, b.p. 156° at 10 mm. (1), which in CHCl₃ on treatment with Cl₂ first adds 2Cl₂, then splits off 2HCl to yield \tilde{C} , see (1); for prepn. from 3,5-dichloro-2-aminobiphenyl via replacement of $-NH_2$ by -H via diazo reactn. see (2)

 \bar{C} (5 g.) in AcOH (12 ml.) on nitration with mixt. (50 ml.) of equal vols. fumg. HNO₃ + AcOH yields (1) mainly 3,5-dichloro-4'-nitrobiphenyl, pale yel. ndls. from alc., m.p. 146° (1), accompanied by a smaller amt. of 3,5-dichloro-2'-nitrobiphenyl, ndls., m.p. 75° (1).

 \tilde{C} on oxidn, with CrO_3 + AcOH yields (1) (2) 3,5-dichlorobenzoic acid (3:4840), m.p. 183° (1), 188° (2).

3:0360 (1) Hinkel, Hey, J. Chem. Soc. 1928, 2786-2791, (2) Scarborough, Waters, J. Chem. Soc. 1927, 93.

M.P. 36.5° (1)

Colorless cryst, from MeOH or from dil, AcOH; eas, sol, usual org, solv. [Note that C has same m.p. as the closely related 3,5-dichlorobenzyl chloride (3:0350) but that a mixture of the two becomes liquid.

[For prepn. of C from 3,5-dichlorobenzaldehyde (3:1475) with PCl₅ (80% yield) see (1).1

 \bar{C} on hydrolysis with fumg. H_2SO_4 as directed gives (71-80% yield (1)) 3,5-dichlorobenzaldehyde (3:1475) (for study of rate of hydrol. in 50% alc. at 83.5° see (2)).

3:0370 (1) Asinger, Lock, Monatsh. 62, 347 (1933). (2) Asinger, Lock, Monatsh. 62, 337-338 (1933).

3: 0372 2,4,6-TRIMETHYLBENZYL CHLORIDE
$$C_{10}H_{13}Cl$$
 Beil. S.N. 469 $(\alpha^2$ -Chloroisodurene) CH_3 CH_2Cl

114-115° at 10 mm. (3)

[See also the isomeric 2,4,5-trimethylbenzyl chloride (3:9702).]

Colorless cryst. from alc. (4). — C blisters skin (3). — [Equiv. conductance of C in liq. SO₂ is 10 times that of benzyl chloride (3:8535) (3) cf. (5).]

PREPARATION OF C

[For prepn. of C from 1,3,5-trimethylbenzene (mesitylene) (1:7455) with formalin $(1:0145) + \text{conc. HCl} + \text{HCl gas at } 55^{\circ} \text{ for } 5\frac{1}{2} \text{ hrs. (yields: } 55-61\% \text{ (1), } 29\% \text{ (3)) (some)}$ α^2 , α^4 -dichloropentamethylbenzene = bis-1,3-(chloromethyl)2,4,6-trimethylbenzene, cryst. from pet. eth., m.p. 105° (1) (3), is also formed) see indic. refs.]

[For prepn. of C from mesitylene (1:7455) with chloromethyl methyl ether (3:7085) + SnCl₄ (yields: 60% (4) cf. (6)), or in AcOH without other cat. (yields: 80-85% (7), 80% (2)), or with chloromethyl ethyl ether (3:7195) + SnCl₄ in CCl₄ soln. at -5° (70% yield (8)), see indic. refs.]

CHEMICAL BEHAVIOR OF C

Reduction. [\overline{C} with H_2 + Pt cat. in alc. soln. gives (80% yield (2) cf. (7)) 1,2,3,5tetramethylbenzene (isodurene) [Beil. V-430, V₂-(329)] (9), liquid, b.p. 195-197° at 760 mm., f.p. -24° , $D_4^{20} = 0.8906$.]

Hydrolysis. C on hydrolysis (no details (2)) gives 2,4,6-trimethylbenzyl alc. (mesitylcarbinol), ndls. from alc., m.p. 89° (2), 88-89° (10) (3) (11), 87° (12) (corresp. N-phenylcarbamate, m.p. 124-125° (11)).

Conversion to ethers. [C with MeOH/KOH at 100° for 3 hrs. gives (79% yield (3)) methyl 2,4,6-trimethylbenzyl ether, oil, b.p. 109-110° at 15 mm. (3); C with EtOH/KOH similarly gives (77% yield (3)) ethyl 2,4,6-trimethylbenzyl ether, oil, b.p. 114-115° at 14 mm. (3).]

Conversion to esters. [C with AgOAc in AcOH at 100° for 3 hrs. gives (70% yield (3)) 2,4,6-trimethylbenzyl acetate, oil, b.p. 136-137° at 15 mm. (3); this ester on hydrolysis with 15% aq. KOH at 100° for 3 hrs. gives (91% yield (3)) 2,4,6-trimethylbenzyl alc., m.p. 88-89°. (See also above.)]

Conversion to nitrile. \bar{C} in alc. with aq. NaCN (1) (13) or KCN (4) (8), or C with CuCN in pyridine (14) cf. (1), gives (yields: almost 100% (13), 89-93% (1)) mesitylacetonitrile, cryst. from pet. eth., m.p. 79-80° (1), 79° (4); b.p. 160-165° at 22 mm. (13), 150-155° at 15 mm. (4), 190° at 11 mm. (8); this nitrile on hydrolysis with abt. 50% H₂SO₄ under reflux for 6 hrs. gives (87% yield (1)) mesitylacetic acid [Beil. IX-563, IX₁-(219)], cryst. from dil. alc. or lgr., m.p. 167-168° (1) (note that partial hydrolysis may give mesitylacetamide, m.p. 216° (8)).

BEHAVIOR OF C WITH ORGANOMETALLIC COMPOUNDS

With MeMgI. [C with MeMgI in dry ether undergoes mainly a coupling reaction giving (86% yield (15)) 1,2-dimesitylethane, m.p. 117.0-117.5°, accompanied by a little ethylmesitylene (1-ethyl-2,4,6-trimethylbenzene), b.p. 212-214° (15), 210° at 725 mm. (16), $D_{20}^{20} = 0.894$ (16), $n_{1}^{20} = 1.5074$ (16) (corresp. dinitro deriv., m.p. 111° (17), 109-111° (17) (15)).]

With misc. reactants. [\bar{C} with diethyl sodiomalonate gives (4) diethyl α -(2,4,6-trimethylbenzyl)malonate, m.p. 36°, b.p. 195–197° at 15 mm. (4). — \bar{C} with ethyl sodiobenzoylacetate gives (21% yield (18)) ethyl α -(2,4,6-trimethylbenzyl)benzoylacetate which upon alk. hydrolysis gives (45% yield (18)) the ketone 1-benzoyl-2-mesitylethane, ndls. from MeOH, m.p. 85.0–85.5° (18).]

OTHER REACTIONS OF C

[C (1 mole) with hexamethylenediamine (1 mole) in CHCl₃ refluxed 3 hrs. gives (96% yield (19)) corresp. quaternary salt, C.C₆H₁₂N₄: this prod. in aq. refluxed 4 hrs. does not give the expected mesitaldehyde but instead (75% yield (19)) di-(2,4,6-trimethylbenzylamino)methane, cryst. from alc., m.p. 151.5-152° (19).

N-(2,4,6-Trimethylbenzyl)phthalimide: ndls. from alc., m.p. 209.5-210° (19). [From C with K phthalimide at 170-180° for 4 hrs. as directed (19) (63% yield (19)).]

3:0372 (1) Fuson, Rabjohn, Org. Syntheses 25, 65-68 (1945).
 (2) Vavon, Bolle, Calin, Bull. soc. chim. (5) 6, 1025-1033 (1939).
 (3) Nauta, Dienske, Rec. trav. chim. 55, 1000-1006 (1936).
 (4) Hoch, Compt. rend. 192, 1465-1466 (1931).
 (5) Nauta, Wuis, Rec. trav. chim. 56, 540 (1937).
 (6) Sommelet, Compt. rend. 157, 1443 (1913).
 (7) Vavon, Bolle, Compt. rend. 204, 1826-1828 (1937).
 (8) Sordes, Compt. rend. 195, 248-249 (1932).
 (9) Smith, Org. Syntheses, Coll. Vol. 2 (1st ed.), 360-362 (1943); 11, 66-69 (1931).
 (10) Fuson, Southwick, Rowland, J. Am. Chem. Soc. 66, 1112 (1944).

(11) Carre, Bull. soc. chim. (4) 7, 842-843 (1910). (12) Bock, Lock, Schmidt, Monatsh, 64, 412 (1934). (13) Fuson, Corse, McKeever, J. Am. Chem. Soc. 62, 3250 (1940). (14) Newman, J. Am. Chem. Soc. 59, 2472 (1937). (15) Fuson, Denton, Kneisley, J. Am. Chem. Soc. 63, 2652-2653 (1941). (16) Smith, Kiess, J. Am. Chem. Soc. 61, 285-286 (1939). (17) Smith, Kiess, J. Am. Chem. Soc. 61, 995-996 (1939). (18) Fuson, Ullyott, Hickson, J. Am. Chem. Soc. 61, 410-411 (1939). (19) Fuson, Denton, J. Am. Chem. Soc. 63, 654-656 (1941).

64

3:0375 14-CHLOROTETRADECANOL-1

C₁₄H₂₉OCl Beil. S.N. 24

 $(\omega$ -Chloro-n-tetradecyl

CH2.(CH2)12.CH2OH alcohol; ω-chloromyristyl alcohol)

M.P. 37-38° (1) B.P. 156-160° at 4 mm. (1)

Colorless cryst.

[For prepn. of \bar{C} from α, ω -tetradecamethylene glycol [Beil. I₂-(564)] (m.p. 85°) with SOCl₂ + dimethylaniline in C₆H₆ (43% yield) or by htg. with conc. HCl (32% yield) see (1); note that by the first method a little 1,14-dichlorotetradecane, cryst. from MeOH, m.p. 40°, is also formed.]

14-Chlorotetradecyl N-phenylcarbamate: lfts. from lt. pet., m.p. 68° (1).

3:0375 (1) Bennett, Gudgeon, J. Chem. Soc. 1938, 1679-1681.

3:0380 2,4,6-TRICHLOROTOLUENE

M.P. 38° (1) 34° (7) 33-34° (2)(3)31.9-32° (4)

Colorless ndls. from alc. (2); eas. volatile with steam (2).

[For prepn. of C from 2,4,6-trichloro-3-aminotoluene [Beil. XII-873] via diazotization and reaction with alc. see (2) (1) (4) (7); from 6-chloro-2,4-diaminotoluene via tetrazotization and use of Cu₂Cl₂ reaction see (3).] .

[C with Cl₂ in pres. of Al/Hg yields (5) 2,3,4,6-tetrachlorotoluene (3:2480), m.p. 89° (5), but \bar{C} with Cl_2 at 200° gives (82% yield (7)) 2,4,6-trichlorobenzal dichloride (3:0142).]

C on mononitration with cold fumg. HNO3 yields (2) (1) (6) 2,4,6-trichloro-3-nitrotoluene [Beil. V-333], ndls. from AcOH + EtOH (2) or dil. AcOH (6), m.p. 54° (2) (6), 50° (1); Č on dinitration (2) yields 2,4,6-trichloro-3,5-dinitrotoluene, cryst. from AcOH, m.p. 178-180° (2).

C on oxidn. with dil. HNO₃ readily yields (2) 2,4,6-trichlorobenzoic acid (3:4545), m.p. 160-161° (2).

3:0380 (1) Bureš, Trpišovska, Časopis Českoslov. Lékárnictva 15, 179-186 (1935); Čent. 1936, I 1209; C.A. 30, 1753 (1936). (2) Cohen, Dakin, J. Chem. Soc. 81, 1335-1336 (1902). (3) Morgan, Drew, J. Chem. Soc. 117, 786 (1920). (4) Maryott, Hobbs, Gross, J. Am. Chem. Soc. 62, 2321 (1940). (5) Cohen, Dakin, J. Chem. Soc. 85, 1284-1285 (1904). (6) Bureš, Trpišovska, Casopis Ceskoslov. Lékárnictva 17, 185-195 (1937); Cent. 1938, I 872; C.A. 32, 923 (1938). (7) Lock, Ber. 66, 1532 (1933).

3: 0395 $d,l-\alpha,\alpha'$ -DICHLOROSUCCINYL (DI)CHLORIDE

, CO—Cl
$$C_4H_2O_2Cl_4$$
 Beil. II — II_1 — II_2 —(558) Cl — Cl — Cl — Cl

M.P. 39° (1) B.P. 78.5° at 7 mm. (1)

[For prepn. of \bar{C} from $d_i l - \alpha_i \alpha'$ -dichlorosuccinic acid (3:4711) with PCl₅ (2 moles) (yield 100%) see (1).]

 $\ddot{\mathbf{C}}$ on hydrolysis yields (1) $d_{l}\mathbf{l}$ - $\alpha_{l}\alpha'$ -dichlorosuccinic acid (3:4711).

[Č with C_6H_6 + AlCl₃ gives (66% yield (1)) solely d,l-1,2-dichloro-1,2-dibenzoylethane (d,l-2,3-dichloro-1,4-diphenylbutandione-1,4), m.p. 86° (2) (3).]

3:0395 (1) Lutz, J. Am. Chem. Soc. 49, 1110 (1927). (2) Conant, Lutz, J. Am. Chem. Soc. 47, 886 (1925). (3) Lutz, J. Am. Chem. Soc. 48, 2908, 2911 (1926).

Ndls. from hot conc. lgr.; spar. sol. aq.; eas. sol. alc., ether, AcOH. — C forms a monohydrate, C.H₂O, m.p. 42° (4) (1). — [For crystallographic data see (2).]

[For prepn. of \mathbb{C} from p-cresol (1:1410) with Cl_2 (1) in CCl_4 (7) (6) or in aq. NaOH (8), or with $\operatorname{SO}_2\operatorname{Cl}_2$ (2 moles) (9), see indic. refs.; from 4-methylphenoldisulfonic acid-2,6 [Beil. XI-261, XI₁-(62)] with Cl_2 in aq. soln. see (3); from 1,2,3,3,5,5,6-heptachloro-1-methylcyclohexanone-4 [Beil. VII-19] by reduction with SnCl_2 (poor yield (7)) or from 3,5-dichloro-1-methyl-1-dichloromethylcyclohexadien-2,5-one-4 [Beil. VII₁-(99)] by reduction with $\operatorname{Zn} + \operatorname{AcOH}$ (4) see indic. refs.; from ethyl 2,6-dichloro-4-methylphenyl ether by cleavage with conc. HCl see (5) although identity of prod. is doubtful.]

[\bar{C} with dry NH₃ gas forms at room temp. a mol. cpd. $\bar{C}.NH_3$; at -15° a mol. cpd. $\bar{C}.2NH_3$ (10); \bar{C} with alc. NH₃ htd. in s.t. short time at 100° gives (1) an NH₄ salt, $C_7H_5Cl_2-ONH_4$, colorless ndls, m.p. 125°, which sublime unchanged and from whose aq. soln. acidification reppts. \bar{C} (1) (dif. from 4,6-dichloro-2-methylphenol (3:1020) q.v.)] — [\bar{C} also yields a yellow silver salt (11) (12) which in light rapidly turns green and decomposes (11) (12).]

[C in AcOH with conc. HNO₃ in cold gives (yield: 92% (6), 82% (7)) 2,6-dichloro-4-methyl-quinitrol, alm. colorless ndls., m.p. 74-76° (6) (7), 80-82° if taken in warm bath (6) (for study of reactions of this prod. with McOH and with EtOH see (13)).]

[\bar{C} with warm dil. HNO₃ (D=1.1) readily oxidizes yielding (1) as the only solid product oxalic acid (1:0445); \bar{C} on oxidn. with CrO₃ in AcOH yields (1) an acid, C₇H₄O₃Cl₂, m.p. 156° u.c., which, however, is *not* the expected 3,5-dichloro-4-hydroxybenzoic acid, m.p. 255-256°.]

[\bar{C} on monosulfonation with fumg. H_2SO_4 (65% SO_3) at 50° yields (14) 2,6-dichloro-4-methylphenolsulfonic acid-3.]

[$\bar{\mathbf{C}}$ in MeOH/KOH with MeI refluxed 5 hrs. gives (15) 2,6-dichloro-4-methylphenyl methyl ether, b.p. 234° (15), which on oxidn with dil. HNO₃ (D=1 15) by refluxing for 50 hrs. yields (15) 2,6-dichloro-4-methoxybenzoic acid, m.p. 200-201° (15); the ethyl ether of $\bar{\mathbf{C}}$ is an oil, b.p. 147-154° at 16 mm., and has been reported by indirect means (5).]

- 2.6-Dichloro-4-methylphenyl acetate: lfts. from dil. AcOH, m.p. 48° (7).
- 2,6-Dichloro-4-methylphenyl benzoate: tbls. from dil. alc., m.p. 91° (7) (4). [From C on htg. with benzoic anhydride (1:0595) (7).]

3:0400 (1) Claus, Riemann, Ber. 16, 1599-1601 (1883). (2) Groth, Miers, Ber. 17, 2532 (1884). (3) Datta, Mitter, J. Am. Chem. Soc. 41, 2034 (1919). (4) von Auwers, Ber. 44, 800 (1911). (5) Autenrieth, Mühlinghaus, Ber. 39, 4104 (1906). (6) Jones, Kenner, J. Chem. Soc. 1931, 1856-1857. (7) Zincke, Ann. 328, 278, 289-291 (1903). (8) Chulkov, Parini, Barshev, Org.

66

Chem. Ind. (U.S.S.R.) 3, 410-412 (1937); Cent. 1938, II 305; C.A. 31, 7047 (1937). (9) Mazzara, Lamberti-Zanardi, Gazz. chim. ital. 26, II 400-401 (1896). (10) Korczynski, Cent. 1909, II 806. (11) Hantzsch, Scholtze, Ber. 40, 4877, 4879 (1907). (12) Hunter, Rathmann, J. Gen. Chem. (U.S.S.R.) 7, 2230-2234 (1937); Cent. 1938, I 3332; C. A. 32, 518 (1938). (13) Jones, Kenner, Chem. Soc. 1931, 1943-1950. (14) Weiler, Better (to I.G.), Ger. 557,450, Aug. 24, 1931; Cent. 1932, II 2371. (15) Bertozzi, Gazz. chim. ital. 29, II 37-38 (1899).

3:0410 2,6-DICHLOROBENZYL CHLORIDE

C7H5Cl3 Beil. S.N. 466

$$C_{\rm Cl}$$
 CH₂Cl

M.P. 39-40° (1)

Colorless cryst. from lgr., ether, or alc. + ether.

[For prepn. of C from 2,6-dichlorotoluene (3:6270) by treatment at b.p. with Cl₂ in u.v. light see (1).]

C with Mg in dry ether gives 90% yield 2,6-dichlorobenzyl MgCl; this prod. upon treatment with CO₂ (1) or with methyl chloroformate (3:5075) followed by appropriate treatment yields 2,6-dichlorophenylacetic acid, cryst. from alc., m.p. 157-158° (1).

3:0410 (1) Austin, Johnson, J. Am. Chem. Soc. 54, 658-659 (1932).

3:0422 OCTACHLOROCYCLOPENTENE

Beil. V - 62 **V**1---

M.P.		B.P.				
41°	(1) (8)	283-284°	at 733 mm.	(5) (6)	$D_4^{50} = 1.817 (4)$	$n_{\rm D}^{50}=1.5660~(4)$
40-4	1° (7)	283°		(1)		
40°	(2)	183°	at 20 mm.	(2)		
39°	(3)	140°	at 10 mm.	(4)		
38°	(4)					
32°	(10)					

[See also hexachlorobutadiene-1,3 (3:6425).]

Colorless cryst. from 95% alc. (4) or EtOH contg. 5% tetrachloroethylene (3:5460) (3). [For prepn. of C from pentachlorocyclopentenone [Beil. VII-49] (7), from either the higher- or lower-melting stereoisomer of hexachlorocyclopentenone [Beil. VII-49] (1). from dibromo-dichloro-cyclopentanetrione [Beil. VII-853] (8), or from xanthogallol (tetrabromocyclopentenedione [Beil. VII₁-(321)] (2), all with PCl₅ in s.t., at elevated temps, as directed, see indic. refs.]

[For formn. from nonachloropentene-1 (itself obtd. from hexachloropropene (3:6370) with trichloroethylene (3:5170) + AlCl₃ (9)) by elimination of 1 HCl with alc. KOH yielding octachloropentadiene-1,3 followed by rearr. to C by boilg. with AlCl3 see (3).1

[For formn. of C (together with CCl₄ (3:5100) and hexachloroethane (3:4835) by highpress./high-temp. chlorination of chloropentanes see (4); by exhaustive chlorination of hexyl iodide, heptaldehyde, heptylic acid, etc. (5), of high-mol.-wt. hydrocarbons (6), or of 3-chloro-5,6-dihydroxy-2-(dichloromethyl)pyridine [Beil. XII-164] (10), see indic. refs.]

Note that C, formerly regarded as hexachlorobutadiene-1,3 (3:6425), is currently (3) believed to have the structure octachlorocyclopentene; for Raman spectra evidence see (11). 3:0422 (1) Zincke, Küster, Ber. 23, 2214-2215 (1890). (2) Hantzsch, Strasser, Ann. 488, 209 (1931). (3) Fruhwirth, Ber. 74, 1700-1701 (1941). (4) McBee, Hass, Pierson, Ind. Eng. Chem. 33, 181-185 (1941). (5) Krafft, Ber. 10, 803-806 (1877). (6) Hartmann, Ber. 24, 1011-1026 (1891). (7) Zincke, Meyer, Ann. 367, 9 (1909). (8) Henle, Ann. 352, 52-53 (1907). (9) Prins, Rec. trav. chim. 57, 661-662 (1938); 51, 1068-1070 (1932). (10) Hoffmann, Ber. 22, 1269-1270 (1889).

(11) Kohlrausch, Wittek, Ber. 75, 227-232 (1942).

3: 0425 2,3,4-TRICHLOROTOLUENE

$$\begin{array}{cccc} {\rm CH_3} & {\rm C_7H_5Cl_3} & & \text{Beil. V - 298} \\ & & & \text{V_1--} \\ & & & \text{V_2-(232)} \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ \end{array}$$

C₅H₉O₂Cl

Beil. S.N. 162

Ndls. from MeOH or EtOH; volatile with steam.

[For prepn. of \bar{C} from 2,3-dichloro-4-aminotoluene [Beil. XII-990] via diazotization and use of Cu_2Cl_2 reaction see (4); from toluene with $AlCl_3 + SO_2Cl_2$ (34% $\bar{C} + 40\%$ 2,4,5-trichlorotoluene (3:2100)) see (2); for formn. of \bar{C} (together with other isomers) from toluene, o-chlorotoluene (3:8245), or p-chlorotoluene (3:8287) with Cl_2 see (1); from 2,3-dichlorotoluene (3:6345) or 2,4-dichlorotoluene (3:6290) with Cl_2 in pres. of Al/Hg see (5); for prepn. of \bar{C} from its sulfonic acid by hydrolysis see (1) (7).]

[C with Cl₂ in pres. of Al/Hg yields (6) 2,3,4,6-tetrachlorotoluene (3:2480).]

 \bar{C} on mononitration (1) (4) by soln. in cold fumg. HNO₃ yields a mononitro \bar{C} [Beil. V-333], ndls. from alc., m.p. 60-61° (4), 60° (1); \bar{C} on dinitration by warming with a mixt. of 2 pts. fumg. HNO₃ and 1 pt. conc. H₂SO₄ (1) (4) cf. (7) yields 2,3,4-trichloro-5,6-dinitro-toluene [Beil. V-345], ndls. from alc., m.p. 141° (1) (2), 140-141° (4).

 \bar{C} on shaking with 2 pts. fumg. H₂SO₄ at 60° yields (1) (7) a monosulfonic acid (use in sepn. of \bar{C} from 2,4,5-trichlorotoluene (3:2100) which is not sulfonated under these conditions (1) (7)).

 \bar{C} on oxidn, with dil. HNO₃ in s.t. at 150° (4) yields 2,3,4-trichlorobenzoic acid (3:4810), m.p. 186-187° (4).

3:0425 (1) Scelig, Ann. 237, 132, 137, 138, 140, 156 (1887). (2) Silberrad, J. Chem. Soc. 127, 2681-2682 (1925). (3) I.G., Brit. 287,178, May 9, 1928; Cent. 1929, II 352. (4) Cohen, Dakin, J. Chem. Soc. 81, 1327-1328 (1902). (5) Ref. 4, pp. 1339-1341. (6) Cohen, Dakin, J. Chem. Soc. 85, 1283 (1904). (7) Prentzell, Ann. 296, 181-182 (1897).

3:0440 CHLOROPIVALIC ACID

(β-Chloro-α,α-dimethylpropionic acid)

CH₂-C-CC

M.P. 40-42° (1) B.P. 126-129° at 30 mm. (1)

[For prepn. of \bar{C} from pivalic acid (trimethylacetic acid) (1:0410) with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 see (1).]

© Chloropivalamide: pl. from aq., m.p. 108-109° (1).

3:0440 (1) Kharasch, Brown, J. Am. Chem. Soc. **62**, 925-929 (1940). (2) Kharasch, Brown (to du Pont Co.), U.S. 2,302,228, Nov. 17, 1942; C.A. **37**, 2018 (1943).

3: 0455 2,6-DICHLORO-2,6-DIMETHYLHEPTANE
$$C_9H_{18}Cl_2$$
 Beil. I - 167 I_1 — I_2 —(129) CH_3 — C — CH_2 . CH_2 . CH_2 — C — CH_3 CH_3

68

M.P. 41-42° (1)

[For prepn. of \bar{C} from 2,6-dimethylheptanediol-2,6 [Beil. I-494] (2) with conc. HCl or AcCl see (1) (2); from the corresponding internal ether, viz., $\alpha,\alpha,\alpha',\alpha'$ -tetramethylpentamethylene oxide (2,2,6,6-tetramethyltetrahydropyran) [Beil. XVII-17], with HCl see (1).]

 \bar{C} on warming with aq. readily hydrolyzes (1) back to 2,6-dimethylheptanediol-2,6 (monohydrate, cryst. from C_6H_6 , m.p. 60-61°; anhydrous form by heating monohydrate at 135-140°, m.p. 76-77° (1).

[\bar{C} in C_6H_6 + AcOH treated with Zn dust in a stream of dry HCl yields (2) mixt. of α - and β -cyclogeraniols [Beil. VI-66, VI₁-(43)].]

3:0455 (1) Bruylants, Bull. acad. roy. Belg. **1909**, 276–282; Cent. **1909**, II 797; C.A. **4**, 1485 (1910); Rec. trav. chim. **29**, 130–133 (1910). **(2)** Staudinger, Widmer, Helv. Chim. Acta **9**, 531, 546–547 (1926).

3: 0460
$$\beta$$
-CHLOROPROPIONIC ACID $C_3H_5O_2Cl$ Beil. II - 249 (3-Chloropropanoic acid) ClCH₂.CH₂.COOH II₁-(111) II₂-(226) M.P. 42° (1) (2) B.P. 204° (11) 41.5° (3) 203-205° at 764 mm. (12)

41.5° (3)203-205° at 764 mm. (12) 41° (4) (19) 127 at 35 mm. (13)40.5° cor. (5) 120° at 30 mm. (27)40° (6)(7)124° at 25 mm. (1) 39° 105-107° at 20 mm. (8) (9) (14)38.5-39.5° (10) 108° at 12 mm. (1)

Lfts. from lgr. or pet. eth. — Very eas. sol. aq., alc., $CHCl_3$; spar. sol. dry ether. — Fairly hygroscopic. — \tilde{C} on boilg. slightly dec. to HCl + acrylic ac. (1:1020). [Note that samples with m.p. higher than 42° may have contd. adipic ac. (8).] [For stability of \tilde{C} in aq. soln. see (8).]

[For prepn. of \bar{C} from acrolein (1:0115) via addn. of HCl to β -chloropropionaldehyde (3:5576) and subsequent oxidn. with fumg. HNO₃ (yield: 65-70% (14), 60-65% (15), 50% (1)) see (15) (14) (7) (1) (16); from 3-chloropropanol-1 (trimethylene chlorohydrin) (3:8285) by oxidn. with conc. HNO₃ (yield: 78-79% (9)) (17) (13) (27) or alk. KMnO₄ (18) see indic. refs.; from β -hydroxypropionitrile (ethylene cyanohydrin) by hydrolysis with HCl see (10); from phosgene + ethylene + AlCl₃ via hydrolysis of intermediate β -chloropropionyl chloride (3:5690) see (19); for other methods see Beil. II-249.]

Č on htg. with aq. alk. or alk. carbonates (1) (7) (19) or on passing over activated carbon at 230-240° at 250-320 mm. (21) loses HCl and yields acrylic ac. (1:1020). [The alk. salts of Č dec. even at ord. temp. giving alk. chlorides (3).] [For example of use of Č as source of acrylic acid in Diels-Alder addn. reactions see under 9,10-dichloroanthracene (3:4916).]

 \tilde{C} with PCl₃ (12) or SOCl₂ (22) yields β -chloropropionyl chloride (3:5690) q.v., b.p. 144°.

Č (1 g.) + pyridine (2 g.) htd. at 100° solidifies after 2 hrs. to give 100% yield addn. cpd. Č.C₅H₅N, pr. from abs. alc., m.p. 160° (26).

- —— Methyl β-chloropropionate: b.p. 148-150° at 760 mm. (3:5765)
- Ethyl β -chloropropionate: b.p. 162-163° at 760 mm. (3:8290).
 - ---- β-Chloropropionamide: unrecorded.
- Φ β-Chloropropionanilide: cryst. from aq. or MeOH, m.p. 119° (23). [From β-chloropropionyl chloride + aniline in acetone in 90% yield (23).]
- **Φ** β-Chloropropion-p-toluidide: cryst. from MeOH, m.p. 121° (23) (22).
- Φ β-Phenoxypropionic acid: ndls. from hot aq. (24) or lgr. (25); m.p. 98° (24), 97-98° (25). [From \bar{C} + phenol + NaOH, 36% yield (25).]

3:0460 (1) Moureu, Murat, Tampier, Ann. chim. (9) 15, 222-228 (1921). (2) Wooten, Hammett, J. Am. Chem. Soc. 57, 2291 (1935). (3) Beckurts, Otto, Ber. 18, 226, 846 (Note) (1885).
(4) Michael, Ber. 34, 4047-4048 (1901). (5) Linnemann, Ann. 163, 96 (1872). (6) Lichty, Ann. 319, 369-370 (1901). (7) Moureu, Ann. chim. (7) 2, 157-158 (1894); Bull. soc. chim. (3) 9, 388 (1893). (8) Simpson, J. Am. Chem. Soc. 40, 675 (1918). (9) Powell, Huntress, Hershberg, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 168-169 (1941). (10) Jacobs, Heidelberger, J. Am. Chem. Soc. 39, 1465-1466 (1917).

(11) de Barr, Am. Chem. J. 22, 334 (1899). (12) Henry, Compt. rend. 106, 114 (1885); J. prakt. Chem. (2) 31, 126 (1885). (13) Powell, J. Am. Chem. Soc. 46, 2879 (1924). (14) Moureu, Chaux, Bull. soc. chim. (4) 35, 1360-1364 (1924). (15) Moureu, Chaux, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 166-168 (1941). (16) Arndt, Ber. 56, 1276-1277 (Note) (1923). (17) Rojahn, Ber. 54, 3116-3117 (1921). (18) Brit. (to I.G.), 479,690, Mar. 10, 1938; Cent. 1938, I 3833; French 824,489, Feb. 9, 1938; C.A. 32, 5857 (1938). (19) Pace, Gazz. chim. ital. 59, 580-582 (1929). (20) Klebanskii, Chevychalova, Cent. 1938, I 1335; C.A. 34, 6222 (1940).

(21) Bauer, Lauth (to Rohm and Haas Co.), U.S. 2,087,466, July 20, 1937; Ger. 646,820, June 23, 1937; Cent. 1937, II 2072; Brit. 526,122, Sept. 11, 1940; C.A. 35, 6981 (1941). (22) Wolffenstein, Rolle, Ber. 41, 736 (1908). (23) Mayer, van Zütphen, Philipps, Ber. 58, 860 (1927); Mayer, Ger. 415,096, June 13, 1925; Cent. 1925, II 1094. (24) Powell, J. Am. Chem. Soc. 45, 2710 (1923). (25) Arndt, Kallner, Ber. 57, 204 (1924). (26) Kirpal, Wojnar, Ber. 71, 1264 (1938). (27) Fieser, Seligman, J. Am. Chem. Soc. 58, 2484 (1936).

3: 0470 PENTACHLOROPROPIONYL CHLORIDE
$$C_3 \circ Cl_6$$
 Beil. II — $Cl_3 \circ Cl_6 \circ C$

M.P. 42° (1)

Colorless not especially hygroscopic ndls.

[For prepn. of \bar{C} from trichloroacrylic acid chloride (3:5845) by addn. of Cl_2 in bright sunlight see (1).]

 \bar{C} with AlCl₃ (1 mole) at 60° decomposes in two ways (1), leading on one hand to CO and hexachlorethane (3:4835), and on the other to phosgene (3:5000) and tetrachloroethylene (3:5460).

[$\ddot{\mathbf{C}}$ with $\mathbf{C}_6\mathbf{H}_6$ + AlCl₃ yields (1) phenyl pentachloroethyl ketone ($\alpha,\alpha,\beta,\beta,\beta$ -pentachloropropiophenone) [Beil. VII₁-(161)], m.p. 83° (1).]

C on hydrolysis yields pentachloropropionic acid (3:4895).

3:0470 (1) Böeseken, Hasselbach, Rec. trav. chim. 32, 11-13 (1913).

3:0475 p-CHLOROPHENOL ClOH C₆H₅OCl Beil. VI - 186 VI₁-(100) VI₂-(174)

M.P.		B.P.					
43°	(1)	219.75	at 760 mm.	(11)	$D_4^{78.1} = 1.2238$		
42.9°	(2) (3)	218.3-2	218.9°	(12)	-		1.5480 (23)
42.5°	(4)	218°	(6)	(15)		$n_{\rm D}^{40} =$	1.5600 (14)
40-41	° (5)	217°	at 760 mm.	(7)			1.5579 (3)
41°	(6) (15)	217°		(10)		$n_{\mathrm{D}}^{20} =$	1.5690 (14)
40°	(7)	216.0°	at 760 mm.	(13)			
38-39	° (8)	99.7°	at 12 mm.	(13)			
37°	(9) (10) (20) (55)					
36°	(39)						

[See also o-chlorophenol (3:5980).]

 \bar{C} has disagreeable and persistent odor (15) for study of strength of which in aq. soln. see (16). — \bar{C} is spar. sol. aq. at ord. temp. (for details see (17)); but \bar{C} is eas. sol. alc., ether, C_6H_6 , $CHCl_3$, CS_2 . — \bar{C} (like its o-isomer (3:5980)) is volatile with steam (for studies see (18)) even from soln. in equiv. aq. NaOH (19) (dif. and sepn. from 2,4-dichlorophenol (3:0560), 2,6-dichlorophenol (3:1595), and 2,4,6-trichlorophenol (3:1673) (19).

The cryoscopic const. of \bar{C} is 85.8 (20).

SELECTED DATA ON BINARY SYSTEMS CONTG. C

 \overline{C} + aq.: for solubility/temp. data see (17).

 $\bar{C} + C_6H_6$: for solubility/temp. data (17) or for vapor-press. data (21) see indic. refs.; for association of \bar{C} in C_6H_6 soln. see (30). $\bar{C} + \text{MeOH}$ (1:6120): for vapor-press. data see (21). $\bar{C} + \text{acetone}$ (1:5400): for vapor-press. data see (21). $\bar{C} + \text{methyl}$ acetate (1:3005): for vapor-press. data see (21).

 $\ddot{\mathbf{C}}$ + nitrobenzene: for f.p./compn. data and diagrams see (24) (25), eutectic m.p. -24.5° contg. 41.5 wt. % $\ddot{\mathbf{C}}$ (24), m.p. -30.5° contg. 50.5 mol. % $\ddot{\mathbf{C}}$ (25).

 \overline{C} + aniline: for D^{25} and D^{50} + viscosity at 25° and 50° sec (26). \overline{C} + p-toluidine: for f.p./compn. and n_D^{54} /compn. data and diagrams see (4) cf. (29); note two eutectics, E_1 , m.p. 21° contg. 28 mol. % \overline{C} , and E_2 , m.p. 7.4° contg. 71 mol. % \overline{C} (4). \overline{C} + benzylamine: for f.p./compn. diagram see (27), noting two molecular cpds., one of compn. 3 \overline{C} .1 benzylamine, m.p. 55°, the other 1 \overline{C} .1 benzylamine, m.p. 16° (27). \overline{C} + phenylhydrazine: for f.p./compn. data and diagram see (1).

 \bar{C} + piperidine: for n_{D}^{65} /compn. data see (23).

 $\bar{\bf C}$ + pyridine: for f.p./compn. diag. of entire system see (4) cf. (28) (note two eutectics, viz., E_1 , m.p. -19.5° contg. 66.6 mol. % $\bar{\bf C}$, E_2 , m.p. -47.3° contg. 13.5 mol. % $\bar{\bf C}$); for n_D^{25} /compn. and n_D^{50} /compn. data over entire system see (14).

 $\ddot{\mathbf{C}}$ + o-chlorophenol (3:5980): for f.p./compn. data and diagram see (3) (note that the eutectic, m.p. about -20.5° , conts. about 38.5 mol. % $\ddot{\mathbf{C}}$). $\ddot{\mathbf{C}}$ + p-dichlorobenzene (3:0980): for f.p./compn. diagram see (4) (note eutectic m.p. 27.2° contg. 73.4 mol. % $\ddot{\mathbf{C}}$); for $n_{\mathbf{D}}^{54}$ / compn. data see (4).

AZEOTROPIC SYSTEMS CONTG. Č

 $\bar{\bf C}$ with naphthalene (1:7200) forms a const.-boilg. mixt., b.p. 216.3° contg. 36.5% $\bar{\bf C}$ (11). $\bar{\bf C}$ with *p*-dibromobenzene forms a const.-boilg. mixt., b.p. 215.05° contg. 35% $\bar{\bf C}$ (11).

PREPARATION OF C

From p-chloroaniline. [For prepn. of \bar{C} from p-chloroaniline [Beil. XII-607, XII₁-(304)] via diazotization to salts of p-chlorobenzenediazonium hydroxide [Beil. XVI-463, XVI₁-(355)] and hydrolysis of the latter (yields not stated) (3) (10) in an inert solvent (31) see indic. refs.; for study of rate of hydrolysis (32) of p-chlorobenzenediazonium chloride and influence of light thereon (33) see indic. refs.]

From phenol. [For prepn. of \bar{C} from phenol (1:1420) with Cl₂ at temps. over range 40°-155° see (3) cf. (6) (35); with Cl₂ + conc. aq. Na₂CO₃ soln. see (34); by use of N,N-dichlorobenzenesulfonamide in CHCl₃ at -15° see (36) (note that evidence obtd. from this reaction in pres. of isobutylene indicates that phenyl hypochlorite is first formed and subsequently rearranges (36)); by use of N,N'-dichlorourea + HCl see (37); with EtOCl (3:7022) in CCl₄ at -20° see (38); or by use of SO₂Cl₂ see (39) (40) (41) (for use of SO₂Cl₂ on NaOC₆H₅ see (7)). — Note that in all these methods some o-chlorophenol (3:5980) is usually also formed.]

From p-aminophenol. [For form. of \bar{C} from p-aminophenol [Beil. XIII-427, XIII₁-(143)] via diazotization, conversion to corresp. PtCl₄ double salt, and dry distn. see (42); or via diazotization, conv. to corresp. ZnCl₂ double salt, and decompn. by addn. of molten phenol (yield 40% accompanied by 41% hydroxybiphenyl + 11% diphenyl ether) see (43).]

From p-dichlorobenzene. [For prepn. of \tilde{C} from p-dichlorobenzene (3:0980) with MeOH/NaOMe in s.t. at 180° (44) (45), or with MeOH/NaOH in s.t. at 190-195° (90%) yield (46)) or at 200° for 25 hrs. under press. (8), see indic. refs.; for use of aq. alk. or alk. earths with MeOH in pres. of copper salts at 150-190° under press. see (47) (note, however, that, although the hydrolysis of p-dichlorobenzene to \tilde{C} is markedly facilitated by presence of Cu, e.g., with aq. NaOH, maximum yield is 30% while with MeOH/NaOH + Cu yield is 85% (48), yet in presence of Cu₂O some ord. phenol (1:1420) is also formed (49); for prepn. of \tilde{C} from p-dichlorobenzene (3:0980) by vapor-phase hydrolysis with steam + cat. at 550-850° see (50).]

From other miscellaneous sources. [For formn. of \bar{C} from various p-chlorophenyl ethers by cleavage, e.g., from p-chloroanisole (3:6300) with conc. HCl in s.t. (51) or with MeOH/NaOMe in s.t. at 176° (45); from p-chlorophenetole (3:0090) with conc. HCl (52) or with HBr in AcOH (85% yield (53)); or from p-chlorophenoxyacetic acid (3:4375) with conc. HCl in s.t. at 150° (34), see indic. refs.]

 $[\bar{C}]$ is also obtainable by hydrolysis of its various esters, but these need not be cited here.] [For formn. of \bar{C} from p-bromophenol with SO_2Cl_2 at ord. temp. see (55); from calcium salt of p-dichlorobenzenesulfonic acid with $Ca(OH)_2 + Cu$ at 200-220° followed by removal of the sulfonic acid group from the resultant p-chlorophenolsulfonic acid see (56).]

BIOCHEMICAL ASPECTS OF C

[For studies involving fate of \bar{C} in animal metabolism see (57) (58) (59); for studies from various aspects of bactericidal and fungicidal action of \bar{C} see (60) (61) (62) (63) (64) (65) (67) (68).]

[For studies from various aspects of effect of \bar{C} and other chlorophenols on taste of water see (69) (70) (71) (72) (73).]

MISCELLANEOUS USES OF C

[For use of \bar{C} in selective solv. refining of mineral oils see (74); as denaturant for alc. see (75); as solv. for lignin see (76).]

QUANT. DETN. OF C

See text below under bromination of $\bar{\mathbf{C}}$, iodination of $\bar{\mathbf{C}}$, and nitration of $\bar{\mathbf{C}}$.

CHEMICAL BEHAVIOR OF C

Pyrolysis of C

[Č on pyrolysis through silica tube at red heat gives (77) 3,6-dichlorodiphenylene oxide, m.p. 188° (77).]

REDUCTION OF C

[\bar{C} with H_2 + Ni cat. in aq. or aq. alc. alk. soln. loses chlorine quant. as HCl (78) (for study of rate see (79)); note also that \bar{C} with Li at 220° (80) or with Ca at 160° (80) followed by treatment with aq. gives (yields 14% and 36% resp.) phenol (1:1420). — Note that \bar{C} with aq. Cu₂O at 250–380° under press. gives (81) phenol (1:1420) (see also above under prepn. of \bar{C} from p-dichlorobenzene). — Note that reduction of \bar{C} to 4-chlorocyclohexanol-1 (3:9376) appears to be unreported.]

OXIDATION OF C

[$\bar{\mathbf{C}}$ on oxidn. with 35% peracetic acid at 25° gives (82) slowly (17 days) in small yield β -chloromuconic acid (2-chlorobutadien-1,3-dicarboxylic acid-1,4), m.p. 223°, accompanied in the mother liquor by some lactone ($C_6H_5O_6Cl$) of 3-chloro-4,5-dihydroxyhexen-2-dioic acid-1,6, m.p. 177° (82). — $\bar{\mathbf{C}}$ on electrolytic oxidn. gives (83) benzoquinone-1,4 (1:9025).].

NUCLEAR SUBSTITUTION OF C

(See also below under condensation reactions of C.)

Halogenation of \tilde{C}. Fluorination. [The fluorination of \tilde{C} has not been reported, and no fluoro- or difluoroderiv. of \tilde{C} is known.]

Chlorination. [\bar{C} with Cl₂ (2 moles) in AcOH in cold gives (80% yield (84)) 2,4-dichorophenol (3:0560), m.p. 45°; presumably \bar{C} with Cl₂ (3 moles) would give 2,4,6-trichlorophenol (3:1673), but such reaction is not actually reported. — For study of rate of chlorination of \bar{C} with Cl₂ in CCl₄ (85) or with NaOCl in alk. soln. at 25° (86), or behavior of \bar{C} with Cl₂ in presence of radioactive HCl in C₆H₆ soln. (87), see indic. refs.]

Bromination. [C with Br₂ (1 mole) in CCl₄ at room temp. gives (62% yield (88)) 2-bromo-4-chlorophenol, m.p. 33-34°, b.p. 121-123° at 10 mm. (corresp. benzoyl deriv., m.p. 99-100°) (88).]

Č with Br₂ (2 moles) in AcOH (89) (90) (91) or Č with Br₂ (2 moles) in aq. KBr soln. (92) gives (yields not stated) 4-chloro-2,6-dibromophenol, ndls. from dil. alc., m.p. 92° (89), 90° cor. (92), 89° (90) (corresp. methyl ether, m.p. 74° (92); 2,4-dinitrophenyl ether, m.p. 145-146° (90), p-toluenesulfonate, m.p. 107-108° (90)). [Note difference from the isomeric 4-chloro-3,5-dibromophenol, m.p. 121° (93), 118° (94) (corresp. Me ether, m.p. 82.5° (93), benzoyl deriv., m.p. 132° (94)).]

[Č with Br₂ (4 moles) in pres. of Fe powder gives (93) 4-chloro-2,3,5,6-tetrabromophenol, m.p. 215° (corresp. methyl ether, m.p. 161°, benzoyl deriv., m.p. 203° (93)).]

[For quant. detn. of C by dibromination with KBrO₃/KBr soln. see (95) (96) (97).]

Iodination. \bar{C} with I₂ (1 mole) in aq. KI + conc. NH₄OH gives (88% yield (98)) 4-chloro-2-iodophenol, ndls. from CHCl₃ or lt. pet., m.p. 78° (98) (99) (corresp. acetyl deriv., m.p. 57° (98); corresp. benzoyl deriv., m.p. 88° (99), 83-84° (98); corresp. N-phenyl-carbamate, m.p. 128° (99)).

 \bar{C} with excess I_2 in eq. KI + conc. NH₄OH (98), or \bar{C} in alk. soln. with I_2 in eq. KI (92),

or \overline{C} in alk. soln. with $I_2 + KIO_3$ followed by dil. H_2SO_4 (89), or \overline{C} with ICl (99), gives (89% yield (98)) 4-chloro-2,6-iodophenol, ndls. from alc. or lt. pet., m.p. 109° cor. (92), 108° (98) (100), 107-108° (89), 106-107° (99) (corresp. methyl ether, m.p. 79° (92); corresp. acetyl deriv., m.p. 128° (98), 127.5° (100)).

[For quant. detn. of \bar{C} by di-iodination using I_2 + borax soln. see (97).]

Nitration of \bar{C} . \bar{C} on mononitration with dil. HNO₃ (101) (102), or with 30% HNO₃ in cold (103), or with nitrosulfonic acid + fumg. HNO₃ (104), or in MeOH with HNO₃ (105), gives (yields 90% (103), 85% (102), 77% (104)) 4-chloro-2-nitrophenol [Beil. VI-238, VI₁-(122)], yel. cryst. from alc., volatile with steam, m.p. 86-87° (101) (102) (corresp. methyl ether, m.p. 98° (44), 97.5° cor. (106); corresp. ethyl ether, m.p. 61-62° (101); corresp. benzyl ether, m.p. 84-85° (99)). — [For use of mononitration in quant. detn. of mixts. of \bar{C} with o-chlorophenol (3:5980) see (107) cf. (112).]

C on dinitration with conc. HNO₃ (108) (or the above 4-chloro-2-nitrophenol on further nitration with fumg. HNO₃ (101)) gives 4-chloro-2,6-dinitrophenol [Beil. VI-260, VI₁-(128)], yel. ndls. or lfts. from aq., ndls. or pr. from alc., ether, or CHCl₃, m.p. 81° (108) (corresp. methyl ether, m.p. 66° (109), 64° (94); corresp. ethyl ether, m.p. 54-55° (110); corresp. N-phenylcarbamate cannot be prepared (111)).

Nitrosation of C. [Unlike the isomeric o-chlorophenol (3:5980) the nitrosation of C has not been reported, and no nitroso-p-chlorophenol is known.]

Sulfonation of \bar{C} . [\bar{C} with equiv. amt. fumg. H_2SO_4 (D=1.90) at 100° (113) (114) gives 4-chlorophenolsulfonic acid-2 [Beil. XI-236], deliquescent tbls. of monohydrate from aq., m.p. 75-76° (113) (for study of acid strength see (115)). — Note also that \bar{C} with very large excess (15 wt. pts.) fumg. H_2SO_4 (20% SO_3) gives (80-85% yield (116)) a bimolecular condensation prod. of the above sulfonic acid.]

Mercuration of \bar{C} . [\bar{C} with HgO/HgSO₄ on warming, followed by neutraliz. with NaOH, gives (117) 4-chloro-2-hydroxymercuriphenol [Beil. XVI₁-(564)]. — For other studies of mono- and di-mercuration of \bar{C} see (118) (119); for patents see (120) (121).]

CONDENSATION REACTIONS INVOLVING NUCLEAR HYDROGEN OF C

With alcohols. \tilde{C} with alcs. contg. more than one C in pres. of conc. HClO₄ at 0-160° gives ultimately (although doubtless through formn. of intermediate esters followed by rearr. or intermediate formn. of olefins followed by addn.) (122) the corresp. 2-alkyl-4-chlorophenols [e.g., \tilde{C} with isopropyl alc. (1:6135) + conc. HClO₄ as directed (122) gives 4-chloro-2-isopropylphenol, sol. aq. NaOH, b.p. 235-250° accompanied by 4-chloro-2,6-diisopropylphenol, insol. aq. NaOH, m.p. 260-265°].

With aldehydes. [$\bar{\mathbb{C}}$ with formaldehyde (1:0145) + conc. HCl + H₂SO₄ is claimed (123) to undergo simple chloromethylation yielding 5-chloro-2-hydroxybenzyl chloride, m.p. 85° (123); note, however, that further condensation (involving 2 additional moles of formaldehyde) may occur giving (67% yield (124)) 6-chloro-8-(chloromethyl)benzodioxane-1,3, cryst. from MeOH, m.p. 103° (124). — $\bar{\mathbb{C}}$ with formaldehyde (1:0145) + aq. alkali gives (125) 4-chloro-2,6-bis-(hydroxymethyl)phenol ("p-chlorophenol dialcohol"), m.p. 154° (126) (corresp. mono-(p-toluenesulfonate), m.p. 151° (127)); note that reaction of $\bar{\mathbb{C}}$ with 1 mole formaldehyde to give 4-chloro-2-(hydroxymethyl)phenol (5-chlorosalicyl alcohol) is not reported although the latter [Beil. VI-893], m.p. 93°, is known.]

With CHCl₃, chloral, or hexamethylenetetramine. [Č with CHCl₃ + EtOH + aq. NaOH (128), or Č with hexamethylenetetramine in anhydrous glyceroboric acid at 150-155° followed by H₂SO₄ hydrolysis (129), or Č with chloral + anhydrous Na₂HPO₄ at 70-75° (giving (4-chloro-2-hydroxyphenyl)-trichloromethyl-carbinol cf. (130)) followed by hydrolysis + oxidation (131), gives (18% yield (129)) 5-chloro-2-hydroxybenzaldehyde (5-chlorosalicylaldehyde) (3:2800), m.p. 99-100°.]

With CCl₄. [C with CCl₄ in aq. NaOH (128) in pres. of Cu or Cu compds. (132) or C with CCl₄ in alc. KOH in s.t. at 140° for 5-6 hrs. (133) gives 5-chloro-2-hydroxybenzoic acid (5-chlorosalicylic acid) (3:4705), m.p. 172°.]

With CO₂ or organic acids. [C (as dry NaA) with CO₂ at 140-150° under press. gives (135) (136) Na salt of 5-chlorosalicylic acid (3:4705) (see also above).]

[C with o-chlorobenzoic acid (3:4150) in MeOH/NaOMe + trace Cu powder evapd., htd. at 200°, then htd. with conc. H₂SO₄ for 15 min. gives (136) 2-chloroxanthone, m.p. 165° (136).]

With acid chlorides of organic acids. The conventional type of reaction of \bar{C} with acyl halides is to form the corresp. p-chlorophenyl esters (see also below under reactions of phenolic hydrogen of \bar{C}); however, with \bar{C} acid chlorides in pres. of AlCl₃ the ultimate product (undoubtedly formed by rearr. of an intermediate ester) is the ketone [e.g., \bar{C} with benzoyl chloride (3:6240) + AlCl₃ in CS₂ (137) or acetylene tetrachloride (3:5750) (138) gives 4-chloro-2-benzoylphenol (5-chloro-2-hydroxybenzophenone), m.p. 95.0-95.5° (138), 94-95° (139), 94° (137), 93-94° (140), frequently accompanied by p-chlorophenyl benzoate, m.p. 87° (see below); for analogous behavior of \bar{C} with p-toluyl chloride (3:8740) see (138)].

With anhydrides. [\bar{C} with phthalic anhydride (1:0725) + AlCl₃ at 140-145° (141) cf. (143) or in acetylene tetrachloride (3:5750) (142) gives (70% yield (142)) o-(5-chloro-2-hydroxybenzoyl)benzoic acid [Beil. X_{1} -(470)], cryst. from hot AcOH, acetone, or alc., m.p. 202°, after sintering at 192° (142); this product ring-closes under the conditions of its formn (141) (142) (143) (144) or with cone. H_2SO_4 at 100° (144) (142) cf. (141) giving 4-chloro-1-hydroxyanthraquinone [Beil. VIII-340, VIII₁-(651)], yel.-or. ndls. from AcOH or pyridine, m.p. 194° (141), 193-194° (145), 192-193° (146), 189° (142), 188° (147) (corresp. methyl ether, m.p. 168° (145), corresp. acetate, m.p. 176-177° (146)), also obtd. (70% yield (145)) directly from \bar{C} with phthalic anhydride (1:0725) + AlCl₃ + NaCl at 200-220° for 3 hrs. (See also next paragraph.)]

[Note, however, that \bar{C} with phthalic anhydride (1:0725) + conc. H_2SO_4 at 200° (148) (149) or in pres. of conc. $H_2SO_4 + H_3BO_3$ at 200° for $3\frac{1}{2}$ hrs. (150) (151) (143) (152) (153) (154) (155) (156) goes further than above giving (yield: 68-74% (150)) 1,4-dihydroxyan-thraquinone (quinizarin) (1:9085), cryst. from AcOH, m.p. 200-202° cor. (150).]

[C with 4-chlorophthalic anhydride (3:2725) + H₃BO₃ + fumg. H₂SO₄ at 175–195° for 20 hrs. gives (157) 6-chloro-1,4-dihydroxyanthraquinone (6-chloroquinizarin), tbls. from toluene, m.p. 188° (158) (corresp. dimethyl ether, m.p. 168.5° (158); diacetate, m.p. 213° (158)). — For completely analogous behavior under similar circumstances of C with 3,4-dichlorophthalic anhydride (3:3695) or C with 4,5-dichlorophthalic anhydride (3:4830) see these cpds.]

[\bar{C} with 4-sulfophthalic anhydride + H_3BO_3 + H_2SO_4 at 200° for 4 hrs. gives (45% yield (159) (160) cf. (161)) 1,4-dihydroxyanthraquinonesulfonic acid-6 (6-sulfoquinizarin) [Beil. XI-357]; for study of Na salt of latter as acid-base indicator see (162).]

[For behavior of \bar{C} with 3-methylphthalic anhydride + AlCl₃ (144) (163), with 4-methylphthalic anhydride + AlCl₃ (163), with naphthalene-1,2-dicarboxylic acid anhydride + AlCl₃ + NaCl (164), or with naphthalene-2,3-dicarboxylic acid anhydride + AlCl₃ + NaCl (165), see indic. refs.]

With esters of keto acids. [\bar{C} (1 mole) with ethyl acetoacetate (1:1710) + conc. H₂SO₄ stood 24 hrs. gives (2.7% yield (166)) 6-chloro-2-methylcoumarin [Beil. XVII-336, XVII₁-(173)], m.p. 186–187° (167), 186° (168), 185° (170), 184–185° (166), 184° (169); note, however, that 4-chloro-2-acetylphenol (5-chloro-2-hydroxyacetophenone) (see below) with Ac₂O + NaOAc at 160–170° for 5 hrs. gives (167) both the above 6-chloro-2-methylcoumarin and the isomeric 6-chloro-2-methylchromone, ndls. from AcOH, m.p. 115–116° (167).]

[Note also that \bar{C} with α -alkylacetoacetates + P_2O_5 gives the corresp. chromones: e.g.,

 $\bar{\mathbf{C}}$ with ethyl α -methylacetoacetate (1:1712) gives (17% yield (171)) 6-chloro-2,3-dimethyl-chromone, m.p. 107°; $\bar{\mathbf{C}}$ with ethyl α -ethylacetoacetate (1:1723) gives (171) 6-chloro-3-ethyl-2-methylchromone, m.p. 109°; $\bar{\mathbf{C}}$ with ethyl α -(n-propyl)acetoacetate gives (172) 6-chloro-2-methyl-3-n-propylchromone, m.p. 108°; $\bar{\mathbf{C}}$ with ethyl α -isopropylacetoacetate gives (172) 6-chloro-2-methyl-3-n-propylchromone, m.p. 108°; $\bar{\mathbf{C}}$ with ethyl α -isopropylacetoacetate gives (172) 6-chloro-3-isopropyl-2-methylchromone, m.p. 127°.]

[C with diethyl oxaloacetate + conc. H₂SO₄ at 0° gives (small yield (170)) ethyl 6-chlorocoumarin-4-carboxylate [Beil. XVIII₁-(493)], yel. ndls., m.p. 96-97°; C with diethyl acetonedicarboxylate (1:1772) + conc. H₂SO₄ gives (6% yield (170)) ethyl 6-chlorocoumarinyl-4-acetate [Beil. XVIII₁-(493)], m.p. 167°.]

With diazonium salts. \bar{C} in alk. soln. couples with diazonium salts giving upon acidification the corresp. chloro-hydroxy-azo derivs. [e.g., \bar{C} with benzenediazonium chloride (aniline diazotized in HCl soln.) gives (173) 4-chloro-2-(benzeneazo)phenol (5-chloro-2-hydroxyazobenzene) [Beil. XVI-93], red-or. ndls. from AcOH, mp. 110-111° (173) (174); \bar{C} with diazotized p-nitroaniline gives (175) 4-chloro-2-(p-nitrobenzeneazo)phenol, m.p. 140-143°; for patent on coupling of \bar{C} with other diazonium salts see (176)].

With other miscellaneous reactants. [For condensation of \bar{C} with indene (di)chloride (2,3-dichloroindane) see (177); for condensation of \bar{C} with o-nitrobenzenesulfinic acid (178) or with 2-chloro-5-nitrobenzenesulfinic acid (179) see indic. refs.; for oxidative condensation of \bar{C} with N,N-dialkyl-p-phenylenediamines, etc., to give various indophenols see (180).] $[\bar{C}$ (2 moles) with SCl₂ (1 mole) in CCl₄ at -10° (181) or in CS₂ at $40-45^{\circ}$ (70% yield (182)) or \bar{C} with S₂Cl₂ in CS₂ at room temp. (42% yield (182)) gives bis-(5-chloro-2-hydroxyphenyl) sulfide [Beil. VI₁-(396)], ndls. or lfts. from C₆H₆, m.p. 175° (183), 174° (182), 173-174° (184), 173° (181) (corresp. dimethyl ether, m.p. 112° (182); diethyl ether, m.p. 145° (185), dibenzoate, m.p. 145° (182)); for use as disinfectant (181) (183) or in mothproofing compositions (186) see indic. refs.]

[\bar{C} (2 moles) with SOCl₂ (1 mole) + AlCl₃ in CS₂ gives (70% yield (184)) bis-(5-chloro-2-hydroxyphenyl) sulfoxide [Beil. VI₁-(396)], pr. from dil. alc., m.p. 202° (corresp. dinitration prod., m.p. 180–181° (184)).]

REACTIONS INVOLVING NUCLEAR HALOGEN OF C

[\bar{C} on fusion with KOH (187) (188) or \bar{C} with aq. alkali or alk. carbonates in pres. of Cu or Cu compds. at elevated temp. under press. (189), or \bar{C} with aq. Ba(OH)₂ at 170–195° under press. (190), or \bar{C} with alkali or alk.-earth hydroxides + Cu salts at elevated temp. under press. (191) gives 1,4-dihydroxybenzene (hydroquinone) (1:1590); note, however, that in such fusions with alkali some 1,3-dihydroxybenzene (resorcinol) (1:1530) is also formed (187) (188) (192) (193), and \bar{C} (as Na \bar{A}) with NaOH at 310° for 5 hrs. gives (194) as high as 38% resorcinol (1:1530) + a trace of 2,4'-dihydroxybiphenyl; however, \bar{C} on fusion with K₂CO₃ is claimed (193) to yield only hydroquinone (1:1590).]

 $[\bar{C} \text{ with Na}_2S + \text{NaOH at 210-215}^\circ \text{ for 24 hrs. gives (195) 4-mercaptophenol (monothiohydroquinone)}$ [Beil. VI-859, VI₁-(419)], m.p. 29-30°.]

 $[\bar{C} \text{ with NH}_3 \text{ in pres. of Cu cpds. htd. under press. gives (196) } p-aminophenol; <math>\bar{C} \text{ similarly with prim. aliphatic amines gives (196) corresp. } N-alkyl-p-aminophenols.]$

REACTIONS OF C INVOLVING PHENOLIC H (I.E., H OF THE OH GROUP)

Acidic strength. $\ddot{\mathbf{C}}$ behaves as weak acid, is soluble in aq. alk. or in large excess (2.75 moles of 2 N (197)) aq. Na₂CO₃ soln. from which it is repptd. by CO₂ (197). — Dissoc. const. of $\ddot{\mathbf{C}}$ in aq. at 28.5° = 6.6 × 10⁻¹⁰ (198); for studies of dissoc. const. in other solutions, e.g., in 50% MeOH at 20° (199) (200) or at 28.5° (198), or at 18° over range 0-95% MeOH by volume (203), in 30% aq. EtOH at 25° (200) (9) (201), or at 18° over range

0-95% EtOH by vol. (202), see indic. refs. — For hydrogen potential of \bar{C} in 48.95 vol. % EtOH or 95 vol. % EtOH at 20° see (204). — For titration of \bar{C} with standard NaOH and indicator see (205).

Salts of C. [NaA; from C in abs. EtOH with equiv. Na, evapd. under H₂, dried at 140-150° (134); very hygroscopic ndls. from conc. alc. soln., turning brown in air; in contrast to Na phenolate is fairly eas. sol. dry ether (206); for behavior with CO₂ at 140-150° giving Na salt of 5-chlorosalicylic acid (3:4705) see (134) (135).]

 $[\bar{C} (38.4 \text{ pts.}) \text{ with KOH } (5.6 \text{ pts.}) \text{ in } C_6H_6 \text{ gives } (207) \text{ KA.}2\bar{C}.]$

[Č with AlCl₃ evolves heat and HCl giving (208) Cl.C₆H₄.OAlCl₂, m.p. 185–187° (208).] [For patents on use of alkali salts of C as anti-gumming agents for motor fuels see (209); for use of aq. solns. of salts of C as wash liquid for fuel gas purification see (210).]

ETHERIFICATION (see also below under D's)

Aliphatic ethers of \tilde{C} . \tilde{C} with alkyl halides usually in presence of an acid acceptor gives the corresponding p-chlorophenyl ethers [e.g., for methyl ether (p-chloroanisole) (3:6300) or for ethyl ether (p-chlorophenetole) (3:0090) see these compds. — p-Chlorophenyl n-propyl ether appears to be unreported; for p-chlorophenyl isopropyl ether, b.p. 101° at 17 mm. (211), 73-75° at 1.5 mm. (212), $n_D^{25} = 1.5127$ (212), see indic. refs. — For p-chlorophenyl isobutyl ether, b.p. 95-97° at 3 mm., $n_D^{25} = 1.5090$, see (213); the n-butyl, sec-butyl and ter-butyl ethers are unreported. — For p-chlorophenyl n-amyl ether, b.p. 132-133° at 12 mm., p-chlorophenyl n-hexyl ether, b.p. 172° at 34 mm., p-chlorophenyl n-heptyl ether, b.p. 162° at 14 mm., and p-chlorophenyl n-hexadecyl ether, m.p. 48°, see (214)].

[\bar{C} with vinyl chloride (3:7010) + aq. NaOH + CuCl₂ at 170–190° for 10 hrs. under press. gives (215) p-chlorophenyl vinyl ether, b.p. 193–194°, $D^{20}_{-}=1.138$. — \bar{C} with allyl bromide + K₂CO₃ in acetone gives (100% yield (216)) p-chlorophenyl allyl ether, b.p. 232–234° at ord. press., 106–107° at 12 mm.; note that distn. at ord. press. causes thermal rearr. to 4-chloro-2-allylphenol, b.p. 137° at 18 mm., 124–125° at 12 mm., mp. 48° (corresp. p-nitrobenzoate, m.p. 82°) (216). — \bar{C} with methallyl chloride (3:7145) + K₂CO₃ in acetone gives (217) p-chlorophenyl methylallyl ether, b.p. 101.5° at 8 mm., $D^{20}_{20}=1.0979$, $n^{20}_{10}=1.5304$; this prod. on thermal rearr. gives (217) 4-chloro-2-methallylphenol, b.p. 113° at 8 mm., $D^{20}_{20}=1.145$, $n^{20}_{10}=1.5622$, accompanied by some 5-chloro-2,2-dimethyl-coumaran, b.p. 96° at 5 mm., $D^{20}_{20}=1.135$, $n^{20}_{10}=1.5300$ (217).]

[$\bar{\mathbf{C}}$ with ethylene oxide (1:6105) in alc. NaOEt adds giving (218) cf. (219) ethylene glycol mono-(p-chlorophenyl) ether (p-chlorophenyl) β -hydroxyethyl ether), m.p. about 28° (corresp. p-nitrobenzoate, m.p. 90-91°) (218); note that the corresp. ethylene glycol bis-(p-chlorophenyl ether) is unreported.

[\tilde{C} (as Na \tilde{A}) with 2-chloropropanol-1 (3:7917) gives (220) p-chlorophenyl β -hydroxyisopropyl ether (propylene glycol β -(p-chlorophenyl) ether), b.p. 151–153° at 18 mm. — \tilde{C} with 3-chloropropanediol-1,2 (glycerol α -monochlorohydrin) (3:9038) in alk. soln. (221), or \tilde{C} with glycerol (1:6540) + NaOAc at 200–210° in atmosphere of illuminating gas (222) gives p-chlorophenyl β , γ -dihydroxy-n-propyl ether (glycerol α -(p-chlorophenyl ether), cryst. from C_6H_6 , m.p. 80° (221), 76° (222); b.p. 214–215° at 19 mm. (221), 173–175° at 17 mm. (223).]

[\bar{C} with diethyl chlorofumarate (3:6864) + NaOEt at 150° gives (224) diethyl p-chlorophenoxyfumarate, b.p. 199–200° at 12 mm. — \bar{C} (as Na \bar{A}) + \bar{C} with ethyl phenylpropiolate as directed gives (224) ethyl β -(p-chlorophenoxy)cinnamate, m.p. 63–64°, b.p. 220–225° at 12 mm.]

Aromatic ethers of \tilde{C} . [p-Chlorophenyl phenyl ether: b.p. 161-162° at 19 mm. (225), 146-150° at 7 mm. (226), $n_D^{25} = 1.5865$ (225); note that although this prod. has not been reported by etherification of \tilde{C} it has been obtd. from diphenyl ether (1:7125) in AcOH

with Cl_2 (226), from K phenolate + p-chloroiodobenzene (225), or from p-aminophenol phenyl ether via diazotization and use of Cu_2Cl_2 reaction (226); for studies of its chlorination, bromination, iodination, and nitration see (226), for metalation see (227); note also that the product first reported (228) was impure (225).]

p-Chlorophenyl p-chlorophenyl ether (bis-(p-chlorophenyl) ether) [m.p. 30° (226) (229), b.p. 168-172° at 7 mm. (226); note that this prod. has not been reported by etherification of Č but has been prepd. from diphenyl ether (1:7125) in AcOH with Cl₂ (226), or from p-aminophenol p-chlorophenyl ether via diazotization and use of Cu₂Cl₂ reaction (226) (229); for mononitration to 4-chlorophenyl 4-chloro-2-nitrophenyl ether, m.p. 75° (see also below) or dinitration to bis-(4-chloro-2-nitrophenyl) ether, m.p. 152° (229), 154° (236), see (229) (236)].

p-Chlorophenyl o-nitrophenyl ether [from \bar{C} (as $K\bar{A}$) with o-chloronitrobenzene on htg. (230) (231) in pres. of Cu bronze (232) (yields: 75% (232), 72% (230)), pale yel. cryst. from MeOH, m.p. 46° (231), 45.5° (230), 44-45° (232), b.p. 220° at 20 mm. (232), 208° at 11 mm. (232); note that this prod. does not (229) react with piperidine at 100°].

p-Chlorophenyl m-nitrophenyl ether [m.p. 60° (233), reported only by indirect means (233)]. p-Chlorophenyl p-nitrophenyl ether: from $\bar{\mathbf{C}}$ (as $K\bar{\mathbf{A}}$) with p-chloronitrobenzene on htg. (81% yield (230)) (229) (233), m.p. 76.5° (230), 76° (233), 75.5-76° (229); b.p. 215° at 12 mm. (229) or as one prod. of nitration of p-chlorophenyl phenyl ether (above) (226). — [For pat. on use as insecticide see (134).]

p-Chlorophenyl 2,4-dinitrophenyl ether: from \bar{C} (as K \bar{A} (230) or Na \bar{A} (235)) with 2,4-dinitrochlorobenzene on htg. (97% yield (230)); yel. tbls. from 1:2 EtOH/AcOH, m.p. 126° (235), 123° (230).

p-Chlorophenyl 2,4,6-trinitrophenyl ether. [This prod. which should easily be obtd. from \bar{C} (as $K\bar{A}$) with 2,4,6-trinitrochlorobenzene (picryl chloride) appears to be unreported.]

p-Chlorophenyl 4-chloro-2-nitrophenyl ether: from \bar{C} (as $K\bar{A}$) with 2,5-dichloronitrobenzene on htg. (84.4% yield (230)) (229) (231) (84), pale yel. ndls. from alc., m.p. 79° (230), 78° (231), 75° (229); b.p. 215-220° at 15 mm. (229).

p-Chlorophenyl 4-bromo-2-nitrophenyl ether: from \bar{C} (as KA) with 2,5-dibromonitrobenzene on htg. (91.9% yield (230)) (236), pale yel. ndls. from AcOH, m.p. 100-101° (236), 100.5° (230).

ESTERIFICATION

Esters of inorganic acids. [\bar{C} with SOCl₂ + pyridine in C₆H₆ as directed gives (237) (238) bis-(p-chlorophenyl) sulfite, b.p. 213-214° at 12 mm., sl. dec.]

- [\bar{C} (3 moles) with PCl₃ (1 mole) at 150° gives (239) tris-(p-chlorophenyl) phosphite, m.p. 49°, b.p. 290–297° at 15 mm. (corresp. MeI addn. prod., m.p. 71° (239)); note, however, that \bar{C} with large excess PCl₃ at 100° gives (240) p-chlorophenylphosphorous dichloride Cl.C₆H₄.OPCl₂, b.p. 128–130° at 12 mm., and di-(p-chlorophenyl)phosphorous chloride (Cl.C₆H₄.O)₂=P-Cl, b.p. 225–227° at 11 mm.]
- [C (3 moles) with POCl₃ (1 mole) under reflux (241), or C with POCl₃ in cold alk. soln. (242) (243), or C (as NaA) with POCl₃ in neutral inert solv. (244), gives tri-(p-chlorophenyl) phosphate [Beil. VI-188, VI₁-(102)], m.p. 117° (241), 112° (244). Note, however, that C with POCl₃ in pres. of Mg at 130–140° gives (245) p-chlorophenylphosphoryl dichloride, Cl.C₆H₄.O—P(O)Cl₂ [Beil. VI-188, VI₁-(102)], b.p. 265° at 760 mm. (246) (247), 141° at 12 mm. (246), 95–115° at 0.1 mm. (245), accompanied by di-(p-chlorophenylphosphoryl chloride (Cl.C₆H₄.O)₂P(O)Cl [Beil. VI-188], b.p. 164–176° at 0.1 mm. (245); these two products may be hydrolyzed, respectively, to p-chlorophenylphosphoric acid [Beil. VI-188] cf. (248), m.p. 80–81° (249), and di-(p-chlorophenyl)phosphoric acid [Beil. VI-188], m.p. 126–127° (242), 133–135° cor. (248) (250).]

[For analogous behavior of C with TiCl₄ see (251).]

Esters of aliphatic organic acids (see also below under D's).

p-Chlorophenyl acetate: from \bar{C} with Ac₂O + NaOAc (252); m.p. 7-8° (252), b.p. 226-228° (253), 100-102° at 15 mm. (254), 108° at 12.5 mm. (252), 90-92° at 2.5 mm. (61), D_4^{20} = 1.2248 (252). — Note that this prod. with AlCl₃ on htg. (255) (254) (61) or \bar{C} with AcCl + FeCl₃ directly (256) gives (100% yield (255)) 4-chloro-2-acetylphenol (5-chloro-2-hydroxy-acetophenone) [Beil. VIII-86], m.p. 55° (256), 54° (61), 53.5-54.5° (167), b.p. 97-99° at 2 mm. (61) (corresp. acetate, b.p. 156-157° (140)).

p-Chlorophenyl propionate: from \bar{C} with propionyl chloride (3:7170) (140) (61); oil, b.p. 234-236° (140), 76-78° at 2 mm. (61). — Note that this prod. with AlCl₃ undergoes Fries rearr. giving (140) (61) 4-chloro-2-propionylphenol (5-chloro-2-hydroxypropiophenone), m.p. 59.7° (61), 56.5-57.5° (140) (corresp. methyl ether, m.p. 41-42°, b.p. 135-140° at 6 mm. (257)).

p-Chlorophenyl n-butyrate: from \tilde{C} with n-butyryl chloride (3:7370) (140) (61); oil, b.p. 249-251° (140), 96-98° at 3 mm. (61). — Note that this prod. with AlCl₃ undergoes Fries rearr. giving (140) (61) 4-chloro-2-(n-butyryl)phenol (5-chloro-2-hydroxy-n-butyro-phenone), m.p. 50.5° (61), 49-50° (140); b.p. 108-112° at 3 mm. (61).

p-Chlorophenyl isobutyrate: from $\bar{\rm C}$ with isobutyric acid (1:1030) + POCl₃ (258); m.p. 29°, b.p. 120° at 11 mm. (258). — Note that this prod. with AlCl₃ undergoes Fries rearr. giving (258) 4-chloro-2-isobutyrylphenol (5-chloro-2-hydroxy-isobutyrophenone), oil, b.p. 130° at 20 mm., $D_4^{20}=1.192, n_{\rm He}^{20}=1.5521$ (258).

[For generally analogous behavior of \bar{C} with *n*-valeryl chloride (3:7740), *n*-caproyl chloride (3:8168), *n*-heptanoyl chloride (3:8520), *n*-octanoyl chloride (3:8680) see (61); with chloroacetyl chloride (3:5235) see (259); with α -bromo-isovaleryl bromide see (260).]

 $\bar{\mathbf{C}}$ (as Na $\bar{\mathbf{A}}$) (2 moles) with COCl₂ (3:5000) in C₆H₆ at 130–180° under press. (261) or $\bar{\mathbf{C}}$ (as K $\bar{\mathbf{A}}$) in conc. aq. soln. with COCl₂ in toluene (262), or $\bar{\mathbf{C}}$ with trichloromethyl chloroformate (diphsogene) (3:5515) + aq. NaOH (263), gives di-(p-chlorophenyl) carbonate [Beil. VI-187], m.p. 147° (263), 144–145° (264).

Esters of aromatic organic acids (see also below under ©'s).

p-Chlorophenyl benzoute: from C with benzoyl chloride (3:6240) (265) (for study of rate at 25° sec (268)) in pres. of aq. NaOH (252) (266) (267); m.p. 87-87.5° (138), 87° u.e. (252), 86° (266) (267). — Note that this prod. with AlCl₃ undergoes Fries rearr. giving (140) 4-chloro-2-benzoylphenol (5-chloro-2-hydroxybenzophenone), m.p. 95.0-95.5° (138), 94-95° (139), 94° (137), 93-94° (140) (corresp. benzoate, m.p. 112° (139)).

p-Chlorophenyl cinnamate: from \bar{C} with cinnamoyl chloride (3:0330) (68% yield (260)), m.p. 105° (260) (269).

- ---- p-Chlorophenyl methyl ether (p-chloroanisole): oil. (See 3:6300.)
- p-Chlorophenyl ethyl ether (p-chlorophenetole): m.p. 20-21°. (See 3:0090.)
- p-Chlorophenyl acetate: m.p. 7-8° (252). [For further details see above under esters of C with aliphatic organic acids.]
 - D p-Chlorophenyl benzoate: m.p. 87.0-87.5° (138), 87° u.c. (252), 86° (266) (267).
 [From \(\tilde{C}\) with benzoyl chloride in pres. of aq. NaOH (252) (266) (267) (see also above under esters of \(\tilde{C}\) with aromatic organic acids).]
 - --- p-Chlorophenyl o-nitrobenzoate: unreported.
 - D p-Chlorophenyl m-nitrobenzoate: m.p. 124.5° (252). [From C with m-nitrobenzoyl chloride + aq. NaOH (252).]
 - D p-Chlorophenyl p-nitrobenzoate: m.p. 171° (270).
 - D p-Chlorophenyl 3,5-dinitrobenzoate: m.p. 186° (271).
 - --- p-Chlorophenyl benzenesulfonate: unreported.

- ---- p-Chlorophenyl p-toluenesulfonate: unreported.
- D p-Chlorophenyl benzyl ether: ndls. from alc., m.p. 71° (272), 70-71° (273). [Note, however, that C with benzyl chloride (3:8535) + AlCl₃ gives not only this prod. but also (273) cf. (274) some Fries rearr. prod., viz., 4-chloro-2-benzylphenol (5-chloro-2-hydroxydiphenylmethane), m.p. 48-49° (273), 48.5° (274) (corresp. benzoate, m.p. 54-55°, benzenesulfonate, m.p. 68-69°, p-toluenesulfonate, m.p. 75.0-75.5° (273)).]
- p-Chlorophenyl p-nitrobenzyl ether: cryst. from alc., m.p. 101.3° (275). [From C + p-nitrobenzyl chloride (m.p. 71°) (or p-nitrobenzyl bromide, m.p. 99°) in alc. NaOEt (275).]
- D p-Chlorophenyl 2,4-dinitrophenyl ether: yel. tbls. from 1:2 EtOH/AcOH, m.p. 126° (235), 123° (230). [From C (as KA (230) or NaA (235)) with 2,4-dinitrochlorobenzene (m.p. 51°) on htg. (97% yield (230)).]
- D p-Chlorophenoxyacetic acid (3:4375): pr. from hot aq., m.p. 156.7-157.2° cor. (279), 155-156.5° u.e. (276), 155-156° (277), 154-155° (278). [From \(\bar{\mathbf{C}}\) with chloroacetic acid in aq. alk. (279) (276) (277) (278).]
- —— p-Chlorophenyl N-phenylcarbamate: cryst. from alc., m.p. 138° (280), 137-138° (263). [From C (as NaA) with phenylisocyanide dichloride on htg. (280); note, however, prepn. from C + phenyl isocyanate has not been reported.
- ① p-Chlorophenyl N-(p-bromophenyl)carbamate: white pl. from $C_6H_6/EtOAc$, m.p. $196-197^{\circ}$ cor. (281). [From \bar{C} with p-bromobenzazide (281) in lgr. (281).]
- D p-Chlorophenyl N-(p-iodophenyl)carbamate; m.p. 214-215° (282). [From C with p-iodobenzazide (282) in lgr. (282).]
- ① p-Chlorophenyl N-(m-nitrophenyl)carbamate: white pl. from lgr., m.p. 136° u.c., 139° cor. (283). [From C with m-nitrobenzazide (283) or m-nitrophenyl isocyanate (283) in lgr. (283)]
- p-Chlorophenyl N-(p-nitrophenyl)carbamate: pale yel. rods from lgr., m.p. 196° cor.
 (284). [From C with p-nitropenzazide (284) in lgr. (284).]
- \bigcirc p-Chlorophenyl N-(3,5-dinitrophenyl)carbamate: yel. pl. from $C_6H_6/EtOAc$, m.p. 197-198° (285). [From \bar{C} with 3,5-dinitrophenzazide (285) in lgr. (285).]
- D p-Chlorophenyl N-(3,5-dinitro-4-methylphenyl)carbamate: pale yel. pl. from lgr., m.p. 206-207° u.c., 212-213° cor. (286). [From C with 3,5-dinitro-4-methylbenzazide (286) in lgr. (286).]
- p-Chlorophenyl N-(α-naphthyl)carbamate: m.p. 165-166° (287). [From C with α-naphthyl isocyanate in lgr. (287).]
- D p-Chlorophenyl N-(β-naphthyl)carbamate: pl. from lgr., m.p. 165-166° u.c., 169-170° cor. (288). [From C with β-naphthyl isocyanate (288) in lgr. (288).]
- p-Chlorophenyl N,N-diphenylcarbamate: m.p. 97° (289). [From C with N,N-diphenylcarbamyl chloride (289).]
- 3:0475 (1) Puschin, Dimitrijevic, Z. physik. Chem. A-184, 231-237 (1939). (2) Holleman; Rinkes, Koninkl. Akad. Wetenschappen Amsterdam 18, 540-541 (1910); Cent. 1910, I 1502; C.A. 5, 1282 (1911). (3) Holleman, Rinkes, Rec. trav. chum. 30, 82-92 (1911). (4) Burnham, Madgin, J. Chem. Soc. 1936, 789-793. (5) Williams, Fogleberg, J. Am. Chem. Soc. 52, 1358 (1930). (6) Dubois, Zeit. für Chemie, 1867, 205; Jahresber. 1867, 206. (7) Durrans, J. Chem. Soc. 121, 47 (1922). (8) Minaev, Fedorov, Sarnit, Org. Chem. Ind. (U.S.S.R.) 4, No. 13, 19-22 (1937); Cent. 1938, II 173; C.A. 31, 8514 (1937). (9) Bennett, Brooks, Glasstone, J. Chem. Soc. 1935, 1823, 1826. (10) Beilstein, Kurbatow, Ann. 176, 30-35 (1875).
- (11) Lecat, Rec. trav. chim. 47, 16 (1928). (12) Kohlrausch, Pongratz, Monatsh. 65, 202 (1935). (13) Jorissen, Z. anorg. allgem. Chem. 104, 161 (1918). (14) Puschin, Matavulj, Z. physik. Chem. A-164, 81-82 (1933). (15) Petersen, Bachr-Predari, Ann. 157, 124-125 (1871). (16) Holleman, Rec. trav. chim. 37, 105-106 (1918). (17) Sidgwick, Turner, J. Chem. Sc. 121, 2256-2259 (1922). (18) Virtanen, Pulkki, J. Am. Chem. Soc. 50, 3138-3151 (1928); Ann. acad. sci. Fennicae 29-A, 28 pp. (1927); Cent. 1928, I 167; C.A. 22, 4351 (1928). (19) Takagi, Ishimasa, J. Pharm. Soc.

Japan, No. 517, 253-260 (1925); Cent. 1926, I 182; C.A. 20, 2669 (1926). (20) Jona, Gazz. chim. ital. 39, II 303-304 (1908).

(21) Weissenberger, Schuster, Lielacher, Monatsh. 46, 295-296 (1925).
(22) von Auwers, Z. physik. Chem. A-158, 418 (1932).
(23) Puschin, Matavulj, Z. physik. Chem. A-158, 291 (1932).
(24) Hrynakowski, Szmyt, Z. physik. Chem. A-182, 110, 113-114 (1938).
(25) Luchinskii, Likhacheva, J. Phys. Chem. (U.S.S.R.) 7, 723-727 (1936); Cent. 1937, 14767; C.A. 30, 7992 (1936).
(26) Thole, Mussell, Dunstan, J. Chem. Soc. 103, 1115 (1913).
(27) Puschin, Rikovski, Ann. 532, 297-299 (1937).
(28) Burnham, Madgin, J. Chem. Soc. 1936, 1303-1306.
(30) Landee, Johns, J. Am. Chem. Soc. 63, 2895 (1941).

(31) Tschunkur, Herdieckerhoff (to I.G.), Ger. 497,412, May 9, 1930; Cent. 1930, II 984; [C.A. 24, 3520 (1930)]. (32) Euler, Ann. 325, 303 (1903). (33) Ruff, Stein, Ber. 34, 1675 (1901). (34) Tishchenko, J. Russ. Phys.-Chem. Soc. 60, 153-162 (1928); Cent. 1928, II 767; C.A. 22, 3397, (1928). (35) Faust, Muller, Ann. 173, 303-304 (1874). (36) Likhosherstov, Arkhangel'skaya J. Gen. Chem. (U.S.S.R.) 7, 1914-1928 (1937); Cent. 1938, I 3330; C.A. 32, 519 (1938). (37) Likhosherstov, J. Russ. Phys.-Chem. Soc. 61, 1019-1023; 1025-1028 (1929); Cent. 1930, I 1294; C.A. 24, 836 (1930). (38) Goldschmidt, Endres, Dirsch, Ber. 58, 576 (1925). (39) Peratoner, Finocchiaro, Gazz. chim. ital. 24, I 238-239 (1894). (40) Peratoner, Gazz. chim. ital. 28, I 210 (1898).

(41) Dubois, Zeit. für Chemie 1866, 705; Jahresber. 1866 283. (42) Schmitt, Cook, Ber. 1, 67-68 (1868). (43) Hodgson, Foster, J. Chem. Soc. 1942, 583. (44) Holleman, de Mooy, Rec. trav. chim. 35, 14, 18, 27-28 (1915). (45) de Lange, Rec. trav. chim. 38, 103-105 (1919). (46) Chemische Werke Ichendorf, Ger. 281,175, Dec. 15, 1914; Cent. 1915, I 180; [C.A. 9, 1830 (1915)]. (47) Lofton, Burroughs (to Pennsylvania Coal Products Co.) U.S. 2,126,648, Aug. 9, 1938; Cent. 1938, II 3006; C.A. 32, 7925 (1938). (48) Kipriyanov, Dashevskii, Ukrain. Khem. Zhur. 7, Wiss-Tech. Abt. 78-86 (1932); Cent. 1933, II 1338; C.A. 27, 3824 (1933). (49) Vorozhtzov, Karlash, Compt. rend. acad. sci. U.R.S.S. 1933, 221-223; Cent. 1935, I 55; C.A. 28, 1991 (1934); Russ. 30,690, June 30, 1933; Cent. 1934, I 767; C.A. 28, 5834 (1934). (50) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994; [C.A. 26, 2747 (1932)].

(51) Autenrieth, Arch. Pharm. 233, 31-32 (1895). (52) Autenrieth, Muhlinghaus, Ber. 39, 4102 (1906). (53) Borosel, J. Am. Chem. Soc. 53, 1408-1409 (1931). (54) Peratoner, Gazz. chim. ital. 28, I 239 (1898). (55) Peratoner, Vitale, Gazz. chim. ital. 28, I 216 (1898). (56) Boehringer und Sohne, Ger. 286,266, July 30, 1915; Cent. 1915, II 566; [C.A. 10, 1254 (1916)]. (57) Shiple, Muldoon, Sherwin, J. Biol. Chem. 60, 59-67 (1924). (58) Muldoon, Shiple, Sherwin, Proc. Soc. Exptl. Biol. Med. 21, 145 (1923); Cent. 1924, II 1363, not in C.A. (59) Coombs, Hele, Biochem. J. 20, 606-612 (1927); Cent. 1926, II 1975; C.A. 21, 3224-3225 (1927). (60) Woodward, Kingery, Williams, J. Lab. Clin. Med. 19, 1216-1223 (1934); Cent. 1935, I 256; C.A. 28, 6849 (1934).

(61) Klarmann, Shternov, Gates, J. Am. Chem. Soc. 55, 2576-2589 (1933). (62) Klarmann, Shternov, Gates, J. Lab. Clin. Med. 19, 835-851 (1934); C.A. 28, 4792 (1934). (63) Engelhardt, Biochem. Z. 190, 217-225 (1927); Cent. 1928, II 691; C.A. 22, 1990-1991 (1928). (64) Kuroda, Arch. exptl. Path. Pharmakol. 112, 60-64 (1926); Cent. 1926, I 3610; C.A. 20, 2705-2706 (1926). (65) Kuroda, Biochem. Z. 169, 281-289 (1926); Cent. 1928, I 3068; C.A. 20, 3315 (1926). (66) Cooper, Forstner, Biochem. J. 18, 941-947 (1924); Cent. 1925, I 104; C.A. 19, 311 (1925). (67) Cooper, Woodhouse, Biochem. J. 17, 600-612 (1923); Cent. 1923, III 1625; C.A. 18, 403 (1924). (68) Uhlenhuth, Hailer, Arch. Hyg. 92, 30-52 (1923); Cent. 1923, IV 435; C.A. 18, 543 (1924). (89) Kohman, Ind. Eng. Chem. 15, 518 (1923). (70) Osborn, J. Am. Water Works Assoc. 17, 586-590 (1927); Cent. 1927, II 312; C.A. 21, 2343 (1927).

(71) Harrison, J. Am. Water Works Assoc. 15, 292-297 (1926); Cent. 1926, I 3501; C.A. 20, 2216 (1926). (72) Harrison, J. Am. Water Works Assoc. 17, 336-340 (1927); Cent. 1927, I 3026; C.A. 21, 1686 (1927). (73) Harrison, J. Am. Water Works Assoc. 21, 542-549 (1929); Cent. 1929, II 618; C.A. 23, 3286 (1929). (74) Saegbarth (to Edeleanu, G. m.b.h.), U.S. 2,138,772, Nov. 29, 1939; Cent. 1939, I 2114; C.A. 33, 2321 (1939). (75) Orelup, Ohlsson, Isermann, U.S. 1,730,850, Oct. 8, 1929; Cent. 1929, II 3254; C.A. 23, 5541 (1929). (76) Hilmer, Cellulosechem. 6,169-187 (1925); Cent. 1926, I 890; not in C.A. (77) Bell, J. Chem. Soc. 1936, 1244. (78) Kelber, Ber. 50, 309 (1917). (79) Kelber, Ber. 54, 2259-2260 (1921). (80) Spencer, Price, J. Chem. Soc. 97, 388-389 (1910).

(81) Vorozhtzov, Karlash, Russ. 30,689, June 30, 1933; Cent. 1934, I 767; C.A. 28, 5834 (1934).
(82) Böeseken, Metz, Rec. trav. chim. 54, 346, 350 (1935).
(83) Fichter, Adler, Helv. Chim. Acta 92, 279-281 (1926).
(84) Groves, Turner, Sharp, J. Chem. Soc. 1929, 516, 519.
(85) Roberts, Soper, J. Chem. Soc. 1932, 1982.
(86) Soper, Smith, J. Chem. Soc. 1926, 1589.
(87) Thomas, J. Am. Chem. Soc. 63, 629-630 (1941).
(88) Raiford, Miller, J. Am. Chem. Soc. 55, 2127 (1933), (89) Hunter, Joyce, J. Am. Chem. Soc. 39, 2643-2644 (1917).
(90) Fox, Turner, J. Chem. Soc. 1930, 1861.

- (91) Lauer, J. Am. Chem. Soc. 48, 449 (1926). (92) Kohn, Rosenfeld, Monatsh. 46, 106-107, 112-115 (1925). (93) Kohn, Dömötör, Monatsh. 47, 228-233 (1926). (94) Kohn, Kramer, Monatsh. 49, 153-155 (1928). (95) Day, Taggart, Ind. Eng. Chem. 20, 545-547 (1928). (96) Feist, Klatt, Pharm. Ztg. 76, 112-113 (1931); Cent. 1931, I 3492; [C.A. 25, 1632 (1931)]. (97) Khaletskii, Yanovitskaya, Farmatsiya i Farmakol (U.S.S.R.) 1938, No. 1, 17-19; C.A. 33, 8143 (1934); Cent. 1938, II 1454. (98) Varma, Yashoda, J. Indian Chem. Soc. 16, 477-478 (1939). (99) Buchan, McCombie, J. Chem. Soc. 1931, 140-144. (100) Brenaus, Girod, Compt. rend. 186, 1553-1555 (1928).
- (101) Faust, Saame, Ann. Suppl. 7, 191-195 (1870). (102) Mottier, Arch. sci. phys. nat. 16, 301-303 (1934); Cent. 1935, I 3278; C.A. 29, 3322 (1935). (103) Neunhoeffer, Ber. 68, 1777-1778 (1935). (104) Varma, Sharma, J. Indian Chem. Soc. 7, 629-630 (1930). (105) Plazek, Roczniki Chem. 10, 761-776 (1930); Cent. 1931, I 1428; [C.A. 25, 1504-1505 (1931)]. (106) Reverdin, Ber. 36, 1689-1690 (1903). (107) Takagi, Tanaka, J. Pharm. Soc. Japan 1925, No. 517, 247-252; Cent. 1926, I 182; C.A. 20, 2669 (1926). (108) Dubois, Zeit. für Chemie, 1867, 206; Jahresber. 1867, 613. (109) Schouten, Rec. trav. chim. 56, 555 (1937). (110) Petersen, Baehr-Predari, Ann. 167, 161 (1871).
- (111) Tarbell, Mallatt, Wilson, J. Am. Chem. Soc. 64, 2229 (1942). (112) Rashevskaya, Zil'berman, Chernyarskaya, Skirvskaya, J. Gen. Chem. (U.S.S.R.) 10, 499-505 (1937); Cent. 1938, I 58; C.A. 31, 6212 (1937). (113) Petersen, Baehr-Predari, Ann. 157, 128-147 (1871). (114) Gauntlett, Smiles, J. Chem. Soc. 127, 2745-2746 (1925). (115) Hamer, Pinching, Acree, J. Research Natl. Bur. Standards 31, 291-304 (1943). (116) Schoepfle, Van Natta, Clarkson; J. Am. Chem. Soc. 50, 1172-1174 (1928). (117) Bayer and Co., Ger. 234,851, May 20, 1911, Cent. 1911, I 1769; C.A. 5, 2912 (1911). (118) Hart, Andersen, J. Am. Chem. Soc. 57, 1060 (1935). (119) Kalinowski, Roczniki Chem. 9, 131-147 (1929); Cent. 1929, I 2301; C.A. 23, 3216 (1929). (120) Engelmann (to du Pont Co.), U.S. 1,748,331, Feb. 25, 1930; Cent. 1930, II 802; C.A. 24, 1927 (1930).
- (121) Engelmann, Funk (to du Pont Co.), U.S. 1,801,145, April 14, 1931; Cent. 1932, I 571; C.A. 25, 3430 (1931). (122) Hinsberg, Ger. 538,376, Nov. 14, 1931; Cent. 1932, I 2094; [C.A. 26, 1617 (1932)]. (123) F. Bayer and Co., Ger. 132,475, June 9, 1902; Cent. 1902, II 82. (124) Buehler, Bass, Darling, Lubs, J. Am. Chem. Soc. 62, 890-891 (1940). (125) Weiler, Berres (to I.G.), Ger. 510,447, Oct. 18, 1930; Cent. 1931, I 2115; C.A. 25, 974 (1931). (126) Hanus, J. prakt. Chem. (2) 158, 253 (1941). (127) Zinke, Hanus, Ziegler, J. prakt. Chem. (2) 152, 142 (1939). (128) Sen, Ray, J. Indian Chem. Soc. 9, 176 (1932). (129) Duff, J. Chem. Soc. 1941, 547-550. (130) Pauly, Schanz, Ber. 56, 979-985 (1923).
- (131) Haakh, Smola, Austrian 141,159, March 25, 1935; Cent. 1935, II 439; C.A. 29, 4021 (1935). (132) Zeitner, Landau, Ger. 258,887, April 17, 1913, Cent. 1913, I 1641; [C.A. 7, 2996 (1913)]. (133) Hasse, Ber. 10, 2190 (1877). (134) Varnholt, J. prakt. Chem. (2) 36, 17-22 (1887). (135) Chem. Fabrik von Heyden, Ger. 33,635; Friedlander 1, 234 (1877-1887). (136) Dhar, J. Chem. Soc. 117, 1068 (1920). (137) Pieroni, Gazz. chim. ital. 62, 390 (1932). (138) Hayashi, J. prakt. Chem. (2) 123, 298-299, 304 (1929). (139) Arventi, Bull. soc. chim. (5) 3, 603 (1936). (140) Wittig, Bangert, Richter, Ann. 446, 194, 198, 186, 188 (1926).
- (141) Ullmann, Ger. 282,493, March 6, 1915; Cent. 1915, I 643; [C.A. 9, 2598 (1915)]. (142) Ullmann, Conzetti, Ber. 53, 829-831 (1920). (143) Rogers, Ogilvie, Crowell (to Natl. Aniline and Chem. Co.), U.S. 1,886,237, Nov. 1, 1932; Cent. 1933, II 1765; C.A. 27, 1366 (1933). (144) Hayashi, J. Chem. Soc. 1927, 2519-2520. (145) Waldmann, J. prakt. Chem. (2) 130, 98-99 (1931). (146) Green, J. Chem. Soc. 1927, 1434-1435. (147) Conant, Fieser, J. Am. Chem. Soc. 46, 1866 (1924). (148) Bayer, Caro, Ber. 8, 152 (1875). (149) Liebermann, Ann. 212, 11-12 (1882). (150) Bigelow, Reynolds, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 476-478 (1941); (1st ed.), 464-465 (1932); 6, 78-80 (1926).
- (151) Reynolds, Bigelow, J. Am. Chem. Soc. 48, 420-422 (1926). (152) Spalding (to Natl. Aniline and Chem. Co.), U.S. 1,845,632, Feb. 16, 1932; Cent. 1933, I 1489; C.A. 26, 2203 (1532). (153) Gubelmann, Wieland (to Newport Chem. Corpn.), U.S. 1,790,915, Feb. 3, 1931; Cent. 1932, I 2238; C.A. 25, 1539 (1931). (154) Orelup, U.S. 1,790,510, Jan. 27, 1931; Cent. 1932, I 2238 [C.A. 25, 1265 (1931)]. (155) Dodd, Sprent and United Alkali Co., Brit. 245,584, Feb. 4, 1921; Cent. 1927, I 360; C.A. 21, 249 (1927) (156) Soc. étude colorantes solides, French 550,362, March 5, 1923; Cent. 1925, I 1245; not in C.A. (157) Scottish Dyes, Ltd., Bangham, Hooley, Thomas, Brit. 339,589, Jan. 8, 1931; Cent. 1932, I 2095; [C.A. 25, 2859 (1931)]. (158) Waldmann, J. prakt. Chem. (2) 126, 255 (1930). (159) Schwenk, Waldmann, Z. angew. Chem. 45, 20-21 (1932). (160) Schwenk (to General Aniline Works), U.S. 1,890,866, Dec. 13, 1932; Cent. 1933, II 613; [C.A. 27, 1642 (1933)].
- (161) Mildner (to I.G.), Ger. 534,930, Oct. 3, 1931; Cent. 1932, I 591; [C.A. 26, 1142 (1932)]. (162) Green, Ind. Eng. Chem., Anal. Ed. 14, 249 (1942). (163) Hayashi, J. Chem. Soc. 1936, 1513-1518. (164) Waldmann, J. prakt. Chem. (2) 131, 77-78 (1931). (165) Waldmann, Mathio-

wetz, Ber. 64, 1718 (1931). (166) Clayton, J. Chem. Soc. 93, 2022 (1908). (167) Wittig, Ber. 57, 88-91 (1924). (168) Mayer, Philipps, Ruppert, Schmitt, Ber. 61, 1971, 1974 (1928). (169) Chakravarti, Dutta, J. Indian Chem. Soc. 17, 65-71 (1940). (170) Dey, J. Chem. Soc. 107, 1642, 1644 (1915).

(171) Simonis, Schuhmann, Ber. 50, 1144-1145 (1917). (172) Chakravarti, J. Indian Chem. Soc. 9, 28 (1932). (173) Krause, Ber. 32, 126 (1899). (174) Hodgson, Rosenberg, J. Soc. Chem. Ind. 497, 405-408 (1930). (175) Ernsberger, Brode, J. Org. Chem. 6, 333 (1941). (176) F. Bayer and Co., Ger. 210,964, June 16, 1909; Cent. 1909, II 243; C.A. 3, 2512 (1909). (177) Suter, Lutz, J. Am. Chem. Soc. 60, 1365-1368 (1938). (178) Kent, Smiles, J. Chem. Soc. 1934, 426. (179) Krishna, J. Chem. Soc. 123, 2785 (1923). (180) M.L.B., Ger. 158,091, Jun. 21, 1905; Cent. 1905, I 478.

(181) F. Dunning, B. Dunning, W. Drake, J. Am. Chem. Soc. 53, 3466-3469 (1931). (182) Richter, Ber. 49, 1024-1025 (1916). (183) Muth (to I.G.), Ger. 568,944, Jan. 1, 1933; Cent. 1933, I 2280, C.A. 27, 2696 (1933). (184) Gazdar, Smiles, J. Chem. Soc. 97, 2251-2252 (1910). (185) Hilditch, Smiles, J. Chem. Soc. 99, 416 (1911). (186) I.G., Brit. 349,004, June 18, 1931; Cent. 1932, I 313; [C.A. 26, 2026 (1932)]. (187) Petersen, Bachr-Predari, Ann. 157, 126-128 (1871). (188) Faust, Ber. 6, 1022-1023 (1873). (189) Bochringer und Sohne, Ger. 269,544, Jan. 22, 1914; Cent. 1914, I 591-592; [C.A. 8, 2221 (1914)]. (190) Bayer and Co., Ger. 249,939, Aug. 1, 1912; Cent. 1912, II 655; [C.A. 6, 3329 (1912)].

(191) Burroughs (to Pennsylvania Coal Products Co.), U.S. 2,041,592, May 19, 1936; Cent. 1937, I 1016; C.A., 30, 4513 (1936). (192) Blanksma, Chem. Weekblad 5, 93-95 (1908); Cent. 1908, I 1051; C.A. 2, 1700 (1908). (193) Tijmstra, Chem. Weekblad 5, 96-101 (1908); Cent. 1908, I 1051; C.A. 2, 1700-1701 (1908). (194) Fierz-Pavid, Stamm, Helv. Chim. Acta 25, 304-370 (1942); C.A. 36, 5469 (1942). (195) Imperial Chem. Ind., Ltd. and Palmer, But. 381,237, Oct. 27, 1932; Cent. 1933, I 675, C.A. 27, 3946 (1933). (196) A.G.F.A., Ger. 205,415, Dec. 28, 1908; Cent. 1909, I 600; [C.A. 3, 1695 (1909)]. (197) Wohlleben, Ber. 42, 4373 (1909). (198) Murray, Gordon, J. Am. Chem. Soc. 57, 110-111 (1935). (199) Kuhn, Wassermann, Helv. Chim. Acta 11, 27 (1928). (200) Jenkins, J. Chem. Soc. 1339, 1139.

(201) Baddeley, Bennett, Glasstone, Jones, J. Chem. Soc. 1935, 1827–1830. (202) Mizutani, Z. physik. Chem. 118, 326 (1925). (203) Mizutani, Z. physik. Chem. 118, 331 (1925). (204) Schwarzenbach, Egli, Helv. Chim. Acta 17, 1176–1182 (1934). (205) Naegel, Kollond-Chem. Beihefte 21, 344,387 (1926). (206) Hantzsch, Mai, Ber. 28, 978 (1895). (207) Schulke-Mayr, Flemming, Ger. 247,410, May 5, 1929; Cent. 1912, II 165; [C.A. 6, 2674 (1912)]. (208) Perrier, Bull. soc. chim. (3) 15, 1183 (1896). (209) Benedict (to Universal Oil Products Co.) U.S. 2,051,-814, Aug. 25, 1936; Cent. 1937, I 495; [C.A. 30, 6938 (1936)]. (210) Vorhees (to Standard Oil Co. of Indiana), U.S. 2,196,281, April 9, 1940; 1942, I 701, C.A. 34, 5275 (1940).

(211) Jones, J. Chem. Soc. 1942, 418–420. (212) Bradfield, Jones, Orton, J. Chem. Soc. 1929, 2815. (213) Bradfield, Jones, J. Chem. Soc. 1929, 3081. (214) Jones, J. Chem. Soc. 1935, 1834. (215) Ernst, Berndt (to I.G.), Ger. 513,679, Dec. 1, 1930; Cent 1931, I 1011–1012, [C.A. 25, 1841 (1931)]. (216) Claisen, Eisleb, Ann. 401, 34–38 (1913). (217) Bartz, Miller, Adams, J. Am. Chem. Soc. 57, 371–376 (1935). (218) Boyd, Marle, J. Chem. Soc. 105, 2123, 2136 (1914). (219) Boyd, Thomas, J. Chem. Soc. 115, 1242 (1919). (220) Bayer and Co., Ger. 282,991, March 24, 1915; Cent. 1915, I 815; C.A. 9, 2568 (1915).

(221) Poulenc Freres, Fourneau, Ger. 219,325, Feb. 23, 1910; Cent. 1910, I 974; [C.A. 4, 2029–2030 (1910)]. (222) Ehlotzky, Monatsh. 36, 664–665 (1909). (223) Nieuwland, Vogt, Foohey, J. Am. Chem. Soc. 52, 1023 (1930). (224) Ruhemann, Bcr. 54, 918,921 (1921). (225) Suter, Green, J. Am. Chem. Soc. 59, 2579 (1937). (226) Brewster, Stevenson, J. Am. Chem. Soc. 62, 3144–3146 (1940). (227) Langham, Brewster, Gilman, J. Am. Chem. Soc. 63, 545–549 (1941). (228) Mailhe, Murat, Compt. rend. 154, 601–603 (1912); Bull. soc. chem. (4) 11, 329–331 (1912). (229) LeFevre, Saunders, Turner, J. Chem. Soc. 1927, 1170–1173. (230) Raiford, Colbert, J. Am. Chem. Soc. 48, 2659–2660 (1926).

(231) McCombie, Macmillan, Scarborough, J. Chem. Soc. 1931, 533-534. (232) Roberts, Turner, J. Chem. Soc. 127, 2007-2008 (1925). (233) Scarborough, J. Chem. Soc. 1929, 2364-2365. (234) Hester (to Röhm and Haas Co.), Ger. 703,189, Jan. 30, 1941; C.A. 36, 212 (1942). (235) Bost, Nicholson, J. Am. Chem. Soc. 57, 2368-2369 (1935). (236) Fox, Turner, J. Chem. Soc. 1930, 1119-1120. (237) Richter, Ber. 49, 2344 (1916). (238) B.A.S.F., Ger. 303,033, Jan. 14, 1918; Cent. 1918, I 499-500; C.A. 13, 324 (1919). (239) Michaelis, Kachne, Rocholl, Ber. 31, 1053 (1898). (240) Strecker, Grossmann, Ber. 49, 85 (1916).

(241) Breusch, Keskin, Rev. faculté sci. univ. Istanbul, 7A, 182–189 (1942); C.A. 38, 1483 (1944). (242) Autenrieth, Ber. 36, 2375–2377 (1897). (243) Autenrieth, Vamossy, Z. physiol. Chem. 25, 446 (1898). (244) A.G.F.A., Ger. 246,871, May 11, 1912; Cent. 1912, I 1875; [C.A. 6, 2497 (1912)]. (245) Rosenmund, Vogt, Arch. Pharm. 281, 317–327 (1943); C.A. 38, 5804–5805 (1943). (246) Anschütz, Molineus, Ann. 415, 53 (1918). (247) Kekulé, Ber. 6, 944 (1873). (248) Zetsche,

Nachmann, Helv. Chim. Acta 9, 425-427 (1926). (249) Kekulé, Barbaglia, Ber. 5, 877 (1872). (250) Kosolapoff, J. Am. Chem. Soc. 64, 2982-2983 (1942).

(251) Luchinskii, J. Gen. Chem. (U.S.S.R.) 7, 2044-2047 (1937); Cent. 1338, I 3909; C.A. 32, 519 (1938). (252) Wohlleben, Ber. 42, 4372-4373 (1909). (253) Seelig, J. prakt. Chem. (2) 39, 175 (1889). (254) Karrer, Yen, Reichstein, Helv. Chim. Acta 13, 1315 (1930). (255) von Auwers, Wittig, Ber. 57, 1275 (1924). (256) Nencki, Stoeber, Ber. 30, 1769 (1897). (257) Chakravarti, Majumdar, J. Indian Chem. Soc. 15, 137 (1938). (258) von Auwers, Baum, Lorenz, J. prakt. Chem. (2) 115, 91-92 (1927). (259) Fries, Hasselbach, Schröder, Ann. 405, 368-370 (1914). (260) Skraup, Beng, Ber. 60, 946, 948 (1927)

(261) von Heyden, Ger. 81,375, Friedländer 4, 1117 (1894–1897). (262) Barral, Morel, Bull. soc. chim. (3) 21, 722–727 (1899). (263) Melnikow, J. prakt. Chem. (2) 127, 236–237 (1930). (264) Barral, Compt. rend. 126, 908 (1898); 138, 910 (1904). (265) Mosso, Jahresber. 1887, 1301. (266) Autenrieth, Muhlinghaus, Ber. 39, 4102 (1906). (267) Autenrieth, Arch. Pharm. 233, 41 (1895). (268) Bernouilli, St. Goar, Helv. Chim. Acta 9, 754–755 (1996). (269) Anschütz, Ber. 60, 1322 (1927). (270) I.G., Danish 59,316, Dec. 22, 1941; Cent. 1942, II 812, not in C.A.

(271) Tseng, Ph.D. Thesis, M.I.T. (unpublished). (272) Baw, J. Indian Chem. Soc. 3, 104 (1926). (273) Huston, Guile, Chen, Headley, Warren, Baur, Mate, J. Am. Chem. Soc. 55, 4641-4642 (1933). (274) Klarmann, Gates, Shternov, J. Am. Chem. Soc. 54, 3323 (1932). (275) Lyman, Reid, J. Am. Chem. Soc. 42, 616 (1920). (276) Koelsch, J. Am. Chem. Soc. 53, 304-305 (1931). (277) Minton, Stephen, J. Chem. Soc. 121, 1600 (1922). (278) Behaghel, J. prakt. Chem. (2) 114, 297-298 (1926). (279) Hayes, Branch, J. Am. Chem. Soc. 65, 1555 (1943). (280) Hantzsch, Mai, Ber. 28, 979-980 (1895).

(281) Sah, Cheng, Rec. trav. chim. 58, 592-593 (1939). (282) Sah, Young, Rec. trav. chim. 59, 357-363 (1940); C.A. 35, 4363 (1941). (283) Sah, Woo, Rec. trav. chim. 58, 1014-1015 (1939). (284) Sah, Cheng, Rec. trav. chim. 58, 596-597 (1939). (285) Sah, Ma, J. Chinese Chem. Soc. 2, 230-231 (1934). (286) Sah, Rec. trav. chim. 58, 587-588 (1939). (287) French, Wirtel, J. Am. Chem. Soc. 48, 1736-1739 (1926). (288) Sah, Rec. trav. chim. 58, 454-458 (1939). (289) Korczynski, Gazz. chim. idal. 53, 96 (1923).

3:0480 4-CHLORO-5-ISOPROPYL-2-METHYLPHENOL C10H13()Cl Beil. VI --

$$(p-(5)\text{Chlorocarvacrol}) \qquad \qquad \text{Cl} \qquad \qquad \textbf{VI}_1--$$

$$(\text{CH}_3)_2\text{CII}--\text{CII}_3 \qquad \qquad \textbf{VI}_2-(\textbf{494})$$

Volatile with steam.

[For prepn. of \bar{C} from 2-hydroxy-p-cymene (carvacrol)(1:1760) with Cl_2 (4) or with SO_2Cl_2 (1) see indic. refs.; from 4-chloro-5-isopropyl-2-methyl-aniline (5-chloro-2-amino-p-cymene) (2) via diazotization and subsequent hydrolysis see (2); from 5-amino-2-hydroxy-p-cymene (5-aminocarvacrol) via diazotization and subsequent reactn. with aq. HCl + Cu powder see (3); from 4-chloro-2-methylphenol (p-chloro-p-cresol) (3:0780) by reactn. with isopropyl alc. + H_2SO_4 at 80° or in decalm soln. with propylene + AlCl₃ see (5).]

[C has outstanding bactericidal properties and is used ("Carvasept" (6)) as disinfectant, antiseptic, germicide, preservative (7), and anthelmintic (8) (9); for reviews of bactericidal actn. see (10) (11) (12) (13).]

[For solubilization of \bar{C} with soap solns. (14) and use of \bar{C} in soap solns. as disinfectant see (14) (15) (16); for prepr. of esters of \bar{C} , e.g., the carbonate, m.p. 83-84° (from \bar{C} + dil. aq. NaOH + phosgene), or the salicylate, m.p. 60-61° (from \bar{C} + salicylic acid + POCl₃), see (17); for mercuration of \bar{C} see (18); for use of \bar{C} in mouth wash see (19).

- ⊕ 4-Chloro-5-isopropyl-2-methylphenyl ethyl ether: m.p. 54-56° (17). [From C in dil. aq. NaOH with Et₂SO₄ (17).]
- 4-Chloro-5-isopropyl-2-methylphenoxyacetic acid: m.p. 160-161° (17). [From C in dil. aq. NaOH with chloroacetic acid (17).]

3:0480 (1) Chem. Fabrik von Heyden, A.G., French 736,304, Nov. 22, 1932; Cent. 1933, 1653. (2) Wheeler, Giles, J. Am. Chem. Soc. 44, 2608 (1922). (3) Philipp (to Chem. Fabrik von Heyden, A.G.), Ger. 522,062, Mar. 30, 1931; Cent. 1931, II 123. (4) Momm, Brit. 411,430, July 5, 1934; Cent. 1934, II 2104. (5) Günther (to I.G.), Ger. 495,717, April 10, 1930; Cent. 1930, II 984. (6) Kuhn, Arch. Hyg. 105, 18-28 (1930). (7) Philipp (to Chem. Fabrik von Heyden, A.G.), Ger. 528,767, Feb. 16, 1935; Cent. 1935, I 3613. (8) Lamson, Stoughton, Buss, J. Pharmacol. 56, 60-62 (1936); Cent. 1938, I 2213; C.A. 36, 3888 (1936). (9) Kochmann, Arch. exptl. Path. Pharmakol. 161, 196-205 (1931); Cent. 1931, II 2030; C.A. 26, 1339 (1932). (10) Heading, Pharm. J. 138, 321-322 (1937); Chemist and Druggist 126, 392-393 (1937); Cent. 1937, II 2208. (11) Weichardt, Münch. Med. Wochschr. 78, 1515-1516 (1931). (12) Kuhn, Med. Klin. 28, 790-791 (1932); Cent. 1932, II 1036; Med. Klin. 26, 1047-1048 (1930); Cent. 1930, II 2282. (13) Hermann, Pharm. Zentralhalle 72, 613 (1931); Cent. 1932, I 1266. (14) Hueter, Engelbrecht (to "Unichem" Chemikalien Handels, A.G.), U.S. 2,267,101, Dec. 23, 1941; C.A. 36, 2376 (1942). (15) Deutsche Hydrierwerke, A.G., French 823,289, Jan. 18, 1938; Cent. 1938, I 2587. (16) Gelinsky, Ger. 649,126, Aug. 16, 1937; Cent. 1937, II 3627. (17) Philipp (to Chem. Fabrik von Heyden), U.S. 1,957,908, May 8, 1934; Ger. 541,316; June 30, 1934; Cent. 1934, II 2104; C.A. 28, 4180 (1934). (18) Christiansen (to E. R. Squibb and Sons), U.S. 2,252,705, Aug. 19, 1941; C.A. 35, 7657 (1941). (19) Pepsodent Co., Brit. 352,397, April 3, 1929; C.A. 27, 375 (1933); French 693,083, Nov. 14, 1930; Cent. 1931, I 1481.

3: 0485 DIMETHYL d,l- α,α' -DICHLOROSUCCINATE $C_6H_8O_4Cl_2$ Beil. II — (Dimethyl allo-dichlorosuccinate; COOCH₃ II₁-(267) dimethyl isodichlorosuccinate) H—C—Cl Cl—C—H

[For prepn. of \tilde{C} from d_l - α,α' -dichlorosuccinic acid (3:4711) in MeOH with H₂SO₄ at ord. temp. see (3); from dimethyl d_l -tartrate (1:2385) (1) or from dimethyl low-melting β -chloro- d_l -malate [Beil. III-438, III₂-(290)] (2) with SOCl₂ in pyridine see indic. refs.] \tilde{C} with dimethylaniline loses 1 HCl yielding (1) dimethyl chlorofumarate (3:6582).

3:0485 (1) Darzens, Séjourne, Compt. rend. 154, 1616 (1912). (2) Kuhn, Wagner-Jauregg, Ber. 61, 514 (1928). (3) Holmberg, Arkiv. Kemi, Mineral. Geol. 8, No. 2, 17, 33 (1920); Cent. 1921, I 820; C.A. 16, 2116 (1922).

3: 0490 2,5-DICHLOROBENZAL (DI)CHLORIDE
$$C_7H_4Cl_4$$
 Beil. V - 302 V_1 — $CHCl_2$ V_2 -(234)

Cryst. from CHCl₃; very eas. sol. org. solvents but spar. sol. in aq. — \bar{C} has faint but not disagreeable odor. — Volatile with steam.

[For prepn. of \bar{C} from 2,5-dichlorobenzaldehyde (3:1145) with PCl₅ (78% yield (1)) or with ClSO₃H in CHCl₃ (3) see indic. refs.; from 2,5-dichlorotoluene (3:6245) at b.p. with Cl₂ see (2).]

 \bar{C} on hydrolysis, e.g., by protracted refluxing (56 hrs.) with aq. + CaCO₃ (2), or by treatment with fumg. H₂SO₄ (3), yields 2,5-dichlorobenzaldehyde (3:1145). [For study of rate of hydrolysis in 50% alc. at 83.5° see (1).]

3:0490 (1) Asinger, Lock, Monatsh. 62, 336–337 (1933). (2) de Crauw, Rec. trav. chim. 50, 773 (1931). (3) Gnehm, Schüle, Ann. 299, 359–360 (1898).

CHAPTER III

DIVISION A. SOLIDS

(3:0500-3:0999)

3: 0520 ISOPHTHALYL (DI)CHLORIDE Cl
$$C_8H_4O_2Cl_2$$
 Beil. IX - 834 IX₁-(372)

C=O

M.P. B.P. (3) $D_4^{46.9} = 1.3872$ (9)

42-43° (2) 200° (7) at 15 mm. (7)

41-43° (18) 156° at 15 mm. (8)

41° (3) (4) 142.6-143° at 14 mm. (5)

(6)Prisms from pet. ether.

143-144°

136°

40.5-41° (5)

40°

[For prepn. of C from isophthalic acid (1:0900) with PCl₅ (3) in a s.t. at 200° (10) or in POCl₃ (8) see indic. refs.; with AcCl (3:7065) in s.t. at 130° for 8 hrs. see (1); with $SOCl_2$ (yield: 100% (6), 92% (18), 67% (2), 62% (7)) (5) see indic. refs.; for prepn. of \overline{C} from 1,3-bis-(trichloromethyl)benzene by partial catalytic hydrolysis see (4) (17).]

at 13 mm.

at 11 mm. (18)

C with excess McOH yields (11) dimethyl isophthalate (1:2244), m.p. 67-68°; cf. also under isophthalic acid (1:0900); C with excess phenol yields (3) diphenyl isophthalate, m.p. 120° (3).

[C on cat. hydrogenation in xylene with Pd cat. as specified (12) gives 83% yield isophthalaldehyde [Beil. VII-675, VII₁-(364)], cryst. from alc., m.p. 88-89° (12) (dioxime, m.p. 178°; bis-phenylhydrazone, m.p. 242-244° (12).

[C with AlCl₃ + benzene yields (13) 1,3-dibenzoylbenzene (isophthalophenone) [Beil. VII-829, VII₁-(443)], m.p. 100-101° (dioxime, m.p. 70-75° (10)); for corresp. reactn. of $\bar{\mathbf{C}}$ with m-xylene (1:7420) see (14); for corresp. reactn. of $\bar{\mathbf{C}}$ with anisole (1:7445) see (15).

[For reactns, of C with ethyl sodio-acetoacetate sec (8) and with ethyl sodio-cyanoacetate see (16).] [For behavior of C with diazomethane see (18).]

C on hydrolysis yields isophthalic acid (1:0900) q.v. for further characterization.

3:0520 (1) Liebermann, Kardos, Ber. 46, 211 (1913). (2) Reindel, Siegel, Ber. 56, 1554 (1923). (3) Schreder, Ber. 7, 708 (1874). (4) I.G., French 820,697, Nov. 16, 1937; Cent. 1938, I 1661; C.A. 32, 3422 (1938). (5) Kohlrausch, Pongratz, Stockmair, Monatsh. 67, 109 (1935). (6) Meyer, Monatsh. 22, 436 (1901). (7) McMaster, Ahmann, J. Am. Chem. Soc. 50, 148 (1928). (8) Ruggli, Gassenmeier, Helv. Chim. Acta 22, 499-500 (1939). (9) von Auwers, Schmidt, Ber. 46, 484 (1913). (10) Münchmeyer, Ber. 19, 1848-1849 (1886).

(11) Baeyer, Villiger, Ann. 276, 258 (1893). (12) Rosenmund, Zetsche, Ber. 54, 2890 (1921). (13) Ador, Ber. 13, 320 (1880). (14) Clar, John, Hawran, Ber. 62, 945 (1929). (15) Weiss, Chledowski, Monatsh. 65, 358, 362-363 (1935). (16) Sacher, Bull. soc. chim. (3) 11, 1097 (1894). (17) I.G., Ger. 708,149, June 5, 1941; C.A. 37, 2746 (1943). (18) Ruggli, Knecht, Helv. chim.

Acta 27, 1108-1115 (1944); C.A. 39, 4857 (1945).

3:0525 16-CHLOROHEXADECANOL-1 C₁₆H₃₃OCl Beil. S.N. 24 (ω-Chloro-n-hexadecyl alcohol; CH₂—(CH₂)₁₄.CH₂OH

ω-Chloropalmityl alcohol)

86

M.P. 43° (1)

Colorless cryst. from lt. pet.

[For prepn. of \bar{C} from α,ω -hexadecamethylene glycol [Beil. I₂-(565)] (m.p. 87-88° (1)) with SOCl₂ + dimethylaniline in C₆H₆ (60% yield) see (1); note that a little 1,16-dichlorohexadecane, cryst. from McOH, m.p. 47°, is also formed.]

3:0525 (1) Bennett, Gudgeon, J. Chem. Soc. 1938, 1679-1681.

[For prepn. of \bar{C} from p-chlorobenzoic acid (3:4940) with MeOH + HCl (2) or MeOH + H₂SO₄ (2) (6) see indic. refs.; from Ag \bar{A} + MeI in s.t. at 100° see (5); from p-chlorobenzoyl chloride (3:6550) with MeOH see (3).]

 $\bar{\mathbf{C}}$ on htg. with sirupy $\mathbf{H}_3\mathbf{PO}_4$ at 200° yields (7) p-chlorobenzoic acid (3:4940), dimethyl ether, and probably some p-chlorotoluene (3:8287).

C̄ added to 5-6 pts. very conc. HNO₃ at 0°, poured onto ice, yields (3) methyl 4-chloro-3-nitrobenzoate [Beil. IX-402], cryst. from MeOH, m.p. 83° (3).

[$\bar{\mathbf{C}}$ with Na + methyl acetate condenses giving (60% yield (6)) methyl p-chlorobenzoylacetate, b.p. 172° at 12 mm., m.p. 36-37° (6); this prod. with excess phenylhydrazine in alc. + AcOH gives on htg. 3-(p-chlorophenyl)-1-phenylpyrazolone-5, or. eryst. from AcOH, m.p. 140° (6); corresp. prod. from p-nitrophenylhydrazine, m.p. 200-205° (6).]

 \bar{C} on hydrolysis (Sap. Eq. = 170.5) yields methyl alcohol (1:6120) + p-chlorobenzoic acid (3:4940). [For studies of hydrolysis under various cond. see (2) (4).] — For the amide, anilide, p-toluidide, and other derivs, corresp. to \bar{C} see p-chlorobenzoic acid (3:4940).

3:0535 (1) Jaeger, Z. Krist. 42, 22 (1907). (2) Kellas, Z. physik Chem. 24, 243-252 (1897). (3) Montagne, Rec. trav. chim. 19, 55-56, 61 64 (1900). (4) Jones, McCombie, Scarborough, J. Chem. Soc. 123, 2694-2697 (1923). (5) Emmelling, Rec. 8, 883 (1875). (6) Wahl, Rolland, Ann. chim. (10) 10, 9-12, 15-17 (1928). (7) Raikow, Tischkow, Chem. Zlq. 29, 1209 (1905). (8) Berger, Rec. trav. chim. 43, 170 (1924). (9) Kahovec, Wagner, Monatsh. 74, 285 (1943).

3:0550 3,4-DICHLOROBENZALDEHYDE
$$C_7H_4OCl_2$$
 Beil. VII - 238 VII_1 -(134)

Colorless adds. from alc. (1), odor like benzaldehyde (2). — Eas. volatile with steam (2) (3).

[For preph. of C from 3,4-dichlorotoluene (3:6355) via chlorination to 3,4-dichlorobenzal

(di)chloride (3:6876) and hydrolysis of the latter with fumg. H₂SO₄ (5% SO₃) (36% yield (3)), conc. H₂SO₄ (4), or CaCO₃ + H₂O (40% yield (3)) see (2) (3) (4); for prepn. from 4-chloro-3-nitrobenzaldehyde via reduction, diazotization, etc., see (1).]

C with satd. aq. NaHSO₃ yields a cpd. C.NaHSO₃ (3). [Use in purification of C (3).]
C on oxidn. with KMnO₄ yields (2) 3,4-dichlorobenzoic acid (3:4925), m.p. 201-202° (3).
C with conc. aq. KOH undergoes Cannizzaro reactn. yielding 3,4-dichlorobenzyl alcohol, ndls. from aq., m.p. 38° (3), and 3,4-dichlorobenzoic acid (see above).

Č on nitration as specified (5) (4) gives (71% yield (4)) 3,4-dichloro-6-nitrobenzalde-hyde [Beil. VII₁-(144)], yel. pr. from C₆H₆, m.p. 73° (5). [This product with NH₄OH/AgNO₃ is oxidized (4) to 3,4-dichloro-6-nitrobenzoic acid, cryst. from C₆H₆, m.p. 165° (6).]

[For conversion of \bar{C} to 3,4-dichlorostyrene (7) (8) cf. (9) via reaction with MeMgI giving (73% yield (7)) 3,4-dichlorophenyl-methyl-carbinol (7) (8) and dehydration of latter with KHSO₄ (yields 83% (8), 64% (7)) see indic. refs.]

- 3,4-Dichlorobenzaldoxime (anti form): m.p. 114-115° (2), 118-119° (1). [The syn isomer, ndls. from alc., m.p. 120° rap. htg., is converted by fusion (2) to the anti form.]
 3,4-Dichlorobenzaldehyde phenylhydrazone: unrecorded.
- 1) 3 4-Dichlorobenzaldehyde p-nitrophenylhydrazone: or. ndls., m.p. 276-277° (1).
- --- 3,4-Dichlorobenzaldehyde 2 4-dinitrophenylhydrazone: unrecorded.
- 3,4-Dichlorobenzaldehyde semicarbazone: unrecorded.

3:0550 (1) Hodgson, Beard, J. Chem. Soc. 1927, 25. (2) Erdmann, Schwechten, Ann. 260, 72-73 (1890). (3) Kraay, Rec. trav. chim. 49, 1086 (1930). (4) Ruggli, Zaeslin, Lang, Helv. Chim. Acta 21, 1248 (1938). (5) Hoechst Farbwerke, Ger. 254,467, Dec. 3, 1912; Cent. 1913, I 199. (6) Ruggli, Zaeslin, Helv. Chim. Acta 19, 437 (1936). (7) Marvel, Overberger, Allen, Johnston, Saunders, Young, J. Am. Chem. Soc. 68, 863-864 (1946). (8) Brooks, J. Am. Chem. Soc. 66, 1295-1297 (1944). (9) Michalek, Clark, Chem. & Eng. News 22, 1559-1563 (1944).

M.P. B.P. (1) (2) 210.2-211.5° u.c. (18)
$$D_{-}^{25} = 1.4723$$
 (8) (43-44° (17) 209-211° (6) (11) $n_{D}^{25} = 1.1729$ (8) (43° (3) (4) 209-210° (4) (16) (18) 206-208° u.c. at 753 mm. (7) (42° (5) 106.2-107.6° at 14-16 mm. (3) (41-42° (11)

Colorless ndls. from C_6H_6 . — \bar{C} has unpleasant and persistent odor suggesting iodoform (1) (for study of strength of odor of aq. solns. of \bar{C} see (1)). — \bar{C} is spar. sol. aq. (100 g. aq. at 20° dis. 0.45 g. \bar{C}), but is eas. sol. alc., ether, C_6H_6 , or CHCl₃. — \bar{C} is volatile with steam; note, however, that from alk. soln. \bar{C} is not volatile with steam (dif. and sepn. from 2-chlorophenol (3:5980) or 4-chlorophenol (3:0475) (9)), although \bar{C} is volatile with steam from aq. solns. contg. PbCO₃ (dif. and sepn. of \bar{C} from 2,4,6-trichlorophenol (3:1673) (9)). — Note that comml. \bar{C} often contains 2,4,6-trichlorophenol, and that \bar{C} prepd. by chlorination of phenol may cont. 2,6-dichlorophenol (3:1595).

[For prepn. of \bar{C} from p-chlorophenol (3:0475) or o-chlorophenol (3:5980) with Cl_2 (1 mole) in AcOH soln. (80% yield) see (6); from phenol (1:1420) with Cl_2 (2 moles) diluted with CO_2 in AcOH and under these cond. giving exclusively \bar{C} see (7).]

[For formn. of \bar{C} (together with other prods.) from phenol (1:1420) with Cl₂ (2 moles) (2) (1) (4) (10), with Cl₂ (2 moles) in alk. soln. (11) (12), with N,N'-dichlorourea in HCl soln. (13), or with SO₂Cl₂ (14) see indic. refs.; for formn. of \bar{C} from salicylic acid (1:0780) in excess aq. KOH with Cl₂ see (15); from 3,5-dichloro-2-hydroxybenzoic acid (3,5-dichloro-salicylic acid) (3:4935) on distn. with lime see (16) (17); from 2,6-dichloro-3-hydroxybenzaldehyde (3:4160) in excess 50% aq. KOH on htg. at 80° (94% yield) see (5).]

Nuclear substitution of \bar{C} . \bar{C} in AcOH with Br₂ (1 mole) (7) (18), or in 50% AcOH with Br₂ (1 mole) in AcOH (19), yields 6-bromo-2,4-dichlorophenol, ndls. from C_6H_6 or lt. pet., m.p. 68-69° (19), 68° (7) (18), b.p. 268° dec. (18), 204° at 19 mm. (19), 198° at 15 mm. (19), 192° at 12 mm. (19) (corresp. methyl ether, m.p. 65° (7); corresp. 2,4-dinitrophenyl ether, yel. lfts. from alc., m.p. 140-141° (19); corresp. p-toluenesulfonate, m.p. 82-83° (19)). — [This 6-bromo-2,4-dichlorophenol with excess Br₂ in pres. of Fe powder and absence of aq. yields (20) 2,4-dichloro-3,5,6-tribromophenol, cryst. from AcOH, m.p. 209° (20) (corresp. methyl ether, m.p. 143-144° (20), corresp. benzoate, m.p. 202° (20)).]

Č in aq. NaOH with I₂ (1 mole) in aq. KI yields (7) 2,4-dichloro-6-iodophenol, ndls. from dil. alc., m.p. 63° (7) (corresp. methyl ether, m.p. 35°, b.p. 278-285° u.c. (7)).

C on nitration by soln. in cold fumg. HNO₃, subsequently poured into aq. (4) cf. (21), yields 2,4-dichloro-6-nitrophenol [Beil. VI-241, VI₁-(122)], yel. cryst. from alc., m.p. 121-122° (4), 124° (22).

Condensation reactions involving nuclear hydrogens. [\tilde{C} with formalin (1:0145) + conc. HCl + conc. H₂SO₄ in pres. of stream of HCl gas at 35-40° (23), or \tilde{C} with trioxymethylene + AcOH/H₂SO₄ at 50° (24), gives (54% yield (23)) 6,8-dichlorobenzodioxane-1,3, volatile with steam, cryst. from MeOH, m.p. 111° (24), 109-109.5° (23). — \tilde{C} with formalin (1:0145) + conc. HCl in stream of HCl gas at 50° for 36 hrs. gives (72% yield (23)) 3,5-dichloro-2-hydroxybenzyl chloride, ndls. from pet. eth., m.p. 82-84° (23); this prod. on hydrol. with aq. at 50° yields (23) 3,5-dichloro-2-hydroxybenzyl alc., ndls. from aq., m.p. 80-81°, also formed as by-product of the dichlorobenzodioxane mentioned above.]

[C with methylal (1:0105), methylene diacetate, or methylene (di)iodide in pres. of conc. H₂SO₄ or ZnCl₂ (25) or \bar{C} + formalin (1:0145) with AcOH/H₂SO₄ (26) yields methylene-bis-(2,4-dichlorophenol) (2,2'-dihydroxy-3,5,3',5'-tetrachlorodiphenylmethane); for use of this prod. as mothproofing cpd., antiseptic, and seed disinfectant see (25) (26) (27) (28) (29) (30). — Note, however, that \bar{C} (as Na salt) with methylene (di)chloride (3:5020) at 120-140° in s.t. for 6 hrs. gives (24) bis-(2,4-dichlorophenoxy)methane, m.p. 98°. — \bar{C} with SCl₂ or S₂Cl₂ + AlCl₃ in CS₂ or CCl₄ yields (31) 2,2'-dihydroxy-3,5,3',5'-tetrachlorodiphenyl sulfide, m.p. 188°. — For condens. of \bar{C} with benzaldehyde o- (or p-) sulfonic acids and use of products as mothproofing agts. see e.g. (26).]

[\bar{C} with phthalic anhydride (1:0725) + AlCl₃ at 150° for 2 hrs. yields (36) cf. (37) (38) 2-(3',5'-dichloro-2'-hydroxybenzoyl)benzoic acid, colorless lfts. from alc., m.p. 204° cor. (36), which with conc. H₂SO₄ ring-closes to 2,4-dichloro-1-hydroxyanthraquinone, yel. ndls. from C₆H₆, m.p. 242° (36), 241-242° (39). — \bar{C} with 4,5-dichlorophthalic anhydride (3:4830) + fumg. H₂SO₄ + H₃BO₃ at 195° yields (40) 2,6,7-trichloro-1,4-dihydroxyanthraquinone (2,6,7-trichloroquinizarin).]

Reactions of the phenolic group of \bar{C} (see also under \oplus below). \bar{C} behaves as a weak acid: \bar{C} is sol, in aq. alk, but largely pptd, by CO_2 . — Dissoc. const. at 25° in aq. is 31. \times 10⁻⁷ (41) cf. (42).

[For study of bactericidal prop. of \bar{C} see (43); for use as insecticide in paper see (44); for prepn. and use of metal complexes as antiseptics see (45).]

[Č with alkali metals gives corresp. alk. 2,4-dichlorophenolates: K 2,4-dichlorophenolate with CO₂ at 140° yields (15) 3,5-dichloro-2-hydroxybenzoic acid (3,5-dichlorosalicylic acid) (3:4935).]

- [\bar{C} with ethyl α -methylacetoacetate (1:1712) + P₂O₅ gives (14.5% yield (46)) 6,8-dichloro-2,3-dimethylchromone [Beil. XVII₁-(177)], ndls. from alc., m.p. 141°.]
- [\bar{C} in 20% aq. KOH htd. 2 hrs. at 100° with Me₂SO₄ (22) cf. (1) yields 2,4-dichlorophenyl methyl ether (2,4-dichloroanisole) [Beil. VI-189, VI₁-(103)], b.p. 232-233° cor. at 743.5 mm.; m.p. 27-28° (47). $-\bar{C}$ with EtI + K₂CO₃ in acetone refluxed 6-8 hrs. gives (90% yield (48)) 2,4-dichlorophenyl ethyl ether (2,4-dichlorophenetole), oil, b.p. 235-236° (48), 236-237° (4) (for study of cleavage of this ether with HBr/AcOH see (48), for study of rate of formation see (49)). $-\bar{C}$ with allyl bromide + K₂CO₃ in acetone yields (50) allyl 2,4-dichlorophenyl ether, b.p. 144-145° at 25 mm. (50).]
 - 2,4-Dichlorophenyl acetate: oil, b.p. 244-245° (4), 167-168° at 80 mm. (51). [From C with AcCl refluxed 40 min. (86% yield (51)); this ester with AlCl₃ at 170° for 40 min. undergoes Fries rearr. giving (75% yield (51)) 3,5-dichloro-2-hydroxyacetophenone, m.p. 95-96° (51).]
 - ② 24-Dichlorophenyl benzoate: cryst. from alc., m.p. 96.5° (5), 96° (1), 97° [Beil. IX-117]. [From C in dil. aq. NaOH shaken with BzCl (5) cf. (1).] [For study of nitration of this ester see (6).]
 - **② 2,4-Dichlorophenyl** *m*-nitrobenzoate: ndls. from alc., m.p. 115-116° (6). [From $\ddot{\mathbf{C}}$ + *m*-nitrobenzoyl chloride in dil. aq. alk.; for study of its nitration see (6).]
 - ---- 2,4-Dichlorophenyl p-nitrobenzoate: unreported.
 - ---- 2,4-Dichlorophenyl 3,5-dinitrobenzoate: unreported.
 - ---- 2,4-Dichlorophenyl benzenesulfonate: unreported.
 - 2,4-Dichlorophenyl p-toluenesulfonate: pr. from alc., m.p. 125° (6).
 - Q 2,4-Dichlorophenyl benzyl ether: pr. from alc., ether, or pet. eth., m.p. 62° (52), 61-62° (53), 60° (54), 59.0-59.5° (55). [From \(\tilde{\mathbb{C}}\) + benzyl chloride (3:8535) + NaOEt in hot alc. (53), or from Na salt of \(\tilde{\mathbb{C}}\) + benzyl chloride in MeOH (55); note, however, that Na salt of \(\tilde{\mathbb{C}}\) with benzyl chloride in toluene at 160° for 5 hrs. undergoes instead nuclear alkylation yielding (55) 2,4-dichloro-6-benzylphenol (3,5-dichloro-2-hydroxydiphenylmethane), cryst. from pet. eth., m.p. 77.0-77.5° (55).]
 - ② 2,4-Dichlorophenyl p-nitrobenzyl ether: ndls. from ether, m.p. 148-150° (53).
 - 2,4-Dichlorophenyl 2,4-dinitrophenyl ether: lfts. from AcOH, AcOH/EtOH, or EtOH, m.p. 119° (56), 118-119° (6), 118° (57). [From Na or K salt of C + 2,4-dinitrochlorobenzene refluxed in alc. (56) (6) (57).]
 - **D** 2,4-Dichlorophenoxyacetic acid (3:4095): cryst. from C_6H_6 , m.p. 138° (58), Neut. Eq. = 221.0. [From \bar{C} + chloroacetic acid in slight excess aq. NaOH, refluxed and then acidified (87% yield (58)); for studies on use of this prod. as plant hormone see (59).]
 - 2,4-Dichlorophenyl N-phenylcarbamate: unreported.
 - 2,4-Dichlorophenyl N(p-iodophenyl)carbamate: m.p. 182-183° (61). [From C + p-iodobenzazide in hot lgr. (61).]
 - **D 2,4-Dichlorophenyl** N-(p-bromophenyl)carbamate: rods from lgr./AcOEt, m.p. 169° cor. (62). [From $\tilde{C}+p$ -bromobenzazide in hot lgr. (62).]
 - **D 2,4-Dichlorophenyl** N-(p-nitrophenyl) carbamate: yel. pl. from lgr./EtOAc, m.p. 205° cor. (62). [From $\bar{C} + p$ -nitrobenzazide in hot lgr. (63).]
 - ② 2,4-Dichlorophenyl N-(3,5-dinitro-4-methylphenyl)carbamate: or.-yel. pr. from lgr. or EtOAc, m.p. 153° u.c., 157° cor. (64). [From C + 3,5-dinitro-4-methylbenzazide in hot lgr. (64).]
 - 2.4-Dichlorophenyl $N-(\alpha$ -naphthyl)carbamate: unreported.
 - D 2,4-Dichlorophenyl N-(β-naphthyl)carbamate: pl. from lgr., m.p. 162° u.c., 166° cor.
 (65). [From C + β-naphthyl isocyanate (or azide) in hot lgr. (65).]

3:0560 (1) Holleman, Rec. trav. chim. 37, 96-107 (1918). (2) van de Lande, Rec. trav. chim. 51, 103, 110 (1932). (3) Kohlrausch, Stockmair, Ypsilanti, Monatsh. 67, 89 (1936). (4) Fischer, Ann. Suppl. 7, 180-190 (1870). (5) Lock, Monatsh. 55, 311-312 (1930). (6) Groves, Turner, Sharp, J. Chem. Soc. 1929, 516, 518, 521-522. (7) Kohn, Sussmann, Monatsh. 46, 590-591, 594 (1925). (8) Sun, Liu, J. Chinese Chem. Soc. 5, 39-40 (1937). (9) Takagi, Ishimasa, J. Pharm. Soc. Japan 1925, No. 517, 253-260 (1925); Cent. 1926, I 182; C.A. 20, 2669 (1926). (10) Rashevskaya, Zil'berman, Chernyavskaya, Skvirskaya, J. Applied Chem. (U.S.S.R.) 10, 499-505 (1937); Cent. 1938, I 58; C.A. 31, 6212 (1937).

(11) Chandelon, Ber. 16, 1751-1752 (1883). (12) Chulkov, Parini, Staroselets, Org. Chem. Ind. (U.S.S.R.) 3, 97-101 (1937); Cent. 1938, I 1419; C.A. 31, 4967 (1937). (13) Likhosherstov, J. Russ. Phys.-Chem. Soc. 61, 1019-1023, 1025-1028 (1929); Cent. 1930, I 1294; C.A. 24, 836. (1930). (14) Steinkopf, Mieg, Herold, Ber. 53, 1145 (1920). (15) Tarugi, Gazz. chim. ital. 30, II 489, 491 (1900). (16) Hecht, Am. Chem. J. 12, 505 (1890). (17) Zincke, Ann. 261, 253-254 (1891). (18) Garzino, Gazz. chim. ital. 17, 495-502 (1887). (19) Rox, Turner, J. Chem. Soc.

1930, 1861-1863. (20) Kohn, Domotor, Monatsh. 47, 215-216 (1926).

(21) Armstrong, J. Chem. Soc. 25, 96 (1872). (22) Kohn, Kramer, Monatsh. 49, 156 (1928). (23) Buehler, Brown, Holbert, Fulmer, Parker, J. Org. Chem. 6, 905-906 (1941). (24) Ziegler, Simmler, Ber. 74, 1871-1879 (1941). (25) Weiler, Wenk, Stotter, Ger. 540,208, Dec. 12, 1931; Brit. 337,832, Dec. 4, 1930; French 39,334, Oct. 12, 1931; Cent. 1932, I 3013. (26) Weiler, Wenk, Stötter, U.S. 1,707,181, March 26, 1929; French 651,646, Feb. 21, 1929; Cent. 1929, II 499. (27) I.G., Austrian 118,640, July 25, 1930; Cent. 1930, II 2978. (28) I.G., Swiss 134,012, Sept. 2, 1929; Cent. 1930, I 1876. (29) I.G., Brit. 334,847, Oct. 9, 1930; Cent. 1931, II 618. (30) I.G., Brit. 337,473, Nov. 27, 1930; Cent. 1931, I 2233.

(31) Muth (to I.G.), Ger. 583,055, Aug. 28, 1933; Cent. 1933, II 3883. (32) I.G., Swiss 137,923-137,929; 138,180-138,183, April 16, 1930; Cent. 1930, II 1453. (33) I.G., Swiss 148,330, Oct. 1, 1931; Cent. 1932, I 1845. (34) Weiler (to I.G.), Ger. 548,822, April 20, 1932; Cent. 1932, II 799. (35) Weiler, Retter (to I.G.), Ger. 604,980, Nov. 3, 1934; Cent. 1935, I 1150. (36) Ullmann, Conzetti, Ber. 53, 827, 831-832 (1920). (37) Scottish Dyes, Ltd. + Thomas + Hooley, Brit. 234,533, June 25, 1925; Ceni. 1926, I 245. (38) Ullmann, Ger. 282,493, March 6, 1915; Cent. 1915, I 643. (39) Zahn, Ber. 67, 2078 (1934). (40) Scottish Dyes, Ltd. + Bangham, Hooley, Thomas, Brit. 339,589, Jan. 8, 1931; Cent. 1932, I 2095.

(41) Hantzsch, Ber. 32, 3070 (1899). (42) Murray, Gordon, J. Am. Chem. Soc. 57, 110-111 (1935). (43) Ordal, Proc. Soc. Exptl. Biol. Med. 47, 387-389 (1941); C.A. 35, 6061 (1941). (44) Ellis (to Insulite Co.), U.S. 2,161,654, June 6, 1939; Cent. 1939, II 4620. (45) I.G., Brit. 356,192, Oct. 1, 1931; Cent. 1931, II 3360. (46) Simonis, Schuhmann, Ber. 50, 1148 (1917). (47) Lock, Monatsh. 62, 184-185 (1933). (48) Birosel, J. Am. Chem. Soc. 53, 1408-1412 (1931). (49) Goldsworthy, J. Chem. Soc. 1926, 1254-1256. (50) Raiford, Howland, J. Am. Chem. Soc. **53,** 1055 (1931).

(51) Chien, Yin, J. Chinese Chem. Soc. 7, 40-45 (1939); C.A. 34, 1979 (1940). (52) Bradfield, Jones, J. Chem. Soc. 1931, 2906. (53) von Auwers, Ann. 357, 92-93 (1907). (54) Baw, J. Indian Chem. Soc. 3, 104 (1926). (55) Huston, Eldredge, J. Am. Chem. Soc. 53, 2263 (1931). (56) Bost, Nicholson, J. Am. Chem. Soc. 57, 2368-2369 (1935). (57) Raiford, Thiessen, Wernert. J. Am. Chem. Soc. 52, 1208 (1930). (58) Pokorny, J. Am. Chem. Soc. 63, 1768 (1941). (59) Zimmermann, Ind. Eng. Chem. 35, 597-599 (1943). (60) Zimmermann, Hitchcock, Contrib. Boyce Thompson Inst. 12, 321-343 (1942); C.A. 36, 6199 (1942).

(61) Sah, Young, Rec. trav. chim. 59, 357-363 (1940); C.A. 35, 4363 (1941). (62) Sah, Gheng. Rec. trav. chim. 58, 592-594 (1939). (63) Sah, Chiao, Rec. trav. chim. 58, 596-599 (1939). (64) Sah, Rec. trav. chim. 58, 587-589 (1939). (65) Sah, Rec. trav. chim. 58, 454-458 (1939).

3: 0563 1,8-DICHLOROPROPANONE-2
$$(\alpha,\alpha'-Dichloroacetone, CH_2-C-CH_2 sym.-dichloroacetone, Cl $(\alpha,\alpha'-Dichloroacetone, CH_2-C-CH_2 sym.-dichloroacetone, Cl $(\alpha,\alpha'-Dichloroacetone, CH_2-C-CH_2 sym.-dichloroacetone, Cl $(\alpha,\alpha'-Dichloroacetone, CH_2-C-CH_2 sym.-dichloroacetone, Cl $(\alpha,\alpha'-Dichloroacetone, CH_2-C-CH_2 sym.-dichloroacetone, CH_2-C-CH_2 sym.-dichloroacetone, CH_2-C-CH_2 sym.-dichloroacetone, CH_2-C-CH_2 sym.-dichloroacetone, CH_2-C-CH_2 sym.-dichloroacetone, CH_2-C-C-CH_2 sym.-dichloro$$$$$$

Colorless tbls. or ndls. volatile even at ord. temp. — Vapors are lachrymatory; liquid blisters skin. — Appreciably sol. in aq. especially on warming, eas. sol. alc., ether. — Volatile with steam.

[For prepn. of \bar{C} from 1,3-dichloropropanol-2 (glycerol α -dichlorohydrin) (3:5985) by oxidn. with Na₂Cr₂O₇ + H₂SO₄ (68-75% yield {10}), with K₂Cr₂O₇ + H₂SO₄ (1) {2} {4} (6) (7) {8} (9) {11} (generally poorer yields) see indic. refs. (note also that b.p. of \bar{C} is very close to that of the precursor 1,3-dichloropropanol-2 (3:5985), a fact which leads to some doubt as to the true yield of \bar{C} in certain of the older reports); for prepn. of \bar{C} from acetone (1:5400) with Cl₂ directly (12), in pres. of I₂, FeCl₃, or SbCl₅ (yield: 28% \bar{C} accompanied by 48.6% unsym.-dichloroacetone (3:5430) {13}), in pres. of NiCl₂ at 70° (other prods. are also formed {14}), or in pres. of aq. + CaCO₃ (yield: 10% \bar{C} accompanied by other prods. (16)) {4} (15), see indic. refs.]

[For prepn. of \bar{C} from epichlorohydrin (3-chloro-1,2-epoxypropane) (3:5358) with S_2Cl_2 (yield: 33% \bar{C} accompanied by 67% 1,3-dichloropropanol-2 (3:5985) (17)), from ethyl γ -(α)-chloro- α (γ)-ethoxyacetoacetate (18) or from ethyl α , γ -dichloracetoacetate (19) by ketonic cleavage with HCl, from allene (propadiene) (20) or 1,2-dichloropropene-2 (21) with HOCl, or from 1,3-diiodoacetone on digestion with AgCl (22) cf. (3) see indicrefs.]

 $[\bar{C}]$ on reduction with yeast gives (53% yield (2)) 1,3-dichloropropanol-2 (3:5985), b.p. 178° (2). — \bar{C} with Zn + AcOH does *not* give acetone but yields (23) a gas formerly supposed to have been cyclopropanone (since it yielded with semicarbazide a semicarbazone, m.p. 156° (23)) although in the light of later work (24) (25) (26) this now appears very doubtful. — For polarographic study of reduction potential of \bar{C} see (27).]

 $\bar{\bf C}$ with aq. alk. presumably yields 3-chloropropanone-2-ol-1 [Beil. I-823] and/or propanone-2-diol-1,3 (dihydroxyacetone) [Beil. I-846, I₁-(428), I₂-(889)] since $\bar{\bf C}$ readily reduces Fehling's soln. (28).

 \bar{C} with satd. aq. NaHSO₃ soln. yields a NaHSO₃ cpd. which seps. with $2\frac{1}{2}$ H₂O (1), 3 H₂O (7). — \bar{C} with aq. K₂SO₃ soln. yields (30) corresp. salt of acetone- α , α '-disulfonic acid [Beil. IV₂-(530)].

[C with KOAc (slightly more than 1 mole) in boilg. AcOH gives (48% yield (29)) chloro-acetylmethyl acetate, b.p. 112-114° at 16 mm. (29). — C with K benzoate refluxed in alc. yields (23) 1,3-dibenzoyloxyacetone, long ndls. from alc., but m.p. not reported.]

[C in dry McOH treated with HCl gas gives (84.5% yield (31)) 1,3-dichloroacetone dimethylketal, cryst. from McOH, m.p. 81.5° (31); C in abs. EtOH similarly treated gives (smaller yield (31)) 1,3-dichloroacetone diethylketal, m.p. 28° (31). — For reactn. of C with ethylene glycol see (32).]

[\bar{C} with equal wt. ethyl mercaptan gives (34% yield (33)) 1,3-bis-(ethylmercapto)-propanone-2, b.p. 117-121° at 15 mm. (33) (corresp. semicarbazone, m.p. 98-99°), but \bar{C} with large excess ethyl mercaptan (4 wt. pts.) gives also 1,2,2,3-tetra(ethylmercapto)-propane, oil (33). — \bar{C} (1 mole) with benzyl mercaptan (2 moles) in alc. NaOH yields (34) 1,3-bis-(benzylmercapto)propanone-2, oil, which on oxidn. in acid soln. with KMnO4 gives the corresp. disulfone, ndls. from alc., m.p. 182° (34).] — [For reactn. of \bar{C} with alk. sulfides and/or polysulfides in prepn. of resins see (37).]

Č with KI even at room temp. (7) yields 1,3-diiodoacetone, pr. from acetone, m.p. 61°. [For reaction of \bar{C} with MeMgBr as means of prepn. of sym.-dichloro-ter-butyl alcohol (3:5977) see the latter.]

[Č with excess conc. aq. or liq. HCN in alc. at 30° for 12 hrs. (11) cf. (35) or with 25% HCN in pres. of a little NH₄OH (36) yields $\beta_{,}\beta'$ -dichloro- α -hydroxyisobutyronitrile (not isolated), which on hydrolysis with HCl (11) (35) (36) gives the corresp. acid, $\beta_{,}\beta'$ -dichloro- α -hydroxyisobutyric acid, in p. 91–92° (11).]

[C with diazotized aniline in pres. of NaOAc yields (3) 1,3-dichloro-1-(benzeneazo)-propanone-2, red-or. cryst. from hot alc., m.p. 156-157° (3); for corresp. homologs using

diazotized o-toluidine or p-toluidine see (3).]

[C with equiv. molar quant. thioacetamide in acetone or alc. followed by htg. with ZnCl₂ (38) (39) gives 4-(chloromethyl)-2-methylthiazole hydrochloride (free base is oil, b.p. 65-67° at 3 mm. (38) (39)); for polymerization of this prod. by htg. see (38). — C with thiobenzamide in acetone followed by htg. of resultant intermediate with HCl in acetone gives 4-(chloromethyl)-2-phenylthiazole hydrochloride (yields: 80-81% (40) (41)) (corresp. free base, m.p. 51° (40), 48.2-51.2° cor. (41)); for reactns. of this prod. see (41). — For analogous reactn. of C with many other substituted thiobenzamides to give corresp. substituted thiazoles see (40) (39).]

 $[\bar{C}$ with equiv. molar amt. carbamyl chloride in dry ether at room temp. for 15 min. is claimed (2) to yield β,β' -dichloroisopropyl carbamate ("Aleudrin"), white cryst. from alc., m.p. 80-81° (2); \bar{C} with 2 molar equivs. of carbamyl chloride similarly treated is claimed (2) to yield β,β -dichloroisopropyl allophanate, cryst. from 60% alc., m.p. 182° (2); note, however, that in view of the facts that the \bar{C} used in the cited work was obtd. from 1,3-dichloropropanol-2, that the b.p.'s of this precursor and \bar{C} are almost identical, and that the \bar{C} employed was purified only by distillation, the indicated esters may have been due to the presence of unoxidized starting material.]

- D 1,3-Dichloropropanone-2 semicarbazone: m.p. 120° (23). [Note that this prod. is very sensitive to heat (care in recrystn. from aq. or C₆H₆) and is also changed by stdg. in solution (23).]
- ① 1,3-Dichloropropanone-2 4-(p-bromophenyl)semicarbazone: ndls. from alc., m.p. 196° cor. dec. (42). [From C + 4-(p-bromophenyl)semicarbazide in alc. refluxed for 12 hrs. (42).]
- © Condensation product (C₁₇H₁₉O₄N₃SCl₂) of C with N-methyl-3-(carbohydrazido)-pyridinium p-toluenesulfonate: cryst. from 1:1 alc./ether, m.p. 115° cor. (43). [From C with nicotinic acid hydrazide metho-p-toluenesulfonate in abs. alc. on refluxing for 15 mins. (43).]

3:0563 (1) Markownikow, Ann. 208, 353-358 (1881). (2) Sen, Barat, J. Indian Chem. Soc. 2, 77-81 (1925). (3) Favrel, Bull. soc. chim. (5) 1, 983-986, 989 (1934). (4) Posner, Rohde, Ber. 42, 3237-3242 (1909). (5) Edwards, Evans, Watson, J. Chem. Soc. 1937, 1944. (6) Glutz, Fischer, J. prakt. Chem. (2) 4, 54-55 (1871). (7) von Hoerman, Ber. 13, 1706-1709 (1880). (8) Cloez, Ann. chim. (6) 9, 167-170 (1886). (9) Erlenbach, Ann. 269, 46-48 (1892). (10) Conant, Quayle, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 211-213 (1941); Coll. Vol. 1 (1st ed.), 206-207 (1932); 2, 13-15 (1922).

- (11) Grimaux, Adam, Bull. soc. chim. (2) 36, 19-21 (1881). (12) Barbaglia, Ber. 7, 467-469 (1874). (13) Consortium für Elektrochem. Ind., French 707,852, July 16, 1931; Cent. 1931, II 2056. (14) Akashi, Bull. Irist. Phys.-Chem. Research (Tokyo) 12, 329-340 (1933); Cent. 1933, I 3066; C.A. 27, 3447 (1933). (15) Kling, Bull. soc. chim. (3) 33, 322-323 (1905); Ann. chim. (8) 5, 474-475 (1905). (16) Fritsch, Ber. 26, 598 (1893); Ann. 279, 315-316 (1894). (17) Malinovskii, J. Gen. Chem. (U.S.S.R.) 9, 832-839 (1939); C.A. 34, 375 (1940). (18) Erlenbach, Ann. 269, 18-19 (1892). (19) Wislicenus, Ber. 43, 3532-3533 (1910). (20) Smirnoff, J. Russ. Phys.-Chem. Soc. 35, 854-872 (1903); Cent. 1904, I 576.
- (21) Henry, Compt. rend. **94**, 1428 (1882). (22) Völker, Ann. **192**, 93-95 (1878). (23) von Romburgh, Verslag Akad. Wetenschappen Amsterdam **31**, 655-656 (1922); Cent. **1924**, I 159; C.A. **18**, 1271 (1924). (24) Ingold, J. Chem. Soc. **119**, 328-329 (1921). (25) Ingold, Sako, Thorpe, J. Chem. Soc. **121**, 1197 (1922). (26) Dem'yanov, Feofilaktov, J. Gen. Chem. (U.S.S.R.) **9**, 340-360 (1939); Cent. **1939**, II 2913; C.A. **34**, 385 (1940). (27) Winkel, Proske, Ber. **69**, 700-701 (1936). (28) Klimont, Chem. Ztg. **69**, 521 (1922). (29) Hess, Fink, Ber. **48**, 2004 (1915). (30) Raschig, Prahl, Ber. **59**, 2027-2028 (1926).
- (31) Prjanischnikow, Leontowitsch, Ber. 68, 1867 (1935). (32) Kuhn, J. prakt. Chem. (2) 156, 124 (1940). (33) Rojahn, Lemme, Arch. Pharm. 263, 615-616 (1925). (34) Fromm, Kapellei, Taubmann, Ber. 61, 1357-1358 (1928). (35) Glattfeld, Schneider, J. Am. Chem. Soc. 60, 417 (1938). (36) Fourneau, Bull. soc. chim. (4) 29, 413-414 (1921). (37) I.G., French 785,705, Aug. 17, 1935; Cent. 1936, I 1134. (38) Hooper, Johnson, J. Am. Chem. Soc. 56, 470-471 (1934). (39) Johnson (to Winthrop Chem. Co.), U.S. 2,014,498, Sept. 17, 1935; Cent. 1936, I 1114; C.A. 29, 7344 (1935). (40) Suter, Johnson, Rec. trav. chim. 49, 1066-1068 (1930).

(41) Huntress, Pfister, J. Am. Chem. Soc. 65, 1668-1670 (1943). (42) Wheeler, J. Am. Chem. Soc. 51, 3654 (1929). (43) Allen, Gates, J. Am. Chem. Soc. 6, 596-601 (1941).

3: 0565 PHENYL CHLOROACETATE C₈H₇O₂Cl Beil. VI - 153 VI₁-(87) ClCH₂.CO.C VI₂-(154) M.P. B.P. $n_{\rm D}^{44} = 1.5146 (9)$ 45° (1) (2)230-235° $D_4^{44} = 1.2202 (9)$ 44-45° 155° (3) at 65 mm. (7) 44° (5) 123-126° at 14 mm. (2) 43° (7) 40.2° (6)

Ndls. or lfts. from alc. — Insol. aq.; eas. sol. alc., ether.

[For prepn. of \bar{C} from phenol (1:1420) with chloroacetyl chloride (3:5235) on htg. alone (7) (6) (3), in ether soln. + pyridine (2), or with AlCl₃ in CS₂ (1) see indic. refs.; with chloroacetic acid (3:1370) + P_2O_5 in CHCl₃ (8) or on htg. with POCl₃ or ZnCl₂ (5) see (8) (5).]

 \bar{C} hydrolyzes rather easily, even slowly on stdg. in moist air (3). \bar{C} on mere refluxing for $\frac{3}{4}$ hr. with abs. alc. or with alc. NaOEt undergoes trans-esterification yielding (3) ethyl chloroacetate (3:5700) and phenol (1:1420).

C in ether treated with NH₃ gas reacts vigorously yielding (3) NH₄ phenolate (sol. in aq.) and chloroacetamide (insol. aq.), m.p. 118° (3).

 \bar{C} with aniline (2 moles) at 80° for 1 hr. gives (4) aniline hydrochloride (sol. in aq.) + phenyl N-phenylaminoacetate [Beil. XII-471] pptd. from alc. by addn. of aq., m.p. 82-83° (4). [Note that \bar{C} on boilg. with aniline yields (4) N-phenylaminoacetanilide (N-phenyl-glycine anilide) [Beil. XII-556], m.p. 111-112° (4).]

C with phenylhydrazine (2 moles) at 50° for ¼ hr. yields (4) phenyl β-phenylhydrazinoacetate [Beil. XV-321], lfts. from C₆H₆ or from alc. by addn. of aq., m.p. 93-94° (4).

C htd. with AlCl₃ for 5 hrs. at 130-140° gives (10) o-hydroxyphenacyl chloride (vol. with steam), m.p. 74°, + p-hydroxyphenacyl chloride (not vol. with steam), m.p. 148°.

 \bar{C} + equal wt. pyridine htd. at 100° gives (1) cpd. $\bar{C}.C_5H_5N.5H_2O$, ndls. from alc., m.p. 165-168° dec. (11), cf. (4).

3:0565 (1) Kunckell, Johannssen, Ber. 30, 1714-1715 (1897). (2) Mannich, Drauzburg, Arch. Pharm. 250, 534 (1912). (3) Morel, Bull. soc. chim. (3) 21, 958-964 (1899). (4) Morel, Bull. soc. chim. (3) 21, 958-964 (1899). (5) Nencki, Ber. 26, Ref., 588 (1893). (6) Prevost, J. prakt. Chem. (2) 4, 379-380 (1871). (7) Fries, Pfaffendorf, Ber. 43, 214-215 (1910). (8) Bakunin, Gazz. chim. ital. 30, II 358 (1900). (9) van der Stichele, J. Chem. Soc. 123, 1228 (1923). (10) von Auwers, Mauss, Ber. 61, 419 (1928).

(11) Barnett, Cook, J. Chem. Soc. 121, 797 (1922).

3: 0572 DI-(β-CHLOROETHYL) OXALATE

C₆H₈O₄Cl₂ Beil. S.N. 170

94

CO.O.CH₂.CH₂Cl CO.O.CH₂.CH₂Cl

M.P. 45° (1) B.P. 132° at 3 mm. (2)

[For prepn. of C from ethylene chlorohydrin (3:5552) with anhydrous oxalic acid (1:0535) by satn. with HCl gas and htg. at 100° see (1).]

[Č with Me₃N in C₆H₆ gives (1) "oxalylcholine chloride," C₁₂H₂₆O₄N₂Cl₂, very hygroscopic cryst. ndls. (chloroaurate, m.p. 256.5° dec.).]

 $[\bar{C} + C_6H_6 + AlCl_3 \text{ gives (2) bibenzyl } (1:7149) + \tan .]$

3:0572 (1) Contardi, Ercoli, Atti IX congresso intern. chim. Madrid 9, V, 163-173 (1934); Cent. **1936**, II 3903-3904; C.A. **31**, 1764 (1937). (2) Markarov-Zemlyanskii, Korshak, Savenkov, J. Gen. Chem. (U.S.S.R.) **11**, 331 334 (1941); Cent. **1942**, I 993; C.A. **35**, 5883 (1941).

3:0580 3,4,5-TRICHLOROTOLUENE



Readily volatile with steam.

[For prepn. of C from 3,5-dichloro-4-aminotoluene [Beil. XII-990] or from 4,5-dichloro-3-aminotoluene [Beil. XII-872] via diazotization and use of Cu₂Cl₂ reactn. see (1); from potassium salt of 3,4,5-trichlorotoluenesulfonic acid-2 by hydrolysis with strong H₂SO₄ see (2).]

[\bar{C} with Cl_2 in pres. of Al/Hg yields (3) 2,3,4,5-tetrachlorotoluene (3:2710), m.p. 97-98° (3).]

C on mononitration with cold fumg. HNO₃ (1) yields 3,4,5-trichloro-2-nitrotoluene [Beil. V-333], pr. from alc., m.p. 81-82° (1); C on dinitration with a mixt. of 6 pts. fumg. HNO₃ and 4 pts. conc. H₂SO₄ (1) yields 3,4,5-trichloro-2,6-dinitrotoluene [Beil. V-346], ndls. from AcOH, m.p. 163-164° (1).

 \bar{C} on oxidn. with dil. HNO3 in s.t. at 130° readily yields (1) 3,4,5-trichlorobenzoic acid (3:4920), m.p. 203° (1).

3:0580 (1) Cohen, Dakin, J. Chem. Soc. 81, 1336-1339 (1902). (2) Wynne, J. Chem. Soc. 61, 1070-1071 (1892). (3) Cohen, Dakin, J. Chem. Soc. 89, 1454 (1906).

M.P. 45.4-46.1° (1) 43.5-44° (2)

[For prepn. of \bar{C} from p-chloro- α -chlorostyrene by elimination of HCl with 25% alc. KOH (36% yield (1)) (2) see indic. refs.]

[For study of dipole moment see (3).]

[\bar{C} with I₂ in liq. NH₃ at -34° readily g ves (98% yield (1)) p-chlorophenyl-iodo-acetylene, m.p. 84.7–85.0° (1).

[Č with NH₃/Cu₂Cl₂ as directed gives (50% yield (5)) di-(p-chlorophenyl)biacetylene, m.p. 258° (5).]

Di-(p-chlorophenylethynyl)mercury: m.p. 221-222° (2), 221.5° (1). [From C in alc. with alk. K₂HgI₄ according to (4); note that m.p. of this prod. is only slightly higher than that (213-214°) for the corresp. prod. from o-chlorophenylacetylene (3:9497).]

3:0590 (1) Vaughn, Nieuwland, J. Am. Chem. Soc. 56, 1207-1209 (1934). (2) Otto, J. Am. Chem. Soc. 56, 1303-1394 (1934). (3) Otto, Wenzke, J. Am. Chem. Soc. 56, 1314-1315 (1934). (4) Johnson, McEwen, J. Am. Chem. Soc. 48, 471 (1926). (5) Zal'kind, Fundyler, J. Gen. Chem. (U.S.S.R.) 9, 1725-1728 (1939); C.A. 34, 3719 (1940).

3: 0610 2,3,5-TRICHLOROTOLUENE CH_3 $C_7H_5Cl_3$ Beil. V - 299 V_1 — V_2 —

M.P. 45-46° (1) B.P. 229-231° at 757 mm. (1)

[For prepn. of \bar{C} from 3,5-dichloro-2-aminotonuene [Beil. XII-837] or from 2,5-dichloro-3-aminotoluene [Beil. XII-872] via diazotization and use of CuCl₂ reactn. see (1); for formn. of \bar{C} from 3,5-dichlorotoluene (3:6310) with Cl₂ in pres. of Al/Hg see (2).]

[C with Cl2 in pres. of Al/Hg yields (3) 2,3,5,6-tetrachlorotoluene (3:2575).]

 \bar{C} on mononitration with cold fumg. HNO₃ (1) yields 2,3,5-trichloro-4(or 6)-nitrotoluene [Beil. V-333], ndls. from alc. or AcOH, m.p. 58-59° (1); \bar{C} on dinitration with 6 pts. fumg. HNO₃ + 4 pts. conc. H₂SO₄ yields 2,3,5-trichloro-4,6-dinitrotoluene [Beil. V-345], ndls. from alc. + AcOH, m.p. 149-150° (1).

 \bar{C} on oxidn. with dil. HNO₃ in a s.t. at 140° yields (1) 2,3,5-trichlorobenzoic acid (3:4485), m.p. 162° (1).

3:0610 (1) Cohen, Dakin, J. Chem. Soc. 81, 1329-1331 (1902). (2) Cohen, Dakin, J. Chem. Soc. 81, 1343-1344 (1902). (3) Cohen, Dakin, J. Chem. Soc. 85, 1284 (1904).

M.P. 46° (1) (2) B.P. 265° (2) 45° (3) 162–163° at 28 mm. (3)

[For prepn. of \bar{C} from m-cresol (1:1730) in aq. alk. with excess Cl_2 (3) or from m-cresol with Cl_2 in the dark (2) see indic. refs. (note that m-cresol with Cl_2 in sunlight yields (2)

3,5,6-trichloro-2-methylbenzoquinone-1,4 [Beil. VII-651, VII₁-(354)], m.p. 238° (2)); from 2,4-dichloro-3-methylphenol (3:1205), from 2,6-dichloro-3-methylphenol (3:0150), and from 4.6-dichloro-3-methylphenol (3:1745) in CHCl₃ with Cl₂ see (1).]

[Č with PCl₅ yields (2) both tris-(2,4,6-trichloro-3-methylphenyl) phosphate, m.p. 230° (2), and bis-(2,4,6-trichloro-3-methylphenyl) phosphate, m.p. 94.5° (2); for study of Hg, Sb, and Bi derivs, of Č see (2).

 $[\tilde{C}$ on sulfonation with fumg. H_2SO_4 (50% SO_3) at 50° yields (4) a monosulfonic acid; for condens, of \tilde{C} with benzaldehyde-p-sulfonic acid and use of prod. as motheroofing agent see (5); for study of use of Na or K salts of \tilde{C} as wood impregnants (preservatives) see (6).]

Č with aqua regia at 100° for 1½ hrs. gives (25% yield (3)) 3,5,6-trichloro-2-methyl-

benzoquinone-1,4 (see above), m.p. 233° (3).

[C in aq. alk. with Me₂SO₄ yields (2) corresp. methyl ether, ndls. from alc., m.p. 46°, b.p. 258° (2); C in aq. alk. with Et₂SO₄ yields (2) corresp. ethyl ether, ndls. from alc., m.p. 35.5°, b.p. 266° (2).]

- --- 2,4,6-Trichloro-3-methylphenyl acetate: m.p. 35°, b.p. 270° (2).
- **② 2,4,6-Trichloro-3-methylphenyl benzoate:** fine prismatic pl. from alc., m.p. 53° (1). [From \bar{C} with BzCl in pyridine (1).]
- **② 2,4,6-Trichloro-3-methylphenyl benzenesulfonate:** prismatic pl. from alc., m.p. 121° (1). [From Č with benzenesulfonyl chloride in pyridine (1).]
- **D 2,4,6-Trichloro-3-methylphenyl** p-toluenesulfonate: prismatic pl. from alc., m.p. 92-93° (1). [From Č with p-toluenesulfonyl chloride in pyridine (1).]

3:0618 (1) Huston, Chen, J. Am. Chem. Soc. 55, 4218 (1933). (2) Burës, Chem. Listy 21, 108-114, 148-162, 221-227, 261-265 (1927); Cent. 1927, II 1345; C.A. 22, 63 (1928). (3) Chulkov, Parini, Barshev, Org. Chem. Ind. (U.S.S.R.) 3, 410-412 (1937); Cent. 1938, II 305; C.A. 31, 7047 (1937). (4) Weiler, Better (to I.G.), Ger. 557,450, Aug. 24, 1931; Cent. 1932, II 2371. (5) Weiler (to I.G.), Ger. 548,822, April 20, 1932; Cent. 1932, II 799. (6) Iwanowski, et al., Przemysl Chem. 16, 205-221 (1932); Cent. 1933, I_867; C.A. 27, 3796 (1933).

3:0625 2.3.6-TRICHLOROTOLUENE

M.P. 45-46° (1) 41-42° (2)

White ndls, from alc.

[For prepn. of \bar{C} from 2,6-dichloro-3-aminotoluene [Beil. XII-872] via diazotization and use of Cu_2Cl_2 reactn. see (1); from p-toluenesulfonyl chloride via chlorination, hydrolysis to acid, and subsequent hydrolytic cleavage of the sulfonic acid radical see (3) (2); for formn. of \bar{C} together with other prods. from 2,5-dichlorotoluene (3:6245) or 2,6-dichlorotoluene (3:6270) with Cl_2 in pres. of Al/Hg see (4).

[C with Cl₂ in pres. of Al/Hg yields (5) 2,3,5,6-tetrachlorotoluene (3:2575).]

Č on mononitration by soln. in cold fumg. HNO₃ yields (1) 2,3,6-trichloro-5-nitrotoluene [Beil. V-333], ndls. from alc., m.p. 57-58° (1); Č on dinitration, e.g., with 6 pts. fumg. HNO₃ + 4 pts. conc. H₂SO₄ (1), yields 2,3,6-trichloro-4,5-dinitrotoluene [Beil. V-346], pr. from AcOH, m.p. 140-142° (1), 140-141° (6).

C on oxidn. with dil. HNO3 in s.t. at 140° yields (1) 2,3,6-trichlorobenzoic acid (3:4500), m.p. 164°.

3:0625 (1) Cohen, Dakin, J. Chem. Soc. 81, 1331-1332 (1902). (2) Austin, Johnson, J. Am. Chem. Soc. 54, 658 (1932). (3) Geigy Co., Ger. 210,856, June 16, 1909; Cent. 1909, II 79. (4) Ref. 1, pp. 1342-1343. (5) Cohen, Dakin, J. Chem. Soc. 85, 1284 (1904). (6) Qvist, Holmberg, Acta Acad. Aboensis Math. Phys. 6, No. 14, 3-28 (1932); Cent. 1932, 2816; C.A. 27, 5726-5727 (1933).

Cryst. from CCl4; spar. sol. alc.; eas. sol. ether, CS2, lgr., or 90% AcOH; sublimes.

[For prepn. of \bar{C} from 3,5-dichloro-2-nitroaniline [Beil. XII-733] via diazotization and use of Cu₂Cl₂ reactn. (note that the nitro group is also replaced by chloride) in 83% yield (4) see (4) (5); from 2,3,4-trichloroaniline [Beil. XII-626] via diazotization and use of Cu₂Cl₂ reaction see (7) (6) cf. (1); from 1,2,3-trichlorobenzene (3:0990) with Cl₂ in CCl₄ in pres. of Al/Hg see (7); for formn. of \bar{C} as by-prod. of actn. of conc. HNO₃ on acet-2,4-dichloroanilide see (2).

[For use of C in mixts. of dielectric liquids see (8).]

[For behavior of \bar{C} with liq. Cl_2 yielding addn. products see (9).]

[For behavior of C with NaOMe see (4) (10).]

 \bar{C} on mononitration by warming with HNO₃ (D=1.52) (1) yields 1,2,3,4-tetrachloro-5-nitrobenzene [Beil. V-247], m.p. 64.5° (1), 62.0-63.5° (7), 66-67° (11); this prod. on further nitration by boilg. 2 hrs. with 10 pts. mixed HNO₃ (D=1.52) + conc. H₂SO₄ yields 1,2,3,4-tetrachloro-5,6-dinitrobenzene, m.p. 151° (11).

3:0655 (1) Beilstein, Kurbatow, Ann. 192, 238-239 (1878). (2) Gotts, Hunter, J. Chem. Soc. 125, 447 (1924). (3) Dadieu, Pongratz, Kohlrausch, Monatsh. 61, 433 (1932). (4) Holleman, Rec. trav. chim. 39, 741-743, 749 (1920). (5) Holleman, van Haeften, Rec. trav. chim. 40, 70 (1921). (6) Körner, Contardi, Atti accad. Lincei (5) 18, I 96 (1904). (7) Cohen, Hartley, J. Chem. Soc. 87, 1365 (1905). (8) Compagnie Française Thomson-Houston, French 48,584, April 5, 1938; Cent. 1938, II 906; C.A. 33, 277 (1939). (9) van der Linden, Rec. trav. chim. 55, 421-430 (1936). (10) de Crauw, Rec. trav. chim. 50, 787 (1931).

(11) Berckmans, Holleman, Rec. trav. chim. 44, 856-857 (1925).

3: 0670 2,4'-DICHLOROBIPHENYL C₁₂H₈Cl₂ Beil. S.N. 479

M.P. 46° (1) B.P. 191° at 30 mm. (2)

Cryst from alc. (1); sol. in C_6H_6 or AcOH (1).

[For prepn. of C from 2-amino-4'-chlorobiphenyl (2), from 4-amino-2,4'-dichlorobiphenyl (1), or 2,4'-diaminobiphenyl (1) by appropriate diazo reactions see (1) (2).]

 \bar{C} on oxidn. with $CrO_3 + AcOH$ yields (2) p-chlorobenzoic acid (3:4940), m.p. 232° (2).

3:0670 (1) Finzi, Bellavita, Gazz. chim. ital. 64, 339 (1934). (2) de Crauw, Rec. trav. chim. 56, 776-777 (1931).

3:0685 2,4-DICHLOROBIPHENYL
$$C_{12}H_8Cl_2$$
 Beil. V — $V_1-V_2-(483)$

Pale yel. cryst. (1).

[For prepn. of C from 3-amino-4-chlorobiphenyl (3) or from 4-amino-3-chlorobiphenyl (1) via appropriate diazo methods see (1) (3).]

C htd. with aq. alk. for 3 hrs. at 290-300° yields (4) phenylpyrocatechol (3,4-dihydroxy-biphenyl) (1:1576), m.p. 144 8-145.2° (4); diacetate, m.p. 77.5-78° (4).

C on oxidn. with CrO₃ + AcOII yields (1) (3) 3,4-dichlorobenzoic acid (3:4925), m.p. 198° (3), 200° (1).

3:0685 (1) Scarborough, Waters, J. Chem. Soc. **1926**, 560. (2) Zerweck, Schutz (to General Aniline and Film Corp.), U.S. 2,280,504, Apr. 21, 1942, C.A. **36**, 5658 (1942). (3) Blakey, Scarborough, J. Chem. Soc. **1927**, 3007. (4) Harvey (to E R. Squibb and Sons), U.S. 1,952,755, March 27, 1934; Cent. **1934**, II 1846; C.A. **28**, 3426 (1934).

Strong camphoraceous odor! — Cryst. from ice-cold lt. pet. ether (3) (2). — Volatile with steam (2).

[For prepn. from 4-chloro-3-aminotolucne (2-chloro-5-methylaniline) [Beil. XII-871] via diazo reaction see (1) (2) (4); from 6-amino-m-cresol (2-amino-5-methylphenol) [Beil. XIII-590] see (1).]

 \tilde{C} treated with $(CH_3)_2SO_4+aq$. NaOH gives its methyl ether, 2-chloro-5-methylanisole, b.p. 212.5° (3). [This methyl ether on oxidn. with dil. KMnO₄ (2.7 hrs. for 5 g.) gave (3) 4-chloro-3-methoxybenzoic ac., pr. from 50% alc. or pl. from CHCl₃, m.p. 211° (3), Neut. Eq. 186.5.]

- © 6-Chloro-3-methylphenyl benzoate: from $\bar{C} + BzCl + pyridine$; pr. contg. alc. (3) from alc., m.p. 31° (3), 38° (1); cryst. from lt. pet. ether, m.p. 40° (3).
- ⊕ 6-Chloro-3-methylphenyl benzenesulfonate: from C
 + benzenesulfonyl chloride +
 pyridine; cryst. from alc., m.p. 99° (1).
- © 6-Chloro-3-methylphenyl p-toluenesulfonate: from \bar{C} + p-toluenesulfonyl chloride + pyridine; hexag. pr. from alc. (3) (1) or acetone (3), m.p. 96° (3), 93-94° (1).

3:0700 (1) Houston, Chen, J. Am. Chem. Soc. 55, 4214-4216 (1933).
 42) Kraay, Rec. trav. chim.
 49, 1090 (1930).
 43) Gibson, J. Chem. Soc. 1926, 1424-1425.
 44) Hodgson, Moore, J. Chem. Soc. 1926, 2038-2039.
 45) Raschig, Ger. 232,071, March 4, 1911; Cent. 1911, I 854.

Tbls. from CHCl₃ + lgr. (3) (4); cryst. from pet. eth. (5). — [For crystallog. data see (5) (8).]

[For prepn. (93% yield (9)) from o-chlorobenzoyl chloride (3:6640) + C_6H_6 + AlCl₃ see (3) (5) (9); for formation (12%) in reaction of BzOH + chlorobenzene + AlCl₃ (main prod. 4-chlorobenzophenone (3:1914)) see (2).]

 \bar{C} on reduction with 10% Na/Hg + ale. (11) or boilg. alc. KOH (12) gives almost exclusively 2-chlorodiphenylcarbinol [Beil. VI-680], m.p. 65° (11) (12), 62° (19). — \bar{C} with Al/Hg + 80% alc. (6) gives mainly 2-chlorodiphenylcarbinol (above) + a little 2,2′-dichlorobenzpinacol. — \bar{C} with Zn + AcOH (11) or \bar{C} in alc. on long exposure to sunlight (11) (13) (14) gives 2,2′-dichlorobenzpinacol [Beil. VI₁-(523)], m.p. 174-175° (6), 178° dec. (11).

Č htd. with aniline 3-4 hrs. at 200° yields (4) 2-chlorobenzophenone anil [Beil. XII-201], pale yel. ndls. or scales from alc., m.p. 128° (4). [Fused subst. or solns. in org. solvents (especially CHCl₃) are yellow.]

Č fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (1) BzOH (1:0715) (90-95% yield) + chlorobenzene (3:7903) but no o-chlorobenzenic acid; however, Č with aq. NaOH + trace CuO in iron bomb (or in pres. of Fe powder) at 240° for 6 hrs. gives (58% yield (20)) fluorenone (1:9014).

 \bar{C} with CH₃MgI yields (15) 1-(o-chlorophenyl)-1-phenylethylene, oil, b.p. 162-163° at 18 mm. (15); \bar{C} with Mg + MgI₂ easily loses nuclear halogen (16).

② 2-Chlorobenzophenone oxime: from C̄ + NH₂OH.HCl + dil. alc. KOH (5) (17) (7) or from C̄ + NH₂OH.HCl + alc. htd. in s.t. for 3 hrs. at 130° (17); cryst. from pet. ether, m.p. 133-134° (17), 121° (5) (7). [With PCl₅ in dry ether, followed by aq. this oxime yields by Beckmann rearr. o-chlorobenzanilide [Beil. XII-266], m.p. 118° (5), 114° (17).] [The above oxime boiled with conc. aq. KOH for 1 day (5) or refluxed 6 hrs. with 20 pts. 30% MeOH/KOH, then diluted with aq. (17) (18), gives 3-phenylindoxazene [Beil. XXVII-71], ndls. or tbls. from ether or alc., m.p. 83-84° (18), 82.5° (5) (11).]

3:0715 (1) Lock, Rödiger, Ber. 72, 867 (1939). (2) Newton, Groggins, Ind. Eng. Chem. 27, 1398 (1935). (3) Overton, Ber. 26, 28-29 (1893). (4) Graebe, Keller, Ber. 32, 1687 (1899). (5) Montagne, Koopal, Rec. trav. chim. 29, 139-145 (1910). (6) Cohen, Böeseken, Rec. trav. chim. 38, 114-115 (1919). (7) von Auwers, Lechner, Bundesmann, Ber. 58, 50 (1925). (8) Jaeger, Z. Krist. 56, 48 (1916). (9) Mayer, Freund, Ber. 55, 2051-2052 (1922). (10) Koopal, Rec. trav. chim. 34, 153 (1915).

(11) Ref. 10, pp. 157-160. (12) Montagne, van Charante, Rec. trav. chim. 31, 311-312 (1912). (13) Cohen, Böeseken, Rec. trav. chim. 39, 258 (1920). (14) Böeseken, Cohen, Langdeijk, Rec. trav. chim. 46, 383-396 (1927). (15) Bergmann, Bondi, Ber. 64, 1473-1474 (1931). (16) Gom-

berg, Bailar, J. Am. Chem. Soc. 51, 2231 (1929). (17) Meisenheimer, Meis, Ber. 57, 295 (1924).
(18) Cathcart, Meyer, Ber. 25, 1498, 3295 (1892). (19) Montagne, Rec. trav. chim. 26, 266 (1907).
(20) Britton, Moyle, Bryner (to Dow Chem. Co.), U.S. 2,377,751, June 5, 1945; C.A. 39, 4097 (1945).

100

[For prepn. of \bar{C} from 2,2'-dichlorobenzilic acid (1) by oxidn. with CrO₃/AcOH (47% yield (1)) or from di-(o-chlorophenyl)carbinol (1) by oxidn. with Na₂Cr₂O₇/H₂SO₄/AcOH see indic. refs.l

① 2,2'-Dichlorobenzophenone 2,4-dinitrophenylhydrazone: m.p. 206-208° (1).

3:6717 (1) Haller, Bartlett, Drake, Newman, Cristol et al., J. Am. Chem. Soc. 67, 1600-1601 (1945).

3: 0720 ETHYLENE GLYCOL bis-CHLOROACETATE C₆H₈O₄Cl₂ Beil. S.N. 160 ClCH₂.CO.O.CH₂ ClCH₂.CO.O.CH₄

Cryst. from ether/pet. eth. — Insol. aq. (dif. from β -hydroxyethyl chloroacetate (3:6780)).

[For prepn. of $\bar{\mathbf{C}}$ from ethylene oxide (1:6105) with chloroacetic acid (3:1370) as by-product of prepn. of β -hydroxyethyl chloroacetate (3:6780) see (1); note also that $\bar{\mathbf{C}}$ is formed (together with ethylene glycol (1:6465)) by disproportionation of β -hydroxyethyl chloroacetate (3:6780) on long stdg. in ord. glass bottles (1).

C on shaking with aq. is hydrolyzed only very slowly (1).

[For use of \bar{C} as insecticide, fungicide, and disinfectant see (2).]

3:0720 (1) Meerwein, Sönke, *J. prakt. Chem.* (2) **137**, 316-318 (1933). (2) Peet (to Rohm and Haas Co.), U. S. 1,816,441, July 28, 1831; *Cent.* **1932**, I 1146; *C.A.* **25**, 5501 (1931); French 667,633, Oct. 18, 1929; *Cent.* **1930**, I 2614.

3: 0730 CHLOROACETIC ACID ANHYDRIDE
$$C_4H_4O_3Cl_2$$
 Beil. II - 199 $II_{1^-}(89)$ $II_{1^-}(89)$ $II_{1^-}(89)$ $II_{1^-}(89)$ $II_{1^-}(89)$ $II_{1^-}(193)$ $II_{1^-}(193)$

Note that the above name of \tilde{C} is so rendered to emphasize that it is the anhydride of chloroacetic acid (not a monochlorinated acetic anhydride).

Pr. from C₆H₆; eas. sol. cold ether, CHCl₃; spar. sol. cold C₆H₆; insol. cold lgr.

[For prepn. of \bar{C} from chloroacetic acid (3:1370) with P_2O_5 in vac. (2), or with Ac_2O_5 (6) (in latter case note also formn. of mixed anhydride acetic-chloroacetic anhydride, b.p. 80-83° at 30 mm. (5), 80-85° at 20 mm. (3), $D_4^{20} = 1.2003$ (5)), or with chloroacetyl chloride (3:5235) + an inorg. acid chloride (7) or $AlCl_3$ (8), see indic. refs.; for prepn. of \bar{C} from sodium chloroacetate with oxalyl (di)chloride (3:5060) in C_6H_6 (54% yield) see (9); for prepn. of \bar{C} from chloroacetyl chloride (3:5235) with Na_2CO_3 (4) or KNO_3 (1) see indic. refs.]

C with aq. K₂CO₃ yields (2) polyglycolide (1:4970), m.p. 220°.

[For reactn. of \bar{C} with AlCl₃ + toluene giving 46-59% ω -chloro-p-methylacetophenone (3:1130) see (10); for reactn. of \bar{C} with AlCl₃ + biphenyl giving 41% yield ω -chloro-p-phenylacetophenone, pale yel. ndls. from dil. alc., m.p. 122-123° see (11); for abnormal reactn. of \bar{C} with benzyl MgCl yielding ω -chloro- σ -methylacetophenone (3:9660) see (12).]

[For behavior of \bar{C} with various carbohydrates (13) and with cellulose (14) see indic. refs.] \bar{C} htd. 4 hrs. at 160–180° with phenyl isothiocyanate yields (15) after distn. at 14–20 mm. 2,4-dioxo-3-phenylthiazolidine [Beil. XXVII-238, XXVII₁-(305)], m.p. 147–148° (15).]

 \bar{C} with aq. hydrolyzes almost instantly yielding chloroacetic acid (3:1370). — For the amide, anilide, p-toluidide, and other derives corresp. to \bar{C} see chloroacetic acid (3:1370).

3:0730 (1) Diels, Okada, Bcr. 44, 3335 (1911). (2) Bischoff, Walden, Bcr. 27, 2949 (1894). (3) Watson, Gregory, J. Chem. Soc. 1929, 1375. (4) Patterson, Bcr. 38, 210-213 (1905). (5) Baroni, Gazz. chim. ital. 63, 29-30 (1933). (6) Clarke, Malm (to Eastman Kodak Co.), U.S. 1,648,540, Nov. 8, 1927; Cent. 1928, I 1459; C.A. 22, 433 (1928). (7) Salmoiraghi, Italian 290,541, June 17, 1930; Cent. 1937, I 185. (8) Strosacker, Schwegler (to Dow Chem. Co.), U.S. 1,713,104, May 14, 1929; Cent. 1929, II 1215; C.A. 23, 3234-3235 (1929). (9) Adams, Ulich, J. Am. Chem. Soc. 42, 607 (1920). (10) Noller, Adams, J. Am. Chem. Soc. 46, 1892-1893 (1924).

(11) Silver, Lowy, J. Am. Chem. Soc. 56, 2429-2430 (1934). (12) Austin, Johnson, J. Am. Chem. Soc. 54, 656 (1932). (13) Brass, Kurz, Cellulosechem. 15, 99-102 (1934). (14) Soc. Chem. Ind. Basel, French 764,308, May 18, 1934; Cent. 1935, I 650. (15) Dubsky, Ber. 56, 1690-1691 (1917). (16) Ballaus, Monatsh. 74, 91 (1943).

3:0738
$$\alpha, \alpha', \beta, \beta, \beta, \beta', \beta' - \beta' - OCl'ACHLORODIETHYL ETHER C4H2OCl8 Beil. I - 624 (bis-($\alpha, \beta, \beta, \beta$ -tetrachloroethyl) ether) Cl Cl I₁— I₂-(681)$$

M.P. 47° (1) B.P. 130-131° at 11 mm. (1) 45-46° (1) 128-130° at 9 mm. (1) 40-42° (2)

Cryst. with agreeable camphoraceous odor from MeOH or EtOH. — Eas. sol. MeOH, C_6H_6 , toluene, or pet. ether; spar. sol. in abs. alc. below 0°.

C slowly sublimes but on attempted distn. at ord. press. decomposes at about 240°.

[For prepn. of $\bar{\mathbb{C}}$ from chloral (3:5210), chloral hydrate (3:1270), or metachloral with ClSO₃H or FSO₃H at not above 50-60° see {1}; note that from chloral (3:5210) with ClSO₃H at -50° for 10-12 hrs. yield of $\bar{\mathbb{C}}$ may be as high as 50%; from metachloral with ClSO₃H at 50° for a few hrs. yield is 60% {1}; note also that various other products including chloralide (3:3510) are also formed. — For form. of $\bar{\mathbb{C}}$ from trichloroethylene (3:5170) with excess Cl₂O in CCl₄ at -20° {2}, or perhaps from α,α' -dichlorodicthyl ether (3:7595) with Cl₂ in sunlight (3), see indic. refs.]

C on htg. in pres. of air gives (2) phosgene (3:5000).

 \overline{C} on reduction with conc. HI (D=1.78) in boilg. AcOH quantitatively yields (2) ethane.

C is fairly stable toward boilg. aq. or aq. alkalies (1).

Č is claimed (1) to react with 2 moles of RMgX cpds. of either aliphatic or aromatic types, but no details are reported.

3:0738 (1) Fuchs, Katscher, *Ber.* **62**, 2381–2386 (1929). (2) Goldschmidt, Schussler, *Ber.* **58**, 569–570 (1925). (3) Roth, *Ber.* **8**, 1017–1018 (1875).

White cryst. (from pet. ether) (1); hygroscopic scales (from lgr.) (2). — Eas. deliquesces absorbing $\frac{1}{2}$ mole H₂O. — Eas. sol. aq. but insol. almost all org. solvents except cold pet. ether or cold lgr.

[For prepn. from catechol (1,2-dihydroxybenzene) (1:1520) by action of SO₂Cl₂ in ether at 0° see (1) (2); for prepn. from o-benzoquinone [Beil. VII-600] by action of ethereal HCl see (2); 4-chlorocatechol (3:2470) is also a by-product of both methods.]

[\bar{C} on oxidn. with PbO₂ in pet. ether gives (12% yield (2)) 3-chloro-o-benzoquinone [Beil. VII₁-(338)]; for use in prepn. of α -chlorophenazine see (1).]

C with FeCl₃ gives a blue-green color, changing to clear red on addn. of Na₂CO₃ (2).

3-Chloropyrocatechol dibenzoate: ndls. from alc., m.p. 108-109° (2); 109° u.c. (1).
 3:0745 (1) Wrede, Mühlroth, Ber. 63, 1932-1933 (1930). (2) Willstätter, Müller, Ber. 44, 2184-

3:0745 (1) Wrede, Mühlroth, *Ber.* **63**, 1932–1933 (1930). **(2)** Willstätter, Müll**er**, *Ber.* **44**, 2184–2189 (1911).

[See also 1-(chloromethyl)naphthalene (3:0250).]

Colorless cryst. from alc. (6) (5); loses HCl on attempted distn. at ord. press.

[For prepn. of \tilde{C} from 2-methylnaphthalene (1:7605) with Cl_2 in sunlight (5) (3) (6) and best at elevated temp., e.g. 220° (7) or even 250-280° (8) (53% yield (11)), see indic. refs.; from β -naphthylcarbinol [Beil. VI-668] (4) (2) with PCl_3 (2) or with $SOCl_2$ in toluene (4) see indic. refs.; from N-(benzoyl)- β -naphthylmethylamine (1) or from N-(benzoyl)- β -naphthylmethyl)amine (1) by htg. with PCl_3 see (1).]

 \bar{C} on oxidn. with aq. Pb(NO₃)₂ soln. yields (6) β -naphthaldehyde (1:0036); \bar{C} on oxidn. with alk. KMnO₄ yields (6) β -naphthoic acid (1:0800).

C on reductn. with Zn/Cu couple yields (2) 2-methylnaphthalene (1:7605).

[\bar{C} with excess Na in dry ether readily gives (8) α,β -bis-(2-naphthylmethyl)ethane, m.p. 182° (9) (picrate, m.p. 198° (9)).] — [For study of reactn. of \bar{C} with 1-(chloromethyl)-naphthalene (3:0250) + AlCl₃ in CS₂ see (7).]

[C with Mg in dry ether + trace C_2H_5I gives corresp. β - $C_{10}H_7$. CH_2MgCl , but reactn. is capricious and requires pure C (4); the RMgCl cpd. with AcCl in ether does not follow a normal course but gives instead 1,3-di-(β -naphthyl)-2-methylpropene-1, cryst. from AcOH, m.p. 184-185° (4).]

[For study of reactn. of \tilde{C} with ethyl acetoacetate + NaOEt in abs. alc. giving (83% yield) ethyl α -(β -naphthylmethyl)acetoacetate see (10).]

 \overline{C} with aq. at 100° for $1\frac{1}{2}$ hrs. is 17% hydrolyzed (1).

[\bar{C} with large excess of conc. C_6H_6 soln. of dimethylamine htd. in s.t. at 100° for 10 hrs. yields (1) N,N-dimethyl- β -naphthylmethyl-amine.]

3:0747 (1) von Braun, Moldaenke, Ber. 56, 2168-2171 (1923). (2) Sah, Rec. trav. chim. 59, 461-470 (1940); C.A. 35, 4763 (1941). (3) Achmatowicz, Lindenfeld, Roczniki Chem. 18, 69-74 (1938); Cent. 1939, II 389. (4) Campbell, Anderson, Gilmore, J. Chem. Soc. 1940, 820. (5) Scherler, Ber. 17, 1529 (1884). (6) Schulze, Ber. 17, 1529 (1884). (7) Clar, Lombardi, Gazz. chim. ital. 62, 542-544 (1932); C.A. 27, 81 (1933). (8) Clar, Wallenstein, Ber. 64, 2080, 2082 (1931). (9) Friedman, Ber. 49, 1354-1355 (1916). (10) Sempronj, Gazz. chim. ital. 68, 263-266 (1938).

(11) Tarbell, Fukushima, Dam, J. Am. Chem. Soc. 67, 198 (1945).

[See also liquid diastereoisomer (3:9068).]

Colorless crystals from alc. (2).

[For prepn. of \tilde{C} (30-50% yield of mixed solid + liquid stereomers (2)) from 1,2-dichloroethylene (3:5030) + 1,1,2-trichloroethane (3:5330) + 1% AlCl₃ for 5 days at 35-40° see (2); for formn. of \tilde{C} from 1,2-dichloroethylene (3:5030) with HCl + AlCl₃ at 50° see (1).]

Č in CCl₄ treated with AlCl₃ remains colorless and the solution does not (2) evolve HCl, even on boilg.

Č in alc. treated with Zn dust gives (80% yield (2)) 1-chlorobutadiene-1,3 (3:7210), b.p. 68° (2).

 \bar{C} dissolved in hot alc. and titrated with N/10 KOH splits off 1.44-1.59 moles HCl (2).

[A pentachlorobutane obtained (3) from trichloroethylene (3:5170) + 1,1-dichloroethane (3:5035) + AlCl₃ may or may not be identical with \tilde{C} .]

3:0750 (1) Müller, Hönn, *J. prakt. Chem.* (2) 133, 289–290 (1932). (2) Prins, *Rec. trav. chim.* 56, 121–123 (1937). (3) Consortium für Elektrochem. Ind., Brit. 453,414, Oct. 8, 1936; *Cent.* 1937, I 1012.

3:0765 p-CHLOROBENZALDEHYDE CLCCHO C7H5OCl Beil. VII - 235 VIII-(133)

M.P.	49°	(1)	R.P.	214.5-216.5°	at	760 mm.	(3)	
	48°	(2) (3)		213-214°			(6)	(8)
	47.5°	(4) (6)		213°	at	748 mm.	(9)	
	47°	(5)		108-111°	at	25 mm.	(7)	
	46-47°	(7)						

Colorless pl. with odor like benzaldehyde. — Volatile with steam. — Somewhat sol. cold aq., more sol. hot aq.; eas. sol. alc., ether, C_6H_6 , CS_2 , AcOH. — Forms spar. sol. NaHSO₃ cpd.

[For prepn. of \bar{C} from p-chlorotoluene (3:8287) with CrO_2Cl_2 (10), or by halogenation to p-chlorobenzal (di)chloride (3:6700) (7) (46) or p-chlorobenzal (di)bromide (11) and their subsequent hydrolysis with fumg. H_2SO_4 (6) (12) (13), conc. H_2SO_4 (7), anhydrous oxalic acid (8), or water in a s.t. at 170° (14) (15) see indicated refs.; from p-aminobenzaldehyde by diazotization and reactn. with CuCl (73% yield (16)) see (16) (17) (1); from p-chlorobenzyl chloride (3:0220) (or bromide) by boilg. with aq. $Pb(NO_3)_2$ in CO_2 (4) (5) or with hexamethylenetetramine (2); from p-chlorobromobenzene vap-chlorophenyl MgBr and its reactn. with ethyl orthoformate (64% yield) (18); from p-chlorobenzonitrile with $SnCl_2$ (19); from chlorobenzene + HCN + $AlCl_3$ (20) or with CO + $AlCl_3$ (21); from p-chlorobenzylamine with hexamethylenetetramine (45) see indic. refs.]

 $\bar{\mathbb{C}}$ with KMnO₄ (2) (4) (5) or even slowly in air oxidizes to p-chlorobenzoic ac. (3:4940), m.p. 236°. [For study of auto-oxidation see (22).] — $\bar{\mathbb{C}}$ on cat. hydrogenation (92% yield (23)) or electrolytic reductn. (24) or by actn. of iodo-magnesium hydrobenzoinate (84% yield (25)) gives p-chlorobenzyl alc., ndls. from $C_6H_6/lgr.$, m.p. 71–72.5° (23). — $\bar{\mathbb{C}}$ with conc. alk. undergoes Cannizzaro reactn. (for study see (26) (28)) although presumable products, p-chlorobenzyl alc. and p-chlorobenzoic ac., have not been (by this reactn.) actually isolated. [For study of $\bar{\mathbb{C}}$ in mixed Cannizzaro reactn. see (27).]

 \bar{C} on reduction with Ni/Al alloy (Raney Ni) in aq. alk. gives (60% yield (48)) toluene (1:7405).

Č with dil. KCN gives benzoin condensation yielding 4,4'-dichlorobenzoin, m.p. 85-87° (29), which on oxidn. with HNO₃ in AcOH yields 4,4'-dichlorodibenzil, m.p. 195-196° (29).

C on htg. with NaOAc + Ac₂O for 8 hrs. at 180-200° undergoes Perkin reactn. giving (yield: 52% (13), 60% (17)) p-chlorocinnamic ac., m.p. 249-250° (17), 247° (13) (31). [This with Br₂ in CHCl₃ gives (30) p-chlorocinnamic acid dibromide, m.p. 191° (30).]—C + malonic acid + pyridine gives alm. quant. yield (31) p-chlorocinnamic acid. [With-

out pyridine reactn. gives (100% yield (31)) p-chlorobenzalmalonic acid, m.p. 197-198° dec. (31).]

 \bar{C} on mononitration with conc. HNO₃ + conc. H₂SO₄ at 80-90° gives (32) (33) 4-chloro-3-nitrobenzaldehyde [Beil. VII-262], ndls. from CHCl₃/lgr. or from aq., m.p. 62° (32) (33); ndls. from dil. alc., m.p. 64.5° (34) [oxime, pale yel. ndls. from alc., m.p. 146° (34), 141.5-142.5° (35); phenylhydrazone, m.p. 148.5-149.5° (35), p-nitrophenylhydrazone, or. ndls., m.p. 278-279° (34); semicarbazone, yel. ndls., m.p. 244-245° dec. (35)].

Č htd. at 100° with 1 mole aniline gives (16) (36) p-chlorobenzalaniline, pale yel. pl., from alc., m.p. 62° (16) (36); Č htd. with 1 mole p-toluidine gives (16) (36) p-chlorobenzal-p-toluidine, colorless ndls. from alc., m.p. 125° (16) (36).

[For conversion of \tilde{C} with MeMgX to p-chlorophenyl-methyl-carbinol and dehydration of latter to p-chlorostyrene see (46).]

- p-Chlorobenzaldoxime (anti form): cryst. from alc., m.p. 106-107° (6) (37). [From C + NH₂OH.HCl + Na₂CO₃ (6); the syn isomer has m.p. 142° (37), 140° (6), and on fusion is converted to anti isomer (6).]
- **p-Chlorobenzaldehyde phenylhydrazone:** lt. yel. cryst. from dil. alc., m.p. 127-127.5° (35), 126-128° (38). [For study of kinetics of formn. see (39).]
- p-Chlorobenzaldehyde p-nitrophenylhydrazone: dk. br. cryst. from alc., m.p. 216.5° u.c. (40), 224° (41), 218-220° (35).
- p-Chlorobenzaldehyde 2,4-dinitrophenylhydrazone: or. cryst., m.p. 270° (42), 265° (45), 264° cor. (43). [Use in detn. of C (43).]
- p-Chlorobenzaldehyde semicarbazone: tbls. from pyridine (10), ndls. from MeOH (44, m.p. 230° (10) (47), 232-233° (44).

3:0765 (1) Blanksma, Chem. Weekblad 6, 909 (1909). (2) Mayer, English, Ann. 417, 78-79 (1918). (3) Kahovec, Kohlrausch, Z. physik. Chem. B-38, 138 (1937). (4) Jackson, White, Ber. 11, 1043 (1887). (5) Jackson, White, Am. Chem. J. 3, 31-32 (1881). (6) Erdmann, Schwechten, Ann. 260, 63-65 (1890). (7) McEwen, Org. Syntheses, Coll. Vol. 2 (1st ed.), 133-135 (1943). (8) Erdmann, Kirchhoff, Ann. 247, 368 (1888). (9) Hoechster Farbwerke, Ger. 207,157; Cent. 1909, I 962. (10) Law, Perkin, J. Chem. Soc. 93, 1636 (1908).

(11) Lock, Bayer, Ber. 72, 1067 (1939). (12) Kaeswurm, Ber. 19, 742 (1886). (13) Böck, Lock, Schmidt, Monatsh. 64, 407 (1934). (14) Beilstein, Kuhlberg, Ann. 146, 328 (1868). (15) Beilstein, Kuhlberg, Ann. 147, 352-353 (1868). (16) von Walther, Ractze, J. prakt. Chem. (2) 65, 259-264 (1902). (17) van der Lee, Rec. trav. chrm. 45, 678-680 (1926). (18) Bodroux, Compt. rend. 138, 701 (1904); Bull. soc. chim. (3) 31, 585-588 (1904). (19) Stephen, J. Chem. Soc. 127, 1874 (1925). (20) Hinkel, Ayling, Benyon, J. Chem. Soc. 1936, 342.

(21) Ger. 281,212, Dec. 15, 1914; Cent. 1915, I 178; Ger. 403,489, Sept. 29, 1924; Cent. 1925, I 1369; Brit. 334,009, Sept. 18, 1930; Cent. 1930, II 3850. (22) van der Beek, Rec. trav. chim. 51, 411-413 (1932). (23) Carothers, Adams, J. Am. Chem. Soc. 46, 1681-1682 (1924). (24) Law, J. Chem. Soc. 99, 1114-1115 (1911). (25) Shankland, Gomberg, J. Am. Chem. Soc. 52, 4975 (1930). (26) Eitel, Lock, Monatsh. 72, 392-409 (1939). (27) Bailar, Barney, Miller, J. Am. Chem. Soc. 58, 2110-2111 (1936). (28) Molt, Rec. trav. chim. 56, 233-246 (1937). (29) Gomberg, Van Natta, J. Am. Chem. Soc. 51, 2241 (1929). (30) Wilstaedt, Ber. 64, 2693 (1931).

(31) K. C. Pandya, R. B. Pandya, Proc. Indian Acad. Sci. 14-A, 112-122 (1941); C.A. 36, 1599 (1942). (32) Erdmann, Ernst, Hugho, Ann. 294, 380 (1897). (33) Hodgdon, Smith, J. Soc. Chem. Ind. 49, T408-410 (1930). (34) Hodgson, Beard, J. Chem. Soc. 1927, 20. (35) van der Lee, Rec. trav. chim. 45, 278-281 (1926). (36) DeGaouck, LeFevre, J. Chem. Soc. 1938, 741-742. (37) Brady, McHugh, J. Chem. Soc. 125, 551 (1924). (38) Charlton, Earl, Kenner, Luciano, J. Chem. Soc. 1932, 40. (39) Bodforss, Z. physik. Chem. 109, 242 (1924). (40) Shoppee, J. Chem. Soc. 1931, 1232.

(41) Hodgson, Handley, J. Chem. Soc. 1928, 1886. (42) Blanksma, Wackers, Rec. trav. chim. 55, 658 (1936). (43) Eitel, Lock, Monatsh. 72, 389-390 (1939). (44) Henderson, Heilbron, J. Chem. Soc. 197, 1749 (1915). (45) Graymore, Davies, J. Chem. Soc. 1945, 294. (46) Ushakov, Matuzov, J. Gen. Chem. (U.S.S.R.) 14, 120-127 (1944); C.A. 39, 916 (1945). (47) Vogelsang, Rec. trav. chim. 62, 5-11 (1943); C.A. 39, 1394 (1945). (48) Schwenk, Papa, Whitman, Ginsburg, J. Org. Chem. 9, 1-8 (1944).

Ndls. (from pet. eth.).

[For prepn. from o-cresol (1:1400) by chlorination with SO₂Cl₂ see (1) (5).]

 \ddot{C} dislyd. in 5 pts. AcOH and treated with small excess of conc. HNO₃ (D=1.42) yields (3) 6-nitro-4-chloro-2-methylphenol [Beil. VI₁-(178)], yel. ndls., m.p. 107° (3), eas. sol. alc., C_6H_6 , less sol. AcOH, acetate, m.p. 88° (3).

 \bar{C} htd. with phthalic anhydride (1:0725) + NaCl.AlCl₃ at 150-200° for 2 hrs. yields (4) after decompn. with HCl, and repeated recrystn. from C_6H_6 , AcOH, xylene, 1-hydroxy-2-methyl-4-chloroanthraquinone, yel.-br. cryst., m.p. 177-179° (4).

 \bar{C} htd. with KOH + CH₃I yields (1) 4-chloro-2-methylanisole, volatile with steam, b.p. 212.6-214.6° cor. at 758 mm. (1).

① 4-Chloro-2-methylphenyl benzoate; from $\ddot{C} + BzCl + aq$. NaOH; lfts. from pet. eth., m.p. $71-72^{\circ}$ (1).

3:0780 (1) Peratoner, Condorelli, Gazz. chim. ital. **28**, I 211 (1898). (2) Klarmann, Shternov Gates, J. Am. Chem. Soc. **55**, 2585 (1933). (3) Zincke, Ann. **417**, 222-223 (1918) (4) Waldmann, Sellner, J. prakt. Chem. **150**, 152 (1938). (5) Sah, Anderson, J. Am. Chem. Soc. **63**, 3165 (1941).

Ndls. from alc. — Volatile with steam. — Sublimes.

[For prepn. of Č from naphthalenedisulfonic acid-1,6 [Beil. XI-213] (16), from K salt of 6-chloronaphthalenesulfonic acid-1 [Beil. XI-161] (4), from 6-chloronaphthalenesulfonyl chloride-1 [Beil. XI-165] (8), from 5-chloronaphthalenesulfonyl chloride-2 [Beil. XI-180] (7), from 5-nitronaphthalenesulfonyl chloride-2 [Beil. XI-180] (7), from 5-nitronaphthalenesulfonyl chloride-2 [Beil. XI-180] (7), from 5-nitronaphthalenesulfonyl chloride-2 [Beil. XI-214] (10) (3) (6) by htg. with PCl₅ as directed see indic. refs.; for prepn. of Č from 5-chloronaphthalenesulfonyl chloride-1 (both above) by htg. at 210-250° see (7); for prepn. of Č from 6-chloronaphthylamine-2 via diazotization and use of Cu₂Cl₂ reactn. see (2); from 6-sulfonaphthylamine-1 [Beil. XIV-758, XIV₁-(735)] or from 5-sulfonaphthylamine-2 [Beil. XIV-748, XIV₁-(733)] via treatment of corresp. diazonium salt with PCl₅ in PCl₅ see (11); from 1,6-diaminonaphthalene [Beil. XIII-204] by tetrazotization in HCl and htg. with Cu pdr. (24% yield (3)) (12) (13) see indic. refs.; for prepn. of Č from 1,6-dichloronaphthalenedisulfonic acid-4,8 [Beil. XI-213] or from 1,6-dichloronaphthalenedisulfonic acid-3,8 [Beil. XI-214] via hydrolysis of the -SO₃H group by htg. with dil. H₂SO₄ in s.t.

at 180-200° see (1); from 1,6-dichloronaphthalenesulfonyl chloride-3 [Beil. XI-182] (14) or from 1,6-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-163] (18) by htg. with conc. HCl in s.t. at 290° see indic. refs.; from sodium α -naphthalenesulfonate [Beil. XI-155, XI₁-(37)] with boilg. dil. HCl + KClO₃ (other products are also formed) see (15).]

[C on mononitration in AcOH with fumg. HNO₃ yields (19) (20) 1,6-dichloro-4-nitro-

naphthalene [Beil. V-556], m.p. 119° (19)]

[C on monosulfonation with mixt. of equal vols. conc. + fumg. H₂SO₄ (17) or with ClSO₃H in CS₂ (18) gives 1,6-dichloronaphthalenesulfonic acid-4 [Beil. XI-163] (corresp. sulfonyl chloride, m.p. 151° (17) (18), corresp. sulfonamide, m.p. 216° (18)).]

[\bar{C} on oxidn, with dil. HNO₃ in s.t. at 150° yields (19) a mixt. of 3-chlorophthalic acid (3:4820) and 4-chlorophthalic acid (3:4820) together with their nitro derivs.]

3:0810 (1) Friedländer, Kielbasinski, Ber. 29, 1980-1982 (1896). (2) Schroeter, Ber. 63, 1318 (1930). (3) Hampson, Weissberger, J. Chem. Soc. 1936, 394. (4) Forsling, Ber. 20, 2105 (1887).
 5) Erdmann, Kirchhoff, Ann. 247, 379 (1888). (6) Ferrero, Bolliger, Helv. Chim. Acta 11, 1146-1150 (1928). (7) Armstrong, Wynne, Chem. News 71, 255 (1895). (8) Sindall, Chem. News 60, 58 (1889). (9) Cleve, Bull. soc. chim. (2) 26, 448 (1876). (10) Armstrong, Wynne, Chem. News 62, 164 (1890).

(11) Érdmann, Ann. 275, 214-215, 256, 279 (1893). (12) Friedlander, Szymanski, Ber. 25, 2081 (1892). (13) Kehrmann, Matis, Ber. 31, 2419 (1898). (14) Armstrong, Wynne, Chem. News 76, 69 (1897). (15) Kozlov, Talybov, J. Gen. Chem. (U.S.S.R.) 9, 1827-1833 (1939); C.A. 34, 4067 (1940). (16) Zil'berman, Rashevaskaya, Martyntsova, J. Applied Chem. (U.S.S.R.) 9, 1832-1840 (1936); Cent. 1937, I 4787, C.A. 31, 2597 (1937). (17) Cleve, Ber. 24, 3477-3478 (1891). (18) Armstrong, Wynne, Chem. News 61, 274-275 (1890). (19) Cleve, Bull. soc. chim. (2) 23, 499 (1878). (20) Armstrong, Wynne, Chem. News 61, 94 (1890).

3:0825 2,4-DICHLOROBENZOPHENONE C₁₃H₈OCl₂ Beil. VII - 420 (2,4-Dichlorophenyl phenyl ketone) C₁₀Cl VII₁—

M.P. 48-49° (1) (2) 52° (3)

Cryst. (from alc. (1)).

[For prepn. from m-dichlorobenzene (3:5960) + BzCl (3:6240) + AlCl₃ at 110-140° see (3) (2); for prepn. (67% yield (1)) from 2,4-dichlorobenzohydrol by oxidn. with CrO₃ in AcOH see (1).]

 \bar{C} fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (1) m-dichlorobenzene (3:5960) and BzOH (1:0715) (92% yield (1)).

[C does not give a smooth reaction with NaOMe (2).]

3:0825 (1) Lock, Rödiger, Ber. 72, 868-869 (1939). (2) van de Lande, Rec. trav. chim. 51, 99, 105 (1932). (3) Böeseken, Rec. trav. chim. 27, 15 (1908).

3:0840 2,7-DICHLORO-2,7-DIMETHYLOCTANE
$$C_{10}H_{20}Cl_2$$
 Beil. I — Cl Cl I_{1-} (66) I_{2-} CH_3 — C — CH_2 . CH_2 . CH_2 . CH_3 — C — CH_3 CH_3

Cryst. (from abs. alc.) with agreeable musk-like odor.

[For prepn. of C from 2,7-dimethyloctanediol-2,7 [Beil. I₁-(257)] with conc. HCl in the cold or with HCl gas in toluene see (1).]

3:0840 (1) Bouvet, Bull. soc. chim. (4) 17, 204 (1915).

Colorless ndls.

[For prepn. of Č from anhydrous chloral (3:5210) with 1 mole n-butyl alcohol (1:6180) (1) (2), or from chloral hydrate (3:1270) under reflux with n-BuOH (yields: 54% in 45 min., 28% in 60 min. (3)) or with tri-n-butyl orthoformate, see indic. refs.; for study of formn. of Č from chloral ethylalcoholate (3:0860) or from chloral n-propyl-hemiacetal by reflux with n-BuOH for 45 min. (yield 40-50%) see (3).]

[\bar{C} with AcCl gives (78% yield (1)) corresp. acetate, b.p. 129–131° at 20 mm. (1).] [For behavior of \bar{C} with diazomethane see (4).]

3:0843 (1) Fourneau, Florence, Bull. soc. chim. (4) 47, 352 (1930). (2) Kuntze, Arch. Pharm. 246, 98 (1908). (3) Post, J. Org. Chem. 6, 832-833 (1941). (4) Meerwein, Bersin, Burneleit, Ber. 62, 1009 (1929).

M.P. 49-50° (1)

[For form. of \bar{C} from 3,5-dimethylphenol (sym.-m-xylenol) (1:1455) with SO_2Cl_2 in CHCl₃ (as by-product of the principal isomer 4-chloro-3,5-dimethylphenol (3:3505)) see (1).]

- --- 2-Chloro-3,5-dimethylphenyl acetate: unreported.
- ---- 2-Chloro-3,5-dimethylphenyl benzoate: unreported.
- 3:0844 (1) Lesser, Gad, Ber. 56, 974 (1923).

3: 0846 1,1,1-TRICHLOROPROPANOL-2
$$C_3H_5OCl_3$$
 Beil. I - 365 $(\beta,\beta,\beta$ -Trichloroisopropyl CH_3 — CH — CCl_3 I_1 -(185) alcohol; "Isopral") OH 12-(385)

Hexag. cryst. from aq. (7); for crystallographic data see (2). — Spar. sol. aq., eas. sol. org. solvents (for data see (7)). — \bar{C} has high vapor press. (for measurement see (2)) and sublimes even at ord. temp. (for study of sublimation of \bar{C} by various methods see (5)).

[For prepn. of $\tilde{\mathbb{C}}$ from 1,1,1-trichloropropanone-2 (3:5620) by reduction with fused Al(OEt)₃ in abs. alc. under H₂ or N₂ (8) or with AlEt₃ etherate in ether (3) (yields: 67% (8), 65% (3)) see indic. refs.; for prepn. of $\tilde{\mathbb{C}}$ from chloral (3:5210) with CH₃MgBr (9) (19) (2) cf. (4) or MeMgI (2) cf. (4) (yield: 40% (9) (2)) see indic. refs. (note that by this method the normal addn. of RMgX leading to $\tilde{\mathbb{C}}$ is accompanied by reduction leading to 2,2,2-trichloroethanol (3:5775) and the relative proportion of these two reactions is profoundly influenced by the pres. of metal salts (9)); for prepn. of $\tilde{\mathbb{C}}$ from chloral (3:5210) with ZnMe₂ see (6).]

Č is used as hypnotic pharmaceutical under the trade name "Isopral" (10), for use as seed disinfectant see (11); for study of disinfectant power and toxicity see (12); for comparative study of narcotic action see (13). — For study of tests for C see (7) (14).

 \bar{C} on reduction in aq. AcOH + Zn dust in cold yields (15) 1,1-dichloropropene-1 (3:5120). \bar{C} on oxidn. with fumg. HNO₃ under reflux for 5 hrs. gives (2) trichloroacetic acid (3:1150); use of $K_2CR_2O_7$ + H_2SO_4 gives only insignificant yields (2) while less strong HNO₃ even after 4 hrs. at 100° has only slight action (2).

 \bar{C} with P_2O_5 on htg. loses H_2O giving (84% yield (19)) (2) 1,1,1-trichloropropene-2 (3:5345), b.p. 114-115° at 757 mm. (2).

[\bar{C} with HNO₃/H₂SO₄ mixt. yields (2) β,β,β -trichloroisopropyl nitrate, oil, $D_{-}^{13} = 1.499$, $n_{\bar{D}} = 1.47892$, but decompg. on htg. — \bar{C} with PCl₃ or PCl₅ yields (2) (1) various partial ester/acid chloride derivs. of phosphorous or phosphoric acids. — \bar{C} with SOCl₂ evolves HCl + SO₂ and also yields (2) a liq. presumably β,β,β -trichloroisopropyl chlorosulfonate.]

 \tilde{C} with aq. or alc. NaOH or conc. aq. Na₂CO₃ gives on htg. (16) (17) mainly acetaldehyde (1:0100) and lactic acid (1:0400), also accompanied by formic acid (1:1005) and carbon monoxide; for use of this reactn. in detection of \tilde{C} see (14). — \tilde{C} with EtOH/NaOEt on htg. gives (15) ethyl α -ethoxypropionate [Beil. III-280, III₁-(109), III₂-(206)], b.p. 155° cor. at 760 mm., $D_4^{20} = 0.9446$, $n_D^{20} = 1.40125$.

[Č with AcCl yields (2) β,β,β -trichloroisopropyl acetate, b.p. 180–181° cor. 766 mm., m.p. + 8°, $D_{13}^{13} = 1.353$, $n_{\overline{D}} = 1.46017$ (2).]

— $\beta_{\gamma}\beta_{\gamma}\beta_{\gamma}$ -Trichloroisopropyl carbamate: cryst. from C_6H_6 , m.p. 125° (18). Prepd. indirectly from $\beta_{\gamma}\beta_{\gamma}\beta_{\gamma}$ -trichloroisopropoxy MgBr with phosgene in toluene, followed by treatment with NH₃ (35% yield (18)).]

3:0846 (1) Henry, Compt. rend. 138, 205 (1904). (2) Vitoria, Rec. trav. chim. 24, 265-287 (1905); Bull. acad. roy. Belg. 1904, 1087-1123; Cent. 1905, I 344-345. (3) Meerwein, Hinz, Majert, Söhnke, J. prakt. Chem. (2) 147, 236-237 (1936). (4) Bayer and Co., Ger. 151,545, May 20, 1904; Cent. 1904, I 1586. (5) Eder, Haas, Mikrochemie (Emich Festschrift), 1930, 59, 67, 78, 80. (6) Garzarolli-Thurnlackh, Ann. 210, 77-79 (1881). (7) Genot, J. pharm. Belg. 12, 735-736 (1930); Cent. 1930, II 3062. (8) Meerwein, Schmidt, Ann. 444, 234 (1925). (9) Kharasch, Kleiger, Martin, Mayo, J. Am. Chem. Soc. 63, 2306-2307 (1941). (10) Cent. 1903, II 899.

(11) von Leuthold, Austrian 145,527, May 11, 1936; Cent. 1936, II 1052. (12) Howard, Stimpert, J. Am. Pharm. Assoc. 14, 487-489 (1925); Cent. 1925, II 1696; C.A. 19, 2864 (1925). (13) Lendle, Arch. expll. Path. Pharmakol. 125, 287-300 (1927); Cent. 1928, I 715; C.A. 22, 639 (1928). (14) Serantes, Anales soc. quim. argentina 12, 199-200 (1924); C.A. 19, 704 (1925). (15) Wohl, Roth, Ber. 49, 215-216 (1907). (16) Hebert, Bull. soc. chim. (4) 27, 49 (1920). (17) Mossler, Monatsh. 29, 583-590 (1908). (18) Yoder, J. Am. Chem. Soc. 45, 479 (1923).

(19) Kharasch, Rossin, Fields, J. Am. Chem. Soc. 63, 2559-2560 (1941).

110

3:0855
$$d_1l-\alpha_1\beta$$
-DICHLOROPROPIONIC ACID $C_3H_4O_2Cl_2$ Beil.II - 252 CH_2 -CH-COOH II_1 -(111) II_2 -

[For prepn. from methyl α,β -dichloropropionate (3:9103) by boilg. with 20% HCl (65% yield) see (3); from 2,3-dichloropropanol-1 ("β-dichlorohydrin") (3:6060) by oxidn. with HNO₃ see (1) (6) (7) (2) (5); from α,β -dichloroacrolein by oxidn. with HNO₃ see (7); from a-chloropropionic acid (3:6125) with Cl₂ at 45° see (8); for forma. of C from α -chloroacrylic acid (3:1445) (6) (9) or from α -chloro- β -hydroxypropionic acid (α -chlorohydracrylic acid) [Beil. III-298] (10), or α,β -dihydroxypropionic acid (glyceric acid) (11) by htg. with fumg. HCl in s.t. at 100°, see indic. refs.]

C with ag. or alc. readily loses HCl yielding (12) (6) (9) \(\alpha\)-chloroacrylic acid (3:1445), m.p. 65°.

Č in MeOH treated as directed (13) with activated Zn gives (72% yield) acrylic acid (1:1020), b.p. 140°.

[\bar{C} with SOCl₂ gives (15) α,β -dichloropropionyl chloride (3:9032).]

C htd. with Ag₂CO₃ yields (5) α-chloro-β-hydroxypropionic acid (α-chlorohydracrylic acid).

- Methyl α,β -dichloropropionate: b.p. 72-75° at 21 mm. (see 3:9103).
- Ethyl $\alpha_0\beta$ -dichloropropionate: b.p. 183-184° (see 3:6090). [For the sec-butyl, β -chloroethyl, and cyclohexyl esters of \bar{C} see (3); for glycol and other esters see (14).
 - --- α,β-Dichloropropionamide: unreported.
 - --- α,β-Dichloropropionanilide: unreported.
 - ---- α,β-Dichloropropion-p-toluidide: unreported.

3:0855 (1) Henry, Bcr. 7, 414 (1874). (2) Bockemuller, Hoffmann, Ann. 519, 190 (1935). (3) Marvel, Dec, Cooke, Cowan, J. Am. Chem. Soc. 62, 3495-3498 (1940). (4) Simpson, J. Am. Chem. Soc. 40, 676, 679 (1918). (5) Koelsch, J. Am. Chem. Soc. 52, 3365 (1930). (6) Werigo, Melikov, Ber. 10, 1499-1500 (1877). (7) Yarnall, Wallis, J. Org. Chem. 4, 287 (1939). (8) Röhm & Haas Co., Ger. 579,654, June 29, 1931, Cent. 1933, II 1587. (9) Otto, Beckurts, Ber. 18, 244 (1885). (10) Melikov, Ber. 13, 274 (1880). (11) Werigo, Melikov, Ber. 12, 178 (1879). (12) Werigo, Werner, Ann. 170, 168 (1873).

(13) Röhm & Haas Co., Ger. 575,423, Apr. 27, 1933; Cent. 1933, II 133. (14) Pollack (to Pittsburgh Plate Glass Co.), U.S. 2,257,021, Sept. 23, 1941; C.A. 36, 95-96 (1942). (15) Leimu.

Ber. 70, 1046, 1050 (1937).

3:0860 CHLORAL ETHYLALCOHOLATE C ₄ H (Chloral alcoholate; tri- chloroacetaldehyde (mono)ethylacetal) Cl ₃ C.CH—OC ₂ H ₅ OH							Beil. I - 621 I ₁ -(330) I ₂ -(681)
-	0°	(1)] (2)(3)	B.P.	115-117° 116.8°	at 771 mm.	(1) (5)	
	7.5° 6.6°	(4) (5)		115-116° 111.0	at 741.4 mm.	(9) . (4)	
4. 4.	6° 5.2° (5°–46.5° 0°	(6) (7) (10) (8) (9)					

[See also chloral (3:5210) and chloral hydrate (3:1270).]

PREPARATION

From chloral. [For prepn. of \bar{C} from chloral (3:5210) with EtOH (1:6130) (yields: 100% (11), 71.3% with 95% EtOH refluxed 2 hrs. (4) (9) (12)) see indic. refs.; for influence of solvents see (13) (14); for form. of \bar{C} from chloral (3:5210) + AcH + Al(OEt)₃ see (8).]

From chloral hydrate. [For prepn. of \bar{C} from chloral hydrate (3:1270) with EtOH (1:6130) (yield: 75% in 60 min., 38% in 24 hrs. reflux (4)), with triethyl orthoformate (1:3241) (25% yield in 105 min. reflux (4)), or with tetraethyl orthosilicate (4% yield in 4 hrs. reflux (4)) see indic. refs.]

From ethyl alcohol. [For formn. of \ddot{C} as end prod. of reaction of ethyl alcohol (1:6130) with Cl_2 see (15).]

PHYSICAL PROFERTIES

 \tilde{C} is less sol. in aq. than chloral hydrate (3:1270) (6) (7). — [For study of toxicity of \tilde{C} as compared with chloral hydrate (3:1270) see (29).]

CHEMICAL BEHAVIOR

Dissociation. \tilde{C} on distillation (7) or in some solns, in org. solvents cf. (17) (2) (18) is partially dissociated into chloral (3:5210) and EtOH (1:6130).

BEHAVIOR WITH INORGANIC REACTANTS

With H_2SO_4 . \bar{C} with cold cone. H_2SO_4 yields (1) chloral (3:5210) (or its polymerization products) and EtHSO₄.

With aq. alkali. \bar{C} with aq. alkali gives (6) CHCl₃ (3:5050) + salts of formic acid (1:1005).

With chlorine. [\bar{C} with Cl₂ at 80° gives (19) trichloroacetaldehyde diethylacetal (3:6317).] With PCl₅. [\bar{C} with PCl₅ in ether below 20° (20) (4) cf. (21) (22) gives (yields: 55-74% (20), 25-33% (11)) α,β,β,β -tetrachloroethyl ethyl ether [Beil. I-623, I₂-(681)], b.p. 189.7° at 758.7 mm. (21), 189.4° at 749.1 mm. cor. (20), 184° at 738 mm. (4), 79° at 16 mm. (20); $D_4^{18} = 1.4225$ (20).]

BEHAVIOR WITH ORGANIC REACTANTS

With other alcohols. [Č with other alcohols may undergo an exchange of alkyl radicals; for studies of such interchange see (4) (2).]

With aic. NaOEt. [C with EtOH/NaOEt yields (23) CHCl₃ (3:5050) + ethyl formate (1:3000).]

With alc. KCN. [C with EtOH/KCN gives within 1 min. (88% yield (24)) ethyl dichloroacetate (3:5850): cf. behavior of chloral (3:5210) with KCN in various alcohols.]

With acid chlorides. [C with AcCl (3:7065) gives (25) the corresp. acetate [Beil. I-153], b.p. 198°. — C with isovaleryl chloride (3:7560) gives (41% yield (26)) the corresp. isovalerate, b.p. 143° at 20 mm. (26).]

With diazomethane. [\bar{C} with CH₂N₂ in EtOH soln. at 0° gives (27) trichloroacetaldehyde ethyl-methyl-acetal [Beil. I-621, I₂-(681)], b.p. 193.4° cor. (28), 78-80° at 13 mm. (27) accompanied by 3,3,3-trichloro-1,2-epoxypropane (3:5760).]

- **Behavior on heating.** Note that \bar{C} on htg. gives off inflammable vapor (EtOH) (dif. from chloral hydrate (3:1270) whose initial ignition cannot be maintained).
- P Behavior with conc. HNO₃. C reacts violently on warming with conc. HNO₃ (dif.) from chloral hydrate (3:1270) which is almost unaffected).
- P Iodoform test. C with aq. alk. + I₂/KI soln. on warming gives iodoform, m.p. 119° accompanied of course by CHCl₃ (3:5050) (dif. from chloral hydrate (3:1270)).

3:0860 (1) Jacobsen, Ann. 157, 244-245 (1871). (2) Willcox, Brunel, J. Am. Chem. Soc. 38, 1821-1841 (1916). (3) Kuntze, Arch. Pharm. 246, 98 (1908). (4) Post, J. Org. Chem. 6, 830-835 (1941). (5) Leopold, Z. physik. Chem. 66, 359-380 (1909). (6) Trillat, Bull. soc. chim. (3) 17, 233-234 (1897). (7) Lieben, Ber. 3, 909-910 (1870). (8) Nagai, Biochem. Z. 152, 268 (1924). (9) Martius, Mendelssohn-Bartholdy, Ber. 3, 444 (1870). (10) Kurnakow, Efrema, Z. physik. Chem. 85, 411-418 (1913).

(11) Magnani, McElvain, J. Am. Chem. Soc. 66, 2212 (1938). (12) Personne, Compt. rend. 69, 1363 (1869). (13) Grabowsky, Herold, Z. physik. Chem. B-28, 290-302 (1935). (14) Buthmann, Z. physik. Chem. B-23, 100-104 (1933). (15) Chattaway, Backeberg, J. Chem. Soc. 125, 1097-1101 (1924). (16) Bruner, Cent. 1902, I 978. (17) Beckmann, Z. physik. Chem. 2, 724-728 (1888). (18) Willcox, Brunel, J. Am. Chem. Soc. 38, 2533-2535 (1916). (19) Byasson, Bull. soc. chim. (2) 32, 304 (1879); Compt. rend. 87, 26 (1878). (20) Neher, Foster, J. Am. Chem. Soc. 31, 410-412 (1909).

(21) Paterno, Pisati, Gazz. chim. ital. 2, 333-338 (1872). (22) Henry, Ber. 4, 101, 435-438 (1871). (23) Kekulé, Ann. 119, 188-189 (1861). (24) Chattaway, Irving, J. Chem. Soc. 1929, 1042. (25) Meyer, Dulk, Ann. 171, 69-72 (1874). (26) Fourneau, Florence, Bull. soc. chim. (4) 47, 353 (1930). (27) Meerwein, Bersin, Burneleit, Bcr. 62, 1002, 1007-1009 (1929). (28) Magnanni, Gazz. chim. ital. 16, 331 (1886). (29) Adams, J. Pharmacol. 78, 340-345 (1943); C.A. 37, 6035 (1943).

3:0870 1,2,3,4-TETRACHLOROBUTADIENE-1,3 C₄H₂Cl₄ Beil. S.N. 12 (Solid stereoisomer) HC=C-C=CH

M.P. 50° (1)

[See also the liquid stereoisomer (3:6150).]

[For isolation of \bar{C} from the high-boilg, fractn. resulting in the preparation of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see (1).]

Č adds Cl₂ (although much more slowly than its liquid stereoisomer) yielding 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), m.p. 80° (1). [This product with Zn/Cu couple in hot alc. regenerates C̄, but in alc. with Ca(OH)₂ or with alk. at room temp. gives the liquid stereoisomer (3:9046) (1).]

Č in CHCl₃ treated with Br₂ gives (100% yield (1)) 1,2-dibromo-1,2,3,4-tetrachloro-butene-2, m.p. 105° (1). [This prod. with Zn/Cu couple in hot alc. regenerates Č (1).]

3:0870 (1) Müller, Hüther, Ber. 64, 589-600 (1931); C.A. 25, 3956 (1931).

α-CHLORO-DIPHENYLACETYL CHLORIDE C14H10OCl2 3:0885 Beil. IX - 675 (Diphenyl-chloro-acetyl chloride) IX₁-(283)

Cryst. from lgr.

[For prepn. of \bar{C} from benzilic acid (α -hydroxy-diphenyl-acetic acid) (1:0770) with 2 moles PCl₅ at 120-130° (2), at 100° (8) (68% yield (9)), or with excess PCl₅ in C₆H₆ at room temp. (7) see indic. refs. (Note that benzilic acid dislvd. in undil. SOCl2 yields (4) benzophenone (1:5150), that benzilic acid treated with 3 moles SOCl₂ in CCl₄ for several days at room temp. ppts. (5) diphenylchloroacetic acid (3:3585), m.p. 118-119° dec., and that benzilic acid in CCl4 with 6 moles SOCl2 refluxed for several days yields (5) on concn. of the soln. diphenyl-chloro-acetic anhydride [Beil. IX₁-(228)], m.p. 129° (5).) - For formn, of C from diphenylketene [Beil. VII-471, VII₁-(254)] with SOCl₂ or SO₂Cl₂ by htg. at 100° in s.t. in absence of air (1), or from diphenyldiazomethane [Beil. VII-418, VII₁-(226)] with liq. phosgene in pet. ether in s.t. (92% yield), see (6).]

[For abnormal reactn. of \bar{C} with C_6H_5MgBr see (9) (10); for reactn. of \bar{C} with Zn filings in dry ether yielding diphenylketene (above) see (11); for reactn. of C with phenylhydroxylamine in ether giving quant, yield of anhydro-[N-phenyl-benzilhydroxamic acid] [Beil. XXVII₁-(290), cryst. from MeOH, m.p. 72-73°, see (12).]

 \bar{C} in ether treated with gaseous NH₃ (2) (13) yields α -chloro-diphenylacetamide, m.p. 115° (2), 111-113° (13). [This product on boilg, with aq. yields (2) benzilamide, m.p. 154° (2).]

C dislyd. in dry ether and treated with 2 moles aniline in dry ether ppts. aniline hydrochloride and from the filtrate addn. of pet. ether ppts. (3) a-chloro-diphenyl-acet-anilide, m.p. 88° (3); this prod. on htg. with more aniline or C warmed with 4 moles aniline yields (3) a-anilido-diphenyl-acet-anilide, ndls. from alc., m.p. 181-182° (3). [Both the first prod. (on treatment with Na₂CO₃) and the latter prod. (on HCl hydrolysis) yield (3) benzilic acid anilide, m.p. 175° (3).]

3:0885 (1) Staudinger, Göhring, Scholler, Ber. 47, 47-48 (1914). (2) Bickel, Ber. 22, 1538-1539 (1889). (3) Klinger, Ann. 389, 255-264 (1912). (4) Meyer, Monatsh. 22, 793 (1901). (5) Stollf, Ber. 43, 2471-2473 (1910). (6) Staudinger, Anthes, Pfenninger, Ber. 49, 1939-1940 (1916). (7) Setlur, Nadkaring, Proc. Indian Acad. Sci. 12-A, 266-269 (1940); C.A. 35, 1398 (1941). (8) Staudinger, Ann. 356, 72-75 (1907). (9) McKenzie, Boyle, J. Chem. Soc. 119, 1137-1139 (1921). (10) Boyle, McKenzie, Mitchell, Ber. 70, 2153-2160 (1937). (11) Staudinger, Ber. 38, 1735-1736 (1905). (12) Staudinger, Jelangin, Ber. 44, 371-373 (1911). (13) Staiptonff, Ber. 41, 3502 (1908).

(1911). (13) Steinkopff, Ber. 41, 3593 (1908).

3: 0900 β-NAPHTHOYL CHLORIDE

B.P. 304-306° (2) M.P. 51° (1) 43° (2)

Cryst. pdr. from C₆H₆ + lt. pet. (1). - Sol. ether, CHCl₃, C₆H₆; insol. aq.

[For prepn. of \tilde{C} from β -naphthoic acid (1:0800) with PCl₅ (2) (3) or with SOCl₂ (100% yield (4)) (1) (5) see indic. refs.]

 \bar{C} with ter bases + $K_2S_2O_5$ (6) or \bar{C} with calcium β -naphthoate at 150-160° (7) yields β -naphthoic acid anhydride, m.p. 134° (7) [cf. α -naphthoyl chloride (3:6930)].

[\bar{C} with AlCl₃ and hydrocarbons yields corresp. β -naphthyl ketones: e.g., with biphenyl (8), with β -methylnaphthalene (9), with 2,3- (10), 2,6- (11), and 2,7- (12) dimethylnaphthalenes, or with anisole (13) see indic. refs.; \bar{C} with RMgX cpds. also yields β -naphthyl ketones; e.g., see (14).]

[For use of C in prepn. of vat dyes from mono- and diamino-anthraquinones see (15).]

 \tilde{C} with hydrazine hydrate yields (5) both β -naphthoylhydrazine (β -naphthoylhydrazide), cryst. from alc., m.p. 147.5° (5), and N,N'-bis-(β -naphthoyl)hydrazine, cryst. from AcOH, m.p. 241° (5).

 $\bar{\mathbf{C}}$ on hydrolysis yields β -naphthoic acid (1:0800), m.p. 184°. — For the amide, anilide, p-toluidide, and other derivs. corresp. to $\bar{\mathbf{C}}$ see β -naphthoic acid (1:0800); in addition see below.

⑤ β -Naphthoic β -naphthalide: ndls. from hot CHCl₃, m.p. 238° (4). [From $\tilde{C} + \beta$ -naphthylamine in C_6H_6 (4).]

3:0900 (1) Bell, J. Chem. Soc. 1930, 1985. (2) Vieth, Ann. 180, 317-319 (1875). (3) Raiford, Lankelma, J. Am. Chem. Soc. 47, 1118 (1925). (4) Beckmann, Liesche, Correns, Ber. 56, 352 (1923). (5) Goldstein, Cornamusaz, Helv. Chim. Acta 15, 941 (1932). (6) Gasopoulos, Praktika 6, 347-353 (1931); Cent. 1932, I 3172; C.A. 27, 3204 (1933). (7) Hausamann, Ber. 9, 1515 (1876). (8) de Ceuster, Cent. 1932, II 1296. (9) Clar, Ber. 62, 356-357 (1929). (10) Cook, J. Chem. Soc. 1933, 1596.

(11) Fieser, Dietz, Ber. **62**, 1831 (1929). (12) Cook, J. Chem. Soc. **1931**, 492. (13) Migita, Bull. Chem. Soc. Japan **7**, 379 (1932). (14) Fieser, Seligman, J. Am. Chem. Soc. **58**, 478-480 (1936). (15) Meyer, Hopff (to I.G.), Ger. 432,579, Aug. 7, 1926; Cent. **1926**, II 2231.

3: 0915 1,2,3,5-TETRACHLOROBENZENE

$$\begin{array}{cccc} & \text{Cl} & \text{C}_6\text{H}_2\text{Cl}_4 & \text{Beil. V - 204} \\ & & \text{V}_1\text{-(113)} \\ & & \text{V}_2\text{-(157)} \end{array}$$

Ndls. from alc. — Spar. sol. cold alc.; eas. sol. C_6H_6 , very eas. sol. CS_2 or lgr. — Volatile with steam.

[For prepn. of \bar{C} from 2,4,6-trichloroaniline [Beil. XII-627, XII₁-(312)] via diazotization and use of Cu₂Cl₂ reactn. (2) (6) (9) or otherwise (5) (yield: 64% (6), 61% (9), 55.8% (2)) see indic. refs.; from 2,3,4,6-tetrachloroaniline [Beil. XII-630, XII₁-(313)] by replacement of $-NH_2$ by -H (3); from 2,6-dichloro-p-phenylenediamine [Beil. XIII-118, XIII₁-(37)] via tetrazotization and warming with Cu₂Cl₂ see (7); for formn. of \bar{C} from p-dichlorobenzene (3:0980) with AlCl₃ + S₂Cl₂ in SO₂Cl₂ at 40° (10% pure \bar{C} + 67% 1,2,4,5-tetrachlorobenzene (3:4115)) see (1); from 2,4,6-trichlorophenol (3:1673) with PCl₃ + PCl₅ in s.t. at 200–300° see Beil. V-204; from 3,5-dibromo-4-chlorobenzenesulfonyl chloride (10) or 2,5-dichlorobenzene-1,3-bis-(sulfonyl chloride) (8) or chlorobenzene-2,4,6-tris-(sulfonyl chloride) (4) on htg. in s.t. with PCl₅ see indic. refs.; for formn. of \bar{C} from 1,3,5-trichloro-

benzene (3:1400) with Cl₂ in pres. of Al/Hg see (11); from benzene (12), chlorobenzene (13), or diphenyl sulfone (14) with Cl₂ followed by treatment with alc. KOH see indic. refs.] [For behavior of \tilde{C} with liq. Cl₂ yielding addn. products see (15).]

[For behavior of C with NaOMe see (2) (16).]

 \bar{C} on mononitration, e.g., by boilg, for $\frac{1}{2}$ hr. with 3 pts. HNO₃ (D=1.52) as directed (17), gives 96.7% yield (17) 1,2,3,5-tetrachloro-4-nitrobenzene, cryst. from spontaneous evapn. of alc. soln., m.p. 40-41° (17) (the m p. of 21-22° previously reported (5) was on impure material).

 \bar{C} on dinitration, e.g., by boilg. with a mixt. of 10 pts. fumg. HNO₃ (D=1.52) + 4 pts. conc. H₂SO₄ for 1 hr. and then pouring into aq. (17), gives (100% yield (17)) (9) 1,2,3,5-tetrachloro-4,6-dinitrobenzene [Beil. V-266], pl. from 90% AcOH, m.p. 162° (9), 161-162° (17). (This prod. on htg. with aniline yields (9) (18) 2-chloro-1,3,5-trianilino-4,6-dinitrobenzene, crimson pl., m.p. 179° (9), 179-180° (18).)

3:0915 (1) Silberrad, J. Chem. Soc. 121, 1020 (1922). (2) Holleman, Rec. trav. chim. 39, 739, 749 (1920). (3) Willgerodt, Wilcke, Ber. 43, 2752 (1910). (4) Olivier, Rec. trav. chim. 39, 197 (1920). (5) Beilstein, Kurbatow, Ann. 192 237-238 (1878). (6) Dadieu, Pongratz, Kohlrausch, Monatsh. 61, 433-434 (1932). (7) Schoutissen, J. Am. Chem. Soc. 55, 4539 (1933). (8) Gebauer-Fulnegg, Figdor, Monatsh. 48, 633 634 (1927). (9) Jackson, Carlton, Ber. 35, 3855 (1902); Am. Chem. J. 31, 365-368 (1904). (10) Anschutz, Molineus, Ann. 415, 62 (1918). (11) Cohen, Hartley, J. Chem. Soc. 87, 1366 (1905). (12) Istrati, Ann. chim. (6) 6, 380, 384, 391 (1885). (13) Jungfleisch, Ann. chim. (4) 15, 299, 302 (1868). (14) Otto, Ostrop, Ann. 141, 105 (1867). (15) van der Linden, Rec. trav. chim. 55, 421-430 (1936). (16) de Crauw, Rec. trav. chim. 56, 787 (1931). (17) Berckmans, Holleman, Rec. trav. chim. 44, 852-856 (1925). (18) Qvist, Salo, Acta Acad. Aboensis Math. et Phys. 8, No. 4 (1934); Cent. 1934, II 595; Cent. 1936, 1540.

3: 0925
$$\alpha,\beta,\beta$$
-TRICHLORO- n -BUTYRIC ACID Cl C₄H₅O₂Cl₃ Beil. II -281 CH₃-C-CH-COOH II₁- II₂- Cl Cl Cl

M.P. 51.5-52° (1)

Tbls. from lgr. — Spar. sol. aq., eas. sol. alc., ether, C₆H₆, CHCl₃, CS₂.

[For prepn. of \bar{C} from either β -chlorocrotonic acid (3:2625) or β -chloroisocrotonic acid (3:1300) in CS_2 soln. with CI_2 stood several days in the dark see (1).]

[\bar{C} in aq. with granulated Zn stood for 6 weeks, then acidified, yields (1) mainly β -chloro-isocrotonic acid (3:1300) accompanied by some β -chlorocrotonic acid (3:2625); note that former is separated from latter by its greater volatility with steam.]

C with aq. Na₂CO₃ soln. on boilg. loses both HCl and CO₂ yielding the higher-boilg. (1) 1,2-dichloropropene-1 (3:5150).

 \bar{C} with alc. KOH (2 moles) loses HCl yielding (1) mainly α,β -dichloroisocrotonic acid [Beil. II-418], m.p. 75.5°, accompanied by a little α,β -dichlorocrotonic acid [Beil. II-418], m.p. 92°; note that these are separated by the greater soly. of the former in lgr. (1).

The acid chloride corresp. to C is unreported.

- Methyl α,β,β -trichloro-n-butyrate: unreported.
- Ethyl α, β, β -trichloro-n-butyrate: unreported.
- ---- α,β,β-Trichloro-n-butyramide: unreported.
- α,β,β-Trichloro-n-butyranilide: unreported.
 α,β,β-Trichloro-n-butyr-α-naphthalide: unreported.

3:0925 (1) Szenic, Taggesell, Ber. 28, 2665-2672 (1895).

M.P. 52° (1)

Cryst. from lt. pet. — Volatile with steam.

[For prepn. of \bar{C} from 6-chloro-2-amino-3,4-dimethylphenol (5-chloro-3-amino-0-4-xylenol) (1) via diazotization and reaction with Cu_2Cl_2 (yield not stated) see (1); from 2,6-dichloro-3,4-dimethylaniline (3,5-dichloro-0-4-xylidine) (2) via diazotization and hydrolysis (yield not stated) see (1).]

The nitration of \bar{C} has not been reported, and the expected 5-nitro-2,6-dichloro-3,4-dimethylphenol is unknown.

2,6-Dichloro-3,4-dimethylphenyl acetate: unreported.

D 2.6-Dichloro-3,4-dimethylphenyl benzoate: m.p. 89° (1).

3:6935 (1) Hinkel, Ayling, Bevan, J. Chem. Soc. 1928, 2532. (2) Hinkel, Ayling, Bevan, J. Chem. Soc. 1928, 1878.

M.P. 52-53° (1) B.P. 80-81° at 40 mm. (1)

Soft waxy solid with characteristic alkyl halide odor; on long stdg. the opaque crystn. structure disappears and \bar{C} becomes transparent (1).

[For prepn. of \bar{C} from 2,2,3,3-tetramethylbutane (hexamethylethane) (1:7090) with Cl_2 in CCl_4 soln. in sunlight (33% yield together with other products) see (1).]

 \bar{C} with Mg + trace of I₂ + a little C₂H₅Br in dry ether gives in 19 hrs. 70% yield corresp. RMgCl (accompanied by 24% 2,2,3,3,6,6,7,7-octamethyloctane, pl. from MeOH, m.p. 74.0-74.5°, from coupling of \bar{C}) (1).

C converted (as above) to RMgCl, treated with wet ether, and poured into dil. H₂SO₄ gives (1) hexamethylethane (1:7090), m.p. 101-102° (1).

 \ddot{C} converted to RMgCl (as above) and the ether soln. treated at -5° with CO₂ gives (59% yield (1)) 3,3,4,4-tetramethylpentanoic acid, cryst. from dil. MeOH, m.p. 66–67° (1). [This acid with SOCl₂ in C₆H₅ gives (80% yield (1)) the corresp. acid chloride, b.p. 87–88° at 20 mm., $D_{-}^{20} = 0.9821$, $n_{D}^{20} = 1.4557$; the latter with dry NH₃ in ether gives (77% yield (1)) the corresp. amide, cryst. from CHCl₃, m.p. 137–138° (a second cryst. form from MeOH has m.p. 149–150° but after fusion melts 137–138°), or with aniline in ether gives the corresp. anilide, cryst. from pet. eth., m.p. 175–176° (1).]

C converted to RMgCl (as above) and the ether soln. treated at -5° with dry O₂ for 4 hrs. gives (53% yield (1)) 2,2,3,3-tetramethylbutanol-1, very volatile solid, m.p. 149-150° [corresp. 3,5-dinitrobenzoate, m.p. 88-90°; N-phenylcarbamate, m.p. 65-66° (1)].

Č converted to RMgCl (as above) and treated with ethereal HgCl₂ gives (35% yield (1)) 2,2,3,3-tetramethylbutyl mercuric chloride, feathery white cryst., m.p. 170-171° (1).

3:0945 (1) Whitmore, Marker, Plambeck, J. Am. Chem. Soc. 63, 1626-1630 (1941).

3:0960 4-CHLORO-2-HYDROXYBENZALDEHYDE C₇H₅O₂Cl Beil. No. 744 (4-Chlorosalicylaldehyde) Cl CHO

M.P. 52.5° (1)

Long colorless ndls. from alc. or dil. AcOH (1). — \tilde{C} has odor of walnuts (1). — \tilde{C} is apprec. sol. in aq. or aq. H_2SO_3 ; readily sol. in org. solvents. — \tilde{C} is very volatile with steam even from its yel. soln. in alk. (1).

[For prepn. of $\tilde{\mathbf{C}}$ from *m*-chlorophenol (3:0255) via Reimer-Tiemann procedure see (1).]

Č does not reduce NH₄OH/AgNO₃ o Fehling soln.; is very resistant to oxidn. by acid, alk., or neutral KMnO₄, and to acetylation (but not benzoylation, q.v. below) (1).

 \bar{C} with FeCl₃ gives brown ppt.; with CuSO₄ or $Cr_2(SO_4)_3$ + dil. aq. alk. gives bright green copper salt and a dark green chromium salt (1).

Č on mononitration as specified (2) yields 5-nitro-4-chloro-2-hydroxybenzaldehyde, pale yel. ndls. from alc., m.p. 116° (2). [This product yields a phenylhydrazone, or.-yel. ndls., m.p. 188° dec.; a p-nitrophenylhydrazone, brn.-yel. ndls. from alc. or AcOH, m.p. 294° dec.; and a semicarbazone, pale yel. ndls. from dil. AcOH, dec. above 300° (2).]

Č on dinitration as specified (2) yields 3,5-dinitro-4-chloro-2-hydroxybenzaldehyde, pale gold.-yel. ndls. from aq., m.p. 153° (2). [This product yields a phenylhydrazone, light brn. cryst. from alc., m.p. 219°; a p-nitrophenylhydrazone, light brn. cryst. from dil. AcOH, m.p. 286° dec.; and a semicarbazone, light yel. cryst. from dil. AcOH, m.p. 225° dec. (2).]

- (1). 4-Chloro-2-hydroxybenzaldoxime: colorless ndls. from alc., m.p. 155° (1).
- 4-Chloro-2-hydroxybenzaldehyde p-nitrophenylhydrazone: or. ndls. from AcOH, m.p. 257° (1).
- 4-Chloro-2-hydroxybenzaldehyde semicarbazone: pale yel. cryst. from AcOH, m.p. 212° (1).
- 4-Chloro-2-benzoxybenzaldehyde: from C + BzCl in ether + pyridine; ndls. from alc., m.p. 98.5° (1).
- 3:0960 (1) Hodgson, Jenkinson, J. Chem. Soc. 1927, 1740-1741. (2) Hodgson, Jenkinson, J. Chem. Soc. 1928, 2273-2274.

3:0980 p-DICHLOROBENZENE CI C₆H₄Cl₂ Beil. V - 203
$$V_{1}$$
-(111) V_{2} -(154)

M.P. B.P. 55° (1) (51) 174° at 764.2 mm. (24) $D_{4}^{80.3}$ = 1.2189 (33) $D_{53.3}^{80.3}$ = 1.52104 (33) 53.3-54.2° (4) 173.5° at 755 mm. (31) $D_{53.2}^{69.9}$ = 1.2310 (33) 53.2° (5) (6) (7) 173.0° (26) (27) $D_{53.0}^{69.9}$ = 1.2310 (33) $D_{53.0}^{69.9}$ = 1.2310 (33) $D_{53.0}^{69.9}$ = 1.52665 (33)

Colorless cryst., alm. insol. aq. (0.077 g. per 1000 g. aq. at 30° (22) cf. (13)); misc. hot alc. (50 ml. abs. alc. + 5 ml. aq. at 25° dis. 4.55 g. \bar{C} (26)), eas. sol. ether, C_6H_6 , CHCl₃, CS₂. — Readily sublimes; eas. volatile with steam.

[For data on crystallographic consts. see (34) (35); for data on rate of evapn. of cryst. \tilde{C} see (11); \tilde{C} has molec. f.p. depression of 77 (36) and because of its accessibility, ease of purification, convenient m.p. and large f.p. depression is often used for making mol. wt. detns.]

[For f.p./compn. data and diagram of system \bar{C} + o-dichlorobenzene (3:6055) (eutectic, m.p. -23.4° contg. 13.3% \bar{C}) see (17) (27); for f.p./compn. data and diagram for system \bar{C} + m-dichlorobenzene (3:5960) (eutectic, m.p. -29.9° contg. 12.0% \bar{C}) see (17); for f.p./compn. data on ternary system of all three dichlorobenzenes see (27). — For f.p./compn. data and diagrams for systems \bar{C} + biphenyl (1:7175) (eutectic, m.p. 26.9° contg. 57.5 mole % \bar{C} (6)) (19), \bar{C} + naphthalene (1:7200) (eutectic, m.p. 30.2° contg. 60.6 mole % \bar{C} (6)), \bar{C} + triphenylmethane (1:7220) (eutectic, m.p. 35.9° contg. 68.5 mole % \bar{C} (6)), \bar{C} + nitrobenzene (eutectic, m.p. -6.8° contg. 32% \bar{C} (9)), \bar{C} + p-chlorophenol (3:0475) (eutectic, m.p. 27.2° contg. 26.6 mole % \bar{C} (18)) see indic. refs. — For thermal anal. of system \bar{C} + SbCl₃ (eutectic, m.p. 39.5° contg. 49.5 wt. % \bar{C} (37)), and of system \bar{C} + SbBr₃ (eutectic, m.p. 48.5° contg. 73.5 wt. % \bar{C} (37)), see (37).

[\bar{C} with p-dibromobenzene gives a series of solid solns. cf. (38) (39) (40) (41) (23) (24) (26); for study of systems \bar{C} + p-chloro-iodobenzene (23) (34) and \bar{C} + p-di-iodobenzene (23) see indic. refs.]

[For data on densities of solns. of \tilde{C} in C_6H_6 (1:6400) and in *n*-hexane (1:8530) see (42); for data on D_{α}^{25} and n_{α}^{25} of solns. of \tilde{C} in C_6H_6 see (7).

 $\bar{\mathbf{C}}$ is widely used as anti-moth agent and vapor fumigant but lit. and patents are so numerous that they cannot be included here; note, however, prevention of caking of $\bar{\mathbf{C}}$ by mixt. with 1-10% paraformaldehyde (43). — [For study of toxicity of $\bar{\mathbf{C}}$ see (44). — For use of $\bar{\mathbf{C}}$ in prepn. of sulfur dyes see (45).]

[For detn. of \bar{C} in air see (46); for detn. of \bar{C} in soil by means of detn. of refractive index of solns. in kerosene see (47).]

[For prepn. of \bar{C} from p-chloroaniline [Beil. XII-607, XII₁-(304)] via diazotization, prepn. of diazonium/ZnCl₂ double salt, and decompn. of latter in molten phenol (41% yield \bar{C} together with 31% hydroxybiphenyl + 15% diphenyl ether) see (48); from p-phenylenediamine [Beil. XIII-61, XIII₁-(18)] via tetrazotization in AcOH (49) or H₃PO₄ (50) with nitrosylsulfuric acid followed by subsequent reactn. with Cu₂Cl₂ (yield: 70% (49) (50)) cf. (51), or by reduction with SnCl₂/HCl to p-phenylenedihydrazine and oxidn. with CuSO₄ (52), see indic. rcfs.]

[For prepn. of $\bar{\mathbb{C}}$ from p-chloro-nitrobenzene [Beil. V-243, V₁-(130)] with conc. HCl in s.t. at 270° (53), or with SOCl₂ in s.t. at 160–200° (54) (55), see indic. refs.; from p-bromonitrobenzene [Beil. V-248, V₁-(132)] (56), phenol-p-sulfonic acid [Beil. XI-241, XI₁-(55)] (57), or p-chlorophenol (3:0475) (16) with PCl₅ on htg. see indic. refs.; from p-chlorophenzenesulfonic acid [Beil. XI-54, XI₁-(14)] with SOCl₂ in s.t. at 160–200° see (54) (55); from 2,5-dichlorobenzophenone (3:2340) by fusion with KOH/NaOH (65% yield) see (58); from di-p-chlorophenyl sulfide or di-p-chlorophenyl sulfoxide with S at 260–270° for 3–8 hrs. see (59); from p-chlorophenyl selenium trichloride by htg. at 184° (90% yield) see (12).]

[For form. of $\bar{\mathbf{C}}$ (together with o- and m-isomers in some cases) from C_6H_6 with Cl_2 in pres. of I_2 (15), $MoCl_5$ (60), $AlCl_3$ (61), or conc. H_2SO_4 (62), by electrolysis of susp. in AcOH+aq. HCl (69) or with aqua regia (70), see indic. refs.: from chlorobenzene (3:7903) with Cl_2+cat . at 600° (17) cf. (63), or with Cl_2 in pres. of $AlCl_3$ (65% yield (27)), $FeCl_3$ (55% yield (27)), or Al/Hg (66), see indic. refs.; from chlorobenzene (3:7903) with $Al_2S_2Cl_3$ (i.e., $2AlCl_3+S_2Cl_2$ (64)) $+SO_2Cl_2$ (64) (65), or by boilg. with $FeCl_3$ (67), or in small amt. by htg. with $PbCl_4.2NH_4Cl$ in s.t. at 210° (68), see indic. refs.]

[\bar{C} with Cl₂ (61) in pres. of Al/Hg (66) or \bar{C} with Al₂S₂Cl₈ (i.e., 2AlCl₃ + S₂Cl₂) + SO₂Cl₂ (64) gives (58% yield (64)) 1,2,4-trichlorobenzene (3:6420); \bar{C} , however, chlorinates less readily than o-dichlorobenzene (3:6055), and if their mixture or eutectic is chlorinated residual \bar{C} can be separated by fractional freezing (71) (72) (73). — \bar{C} with Cl₂ in pres. of Fe (74) or with Al₂S₂Cl₈ (i.e., 2AlCl₃ + S₂Cl₂) + SO₂Cl₂ as directed (64) gives (yields: 67% (64), 39% (74)) (75) 1,2,4,5-tetrachlorobenzene (3:4115). — \bar{C} with liq. Cl₂ + sunlight + cat. (76) (77) or \bar{C} in CCl₄ under 1% aq. NaOH in sunlight (76) adds 3Cl₂ yielding a mixt. of β - (m.p. 262° (76)) and α - (m.p. 89.6° (76)) p-dichlorobenzene hexachlorides (use as insecticide (77)). — For study of photochem. chlorination of \bar{C} see (78).]

[\bar{C} when pure can be recovered unchanged after boiling with liq. Br₂ (79); however, \bar{C} warmed with Br₂ in pres. of Fe (79) or htd. with Br₂ + NaNO₂ + fumg. H₂SO₄ in s.t. at 200° for 4 hrs. (80) gives (19% yield (79)) 2,5-dibromo-1,4-dichlorobenzene, ndls. from hot alc., m.p. 148° (79), 146° (80). — \bar{C} with excess Br₂ + AlCl₃ as directed (81) gives 2,3,5,6-tetrabromo-1,4-dichlorobenzene, m.p. 278-278.5° (81).]

[C passed over Pt spiral at bright red heat yields (82) 2,5,2',5'-tetrachlorobiphenyl, m.p. 84-85° (82). — C in EtOH at 55° in pres. of Adams' cat. (PtO₂) with excess H₂ at 3 atm. press. yields (83) cyclohexane (1:8405). — C in alc. KCN with NiCl₂ htd. in s.t. 20 hrs. at 260-270° gives (12% yield (84)) terephthalic acid (1:0910).]

[\bar{C} with Na + n-butyl chloride (3:7160) in xylene at 150° gives small yield (85) p-di-n-butylbenzene, b.p. 224-225.5° at 759 mm. (85). — \bar{C} with Mg + I₂ (0.25 equiv.) gives in 6 hrs. 58% yield (86) p-chlorophenyl MgCl.]

[\bar{C} with ethylene + AlCl₃ gives a mixt. (87) of mono-, di-, tri-, and tetra-ethyl-p-dichlorobenzenes.]

[\bar{C} (3 moles) with CHCl₃ (1 mole) + AlCl₃ gives (14% yield (88)) tris-(2,5-dichlorophenyl)methane, colorless cryst. from C_6H_6 , m.p. 206-208° (88). — \bar{C} with CCl₄ + AlCl₃ at room temp. (88) or in CS₂ (89) (90) gives (26% yield (88)) 2,5,2',5'-tetrachlorobenzophenone dichloride, m.p. 173-174° (89) (88); this with dil. alc. on boilg. or htg. in s.t. at 130° hydrolyzes to 2,5,2',5'-tetrachlorobenzophenone, colorless cryst. from alc., m.p. 128° (89) (90). — \bar{C} with CCl₄ + AlCl₃ at 55° for 10 hrs. presumably first yields tris-(2,5-dichlorophenyl)methyl chloride (not isolated) which then loses 1 HCl giving (23% yield (88)) 1,4,7-trichloro-9-(2,5-dichlorophenyl)fluorene (?), m.p. 179-180° (88).]

[C with acetyl chloride (3:7065) + AlCl₃ gives (91) 2,5-dichloroacetophenone, b.p. 251° at 756 mm., m.p. 14° (91) (oxime, m.p. 130°, via Beckmann rearr. with conc. H₂SO₄ gives acet-2,5-dichloroanilide, m.p. 133° (91)). — C with benzoyl chloride (3:6240) + AlCl₃ yields (91) (92) 2,5-dichlorobenzophenone, white ndls. from alc., m.p. 88° (91), 85-86° (92) (oxime, m.p. on slow htg. 207°, via Beckmann rearr. with conc. H₂SO₄ gives benz-2,5-dichloroanilide, m.p. 122° (91)). — C with o-chlorobenzoyl chloride (3:6640) + AlCl₃ gives (92) 2,2',5-trichlorobenzophenone, m.p. 145-147° (92). — C with 2,4-dichlorobenzoyl chloride + AlCl₃ gives 2,5,2',4'-tetrachlorobenzophenone, m.p. 176° (92).] — [Note that C fails to react with sym-dichlorodimethyl ether (3:5245).]

[\bar{C} with phthalic anhydride (1:0725) + AlCl₃ gives (59.3% (94), 27% (93)) o-(2,5-dichlorobenzoyl)benzoic acid, colorless pr. from C_6H_6 , m.p. 169° cor. (93), 167° (94); this prod. on ring closure with fumg. H_2SO_4 (94) or conc. H_2SO_4 (93) at 150° gives (yields: 83.5% (94), 83% (93)) 1,4-dichloroanthraquinone [Beil. VII-787, VII₁-(111)], or.-yel. ndls. from AcOH, m.p. 187.5° cor. (93), 186° (94). — Note that \bar{C} reacts with phthalic anhydride + AlCl₃ less readily than o-dichlorobenzene (3:6055) (use in sepn. of the two isomers (95)). — For corresp. condens. of \bar{C} with 3-sulfophthalic anhydride and 4-sulfophthalic anhydride in pres. of AlCl₃ see (96).]

[C on partial hydrol. with aq. MeOH alk., alk. carbonates, or best alk. earths in pres. of Cu or Cu salts at elevated temps. under press. gives in excellent yield (98) (99) (100) (101) (102) (103) (104) (105) p-chlorophenol (3:0475) (some phenol (1:1420) is also formed (102)); if the hydrolysis of C is carried further (100) (106) hydroquinone (1:1590) is also obtd.]—[For study of kinetics of reactn. of C with MeOH/alk. see (99) (107) (108).]

[C with anhyd. NH₃ in alc. in pres. of CuCl₂ + Cu under press. at 150-200° yields (109) p-chloroaniline [Beil. XII-607, XII₁-(304)]; C with conc. aq. NH₄OH in pres. of CuO under press. at 150-200° gives (110) (111) (112) (113) (114) p-phenylenediamine [Beil. XIII-61, XIII₁-(18)]. — [C with K diphenylamine at 240-245° gives (115) not only the expected N,N,N',N'-tetraphenyl-p-phenylenediamine, tbls. from acctone, m.p. 199-200°, but also by rearr. N,N,N',N'-tetraphenyl-m-phenylenediamine, m.p. 137.5-138°.]

[\bar{C} on mononitration, e.g., with 5 wt. pts. abs. HNO₃ at 0° (116) (99), with 2 wt. pts. HNO₃ (D=1.48) below 50° (120), or with 1.5 pts. of a mixt.contg.2 pts. HNO₃ (D=1.54) + 3 pts. conc. H₂SO₄ (117) (118) (119) at 70-100° for 30-60 min., yields 1,4-dichloro-2-nitrobenzene [Beil. V-245, V₁-(131)], cryst. from alc., m.p. 55° (120), 54.5° (99), 54° (119), 53° (116) (note close proximity of this m.p. to that of the initial \bar{C}).]

[C on dinitration, e.g., with 4 wt. pts. fumg. HNO₃ (D=1.52) + 10 wt. pts. conc. H₂SO₄ at b.p. for 5 hrs. (8) (121), or with 3 wt. pts. HNO₃ (D=1.52) + 7.5 wt. pts. conc. H₂SO₄ at b.p. for 2 hrs. (122), finally poured into aq., gives a mixt. contg. all three possible dinitrop-dichlorobenzenes; of these the chief prod. is 1,4-dichloro-2,6-dinitrobenzene [Beil. V-265, V₁-(138)], m.p. 106° (123) (119), 105-106° (122), 105° (121), obtd. by recrystn. (repeated if necessary) of the crude dinitration prod. from 30 pts. 95% alc. (121); the mother liquors contain the more soluble 1,4-dichloro-2,3-dinitrobenzene, m.p. 102-103° (122), 101.2° (119),

- 101° (121), and 1,4-dichloro-2,5-dinitrobenzene, m.p. 119° (122) (121) (124). For f.p. compn. data and diagrams of mixtures of the 2,6- and 2,3-dinitro-p-dichlorobenzenes see (119), of mixtures of the 2,6- and 2,5-dinitro-p-dichlorobenzenes see (121). Note also that the prod., m.p. 81°, formerly (8) supposed to be the 2,5-dinitro isomer, has since (121) been proved to be a compound of the 2,6- and 2,5-dinitro-1,4-dichlorobenzenes. The relative proportion of the three dinitration products varies with conditions (119) (121) (122) (124).]
- [\bar{C} on monosulfonation, e.g., with 1.5 wt. pts. fumg. H₂SO₄ (10–12% SO₃) at 140–150° for 45 min. (118) cf. (27), gives on pouring into aq. (85–90% yield (118)) 1,4-dichlorobenzene-sulfonic acid-2, cryst. from aq. as monohydrate (for derivs. see below). Note that \bar{C} is not sulfonated by conc. H₂SO₄ even at 210° (16) (dif. from o-dichlorobenzene (3:6055) and use in sepn. from \bar{C}); for removal of chlorobenzene (3:7903) from mixt. with dichlorobenzenes via sulfonation of former with 95% H₂SO₄ see (17). For use of reactn. prod. of \bar{C} with SO₃ as dye intermed. or for mothproofing of wool see (125). For reactn. of sodium p-dichlorobenzenesulfonate with fused NaOH to yield hydroquinone (1:1590) see (126).]
- [C with 5 moles ClSO₃H at 150° for 1 hr. (127) (128) gives (85% yield (127) (128)) 1,4-dichlorobenzenesulfonyl chloride-2, cryst. from lgr., m.p. 39° (127) (128), 38° (129), 36.8° (27) (corresp. amide, see below; corresp. sulfonanilide, m.p. 160° (128)); for use in prepn. of tetrachlorothioindigo see (130). C with 30 pts. ClSO₃H at 140° for 48 hrs. (128) gives both 1,4-dichlorobenzene-bis-(sulfonyl chloride)-2,6, m.p. 114° (corresp. bis-sulfonanilide, m.p. 215-217° dec. (128)) and 1,4-dichlorobenzene-bis-(sulfonyl chloride)-2,5, m.p. 182° (corresp. bis-sulfonanilide, m.p. not given). Note that C reacts with ClSO₃H much less easily than o-dichlorobenzene; for use in sepn. of the two isomers via formn. of o-dichlorobenzenesulfonyl chloride and sepn. from unchanged C by distn. see (131).]
 - D 1,4-Dichlorobenzenesulfonamide-2 (2,5-dichlorobenzenesulfonamide-1): cryst. from dil. alc., m.p. 179.5-180° u.c. (129), 181° (127), 185-186° (27). [From Č via treatment with ClSO₃H as directed (129) to 1,4-dichlorobenzenesulfonyl chloride-2 (see above) and subsequent conv. with (NH₄)₂CO₃ to desired sulfonamide.] [Note that, although the m.p. of this sulfonamide is practically identical with that from m-dichlorobenzene (3:5960), each depresses the m.p. of a mixt. with the other; the m.p.'s of the precursor sulfonyl chlorides, viz. 52-53° for the isomer from m-dichlorobenzene, 38° for that from Č, may also serve to distinguish them (129).] [For similar prepn. and use of 1,4-dichlorobenzenesulfonamide-2 see (132).]
- 3:0980 (1) Paulsen, Monatsh. 72, 257 (1939). (2) Rule, McLean, J. Chem. Soc. 1931, 690. (3) Sugden, J. Chem. Soc. 125, 1173 (1924). (4) Dadieu, Pongratz, Kohlrausch, Monatsh. 61, 431 (1932). (5) Perkin, J. Chem. Soc. 69, 1202 (1896). (6) Morris, Cook, J. Am. Chem. Soc. 57, 2404-2406 (1935). (7) Martin, George, J. Chem. Soc. 1933, 1414. (8) Nason, J. Am. Chem. Soc. 40, 1602-1604 (1918). (9) Hrynakowski, Samyt, Z. physik. Chem. A-182, 112-113 (1938). (10) Groves, Sugden, J. Chem. Soc. 1937, 1783.
- (11) Tammann, Dreyer, Z. physik. Chem., Bodenstein Festband, 4 (1931). (12) Foster, Rec. trav. chim. 53, 412-413 (1934). (13) Klemenc, Löw, Rec. trav. chim. 49, 637-640 (1930). (14) Müller, Jahresber. 1864, 524. (15) Jungfeisch, Ann. chim. (4) 15, 252-264 (1868). (16) Beilstein, Kurbatow, Ann. 176, 32-33 (1876). (17) Wibaut, van de Lande, Wallagh, Rec. trav. chim. 56, 65-70 (1937). (18) Burnham, Madgin, J. Chem. Soc. 1936, 790-791. (19) Warner, Scheib, Svirbley, J. Chem. Phys. 2, 591-593 (1934). (20) Glass, Madgin, J. Chem. Soc. 1933, 1432.
- (21) Narbutt, Ber. 52, 1030 (1919). (22) Gross, Saylor, J. Am. Chem. Soc. 53, 1748-1750 (1931). (23) Nagornov, Z. physik. Chem. 75, 578-581 (1911). (24) Kruyt, Z. physik. Chem. 79, 667-668 (1912). (25) Mills, Jahresber. 1882, 103. (26) Küster, Würfel, Z. physik. Chem. 59, 66-71 (1904). (27) Holleman, van der Linden, Rec. trav. chim. 30, 317-332 (1911). (28) Block, Z. physik. Chem. 78, 397 (1911). (29) C. G. LeFevre, R. J. W. LeFevre, J. Chem. Soc. 1336, 490. (30) Bruni, Gorni, Atti accad. Lincei (5) 9, II 327 (1900); Cent. 1901, I 162.

(31) Jaeger, Z. anorg. allgem. Chem. 101, 115 (1917). (32) Quick, J. Am. Chem. Soc. 42, 1035-1040 (1920). (33) von Auwers, Ann. 422, 164 (1921). (34) Hendricks, Z. Krist. 84, 85-96 (1932). (35) Huggins, J. Am. Chem. Soc. 45, 272 (1923). (36) von Auwers, Z. physik. Chem. 30, 312 (1899). (37) Menschutkin, J. Russ. Phys.-Chem. Soc. 43, 416 (1911); Cent. 1910, 11 379-381. (38) Deffet, Bull. soc. chim. Belg. 47, 464-470 (1938). (39) Vuks, Acta Physicochim. U.R.S.S. 6, 327-338 (1937). (40) Meyer, Rec. trav. chim. 42, 306-312 (1923).

(41) Nagornov, Zemcuzny, Kurnakov, Z. physik. Chem. 76, 241-250 (1911). (42) Smyth, Morgan, Boyco, J. Am. Chem. Soc. 50, 1542 (1928). (43) Hinegardner (to du Pont Co.), U.S. 2,081,326, May 25, 1937; Cent. 1937, II 3381; C.A. 31, 5112 (1937). (44) Cameron, Thomas et al., J. Path. Bact. 44, 281-296 (1937); C.A. 31, 4399 (1937). (45) Palmer, Lloyd, J. Am. Chem. Soc. 52, 3388-3395 (1930). (46) Darkis, Vermillion, Gross, Ind. Eng. Chem. 32, 946-949 (1940). (47) Chisholm, Koblitsky, J. Assoc. Oficial Agr. Chem. 26, 273-277 (1943). (48) Hodgson, Foster, J. Chem. Soc. 1942, 581-583. (49) Hodgson, Walker, J. Chem. Soc. 1935, 530. (50) Schoutissen, J. Am. Chem. Soc. 55, 4537 (1933).

(51) Sandmeyer, Ber. 17, 2652 (1884).
(52) Schoutissen, J. Am. Chem. Soc. 55, 4546 (1933).
(53) Lobry de Bruyn, van Leent, Rec. trav. chim. 15, 86 (1896).
(54) Meyer, Monatsh. 36, 721, 724 (1915).
(55) Kinzlberger & Co., Ger. 280,739, Nov. 26, 1914; Cent. 1915, I 104. (56) Schmidt, Wagner, Ann. 387, 164-165 (1911).
(57) Kekulé, Ber. 6, 944 (1873).
(58) Lock, Ródiger, Ber. 72, 869 (1939).
(59) Billman, Dougherty, J. Am. Chem. Soc. 61, 387-389 (1938).

(60) Aronheim, Ber. 8, 1400-1401 (1875).

(61) Mouneyrat, Pouret, Compt. rend. 127, 1026 (1898). (62) Battegay, French 641,102. July 28, 1928; Cent. 1928, II 1718. (63) Imperial Chem. Ind. & Wheeler, Bitt. 388,818, March 30, 1933; Cent. 1933, I 4037. (64) Silberrad, J. Chem. Soc. 121, 1017-1020 (1922). (65) Silberrad, J. Chem. Soc. 119, 2029-2036 (1921). (66) Cohen, Hartley, J. Chem. Soc. 87, 1362 1364 (1905). (67) Thomas, Compt. rend. 126, 1212 (1898). (68) Seyewetz, Trawitz, Compt. rend. 136, 242 (1903). (69) Fichter, Glantzstein, Ber. 49, 2475-2481 (1916). (70) Datta, Fernandes, J. Am. Chem. Soc. 36, 1009 (1914).

(71) Zil'berman, Slobodnik, J. Applied Chem. (U.S.S.R.) 10, 1080-1085 (1937); Cent. 1938, II 1580 (1938); C.A. 32, 1664 (1938). (72) Slobodnik, Zil'berman, Russ. 48,285, Aug. 31, 1936; Cent. 1937, II 288. (73) Britton (to Dow Chem. Co.), U.S. 1,923,419, Aug. 22, 1933; Cent. 1933, II 3049; C.A. 27, 5086 (1933). (74) Holleman, Rec. trav. chim. 39, 737 (1920). (75) Roberts & Co., Ltd., & Silberrad, Brit. 193,200, March 15, 1923, Cent. 1925, I 904. (76) van der Linden, Ber. 45, 412-414 (1912). (77) Bender (to Great Northern Electrochem. Co.), U.S. 2,010,841, Aug. 13, 1935; Cent. 1936, I 1112. (78) Fisk, Noyes, J. Am. Chem. Soc. 58, 1707-1714 (1936). (79) Wheeler, McFarland, Am. Chem. J. 19, 366 (1897). (80) Varma, Shankarayan, J. Indian Chem. Soc. 13, 31-33 (1936).

(81) Mouneyrat, Pouret, Compt. rend. 129, 607 (1899). (82) Meyer, Hofmann, Monatsh. 38, 145 (1917). (83) Brown, Durand, Marvel, J. Am. Chem. Soc. 58, 1595-1596 (1936). (84) Slebodzinski, J. prakt. Chem. (2) 143, 120 (1935). (85) Morgan, Hickinbottom, J. Chem. Soc. 121, 1891-1892 (1921). (86) E. L. St. John, N. B. St. John, Rec. trav. chim. 55, 587 (1936). (87) Istrati, Ann. chim. (6) 6, 475-487 (1885). (88) Wilson, Huang, J. Chinese Chem. Soc. 4, 142-148 (1936). (89) Nortis, Green, Am. Chem. J. 26, 497-499 (1901). (90) Boeseken, Rec. trav. chim. 27, 8-9 (1908).

(91) de Crauw, Rec. trav. chim. 50, 797-769 (1931). (92) Ganzmuller, J. prakt. Chem. (2) 138, 311-312 (1933). (93) Phillips, J. Am. Chem. Soc. 48, 3198-3199 (1926). (94) Kogan, Ganina, Ind. Org. Chem. U.S.S.R. 1, 89-91 (1936); Cent. 1936, II 1341; C.A. 30, 5216 (1936). (95) Dodd, Sprent & United Alkali Co., Ltd., Brit. 204,528, Oct. 25, 1923; Cent. 1925, II 1228. (96) Schwenk, Waldmann, Z. angew. Chem. 45, 17-21 (1932). (97) Stephen, Short, Gladding, J. Chem. Soc. 117, 513 (1920). (98) Chemische Werke Ichendorf, Ger. 281,175, Dec. 15, 1914; Cent. 1915, I 180. (99) Holleman de Mooy, Rec. trav. chim. 35, 8-9, 18, 27-28 (1915). (100) Lloyd, Kennedy. U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994.

(101) Vorozhtzov, Karlash, Russ. 30,690, June 30, 1933; Cent. 1934, I 767. (102) Vorozhtzov, Karlash, Compt. rend. acad. sci. U.R.S.S. 1933, 221-223; Cent. 1935, I 55; C.A. 28, 1991 (1934), (103) Kiprianov, Dashevskii, Ukrain. Khem. Zhur. 7, Wiss.-Tech. Abt. 78-87 (1932); Cent. 1933, II 1338; C.A. 27, 3824 (1933). (104) Lufton, Burroughs (to Pennsylvania Coal Prod. Co.), U.S. 2,126,648, Aug. 9, 1938; Cent. 1938, II 3006; C.A. 32, 7925 (1938). (105) Minaev, Fedorov, Sarnit, Org. Chem. Ind. (U.S.S.R.), 4, No. 13, 19-22 (1937); Cent. 1938, II 173; C.A. 31, 8514 (1937). (106) Popov, Popova, J. Applied Chem. (U.S.S.R.), 9, 1303-1307 (1936); Cent. 1937, I 2362; C.A. 31, 2589 (1937). (107) Holleman, Rec. trav. chim. 37, 203 (1918). (108) de Lango, Rec. trav. chim. 38, 101-105 (1919). (109) Hale, Cheney (to Dow Chem. Co.), U.S. 1,729,775, Oct. 1, 1929; Cent. 1936, I 2007; C.A. 23, 5474 (1929). (110) Quick, J. Am. Chem. Soc. 42, 1035-1040 (1920).

(111) Grosvenor, Miller, U.S. 1,445,637, Feb. 20, 1923; Cent. 1925, II 1800. (112) Williams (to Dow Chem. Co.), U.S. 1,775,360, Sept. 9, 1930; Cent. 1931, II 1195. (113) Federal Phosphorus Co., Brit. 370,774, May 5, 1932; Cent. 1932, II 1237. (114) Booth (to Swann Research, Inc.), U.S. 1,954,469, April 10, 1934; Cent. 1934, II 1846. (115) Haeussermann, Bauer, Ber. 32, 1914–1915 (1899); Haeussermann, Ber. 33, 939–941 (1900); Ber. 34, 38–40 (1901). (116) Booy, Dienske, Rec. trav. chim. 45, 449–450 (1926). (117) Morgan, J. Chem. Soc. 81, 1382 (1902). (118) Crowell, Raiford, J. Am. Chem. Soc. 42, 147–149 (1920). (119) Page, Heasman, J. Chem. Soc. 123, 3247–3255 (1923). (120) Lock, Ber. 68, 1510 (1935).

(121) Macleod, Pfund, Kilpatrick, J. Am. Chem. Soc. 44, 2260-2271 (1922). (122) Holleman, den Hollander, Rec. trav. chim. 39, 440-446 (1920). (123) Misslin, Helv. Chim. Acta 3, 631 (1920). (124) Holleman, den Hollander, van Haeften, Rec. trav. chim. 40, 323-326 (1921). (125) Seel, U.S. 2,171,166, Aug. 29, 1939; C.A. 34, 272 (1940); Ger. 680,329, Aug. 3, 1929; C.A. 36, 2158 (1942). (126) von Bramer (to Eastman Kodak Co.), U.S. 1,421,869, July 4, 1922; Cent. 1924, I 2823; C.A. 16, 2867 (1922). (127) Stewart, J. Chem. Soc. 121, 2557-2558 (1922). (128) Gebauer-Fulnegg, Figdor, Monatsh. 48, 627-637 (1927); Gebauer-Fulnegg, Neumann, Monatsh. 50, 236 (1928). (129) Huntress, Carten, J. Am. Chem. Soc. 62, 511-514 (1940). (130) United Alkali Co., Dodd, Sprent, Brit. 251,321, May 27, 1926; Cent. 1926, II 2356.

(131) Imperial Chem. Ind., & Bennet, Brit. 440,205, Jan. 23, 1936; Cent. 1936, I[4367. (132) Kyrides (to Monsanto Chem. Co.), U.S. 1,993,722, March 5, 1935; Cent. 1935, II 1446.

3: 0985 18-CHLORO-OCTADECANOL-1 C₁₈H₃₇OCl Beil. S.N. 24 (ω-Chloro-n-octadecyl CH₂.(CH₂)₁₆.CH₂OH alcohol; ω-chlorostearyl alcohol) M.P. 53-54.5° (1)

Colorless crystals.

[For prepn. from α , ω -octadecamethylene glycol (m.p. 97-98°) with SOCl₂ + dimethylaniline in C₆H₆ (50% yield) see (1); note that a little 1,18-dichloro-octadecane with m.p. 54° (i.e., practically the same as $\bar{\mathbf{C}}$) is also formed.]

C is only slightly attacked by KOH (2).

D 18-Chloro-octadecyl N-phenylcarbamate: lfts. from ale. or lt. pet., m.p. 77° (1).

3: 9985 (1) Bennett, Gudgeon, J. Chem. Soc. 1938, 1679-1681. (2) Seck, Dittmar, Chem. Umschau Fette, Öle, Wachse, Harze 39, 226-229 (1932); Cent. 1933, I 1757; [C.A. 27, 703 (1933)].

3: 0990 1,2,3-TRICHLOROBENZENE Cl
$$C_6H_3Cl_3$$
 Beil. V - 203 (vic-Trichlorobenzene) C_1 C_1 V_1 -(112) V_2 -(156)

M.P.	54°	(1)	B.P. 218-219	(3)
	53-54°	(2) (3)		
	52.3-53.0°	(4)		
	52.4°	(5)		
	52°	(6)		
	50.8°	(7)		

Tbls. from alc.; eas. sol. CS_2 or C_6H_6 ; spar. sol. alc.; volatile with steam. [For use as component of mixtures for dif. inflammable electric insulating materials see (8).] [For thermal anal. of mixts. of \bar{C} with 1,2,4-trichlorobenzene (3:6420) and with 1,3,5-trichlorobenzene (3:1400) see (5).]

[For prepn. of C from 2,3,4-trichloroaniline [Beil. XII-626] with ethyl nitrite (3) or by diazotization and reaction with alc. (35% yield (4)), or from 3,4,5-trichloroaniline [Beil.

XII-630, XII₁-(313)] via diazotization (9) (6) and reaction with alc. (9), or by reduction to 3,4,5-trichlorophenylhydrazine and reaction of this with Fehling soln. (poor yield (6)) (5), see indic. refs.; for prepn. of \bar{C} from 2,3-dichloroaniline [Beil. XII-621] (7) or from 2,6-dichloroaniline [Beil. XII-626] (7) (4) via diazotization and use of Cu_2Cl_2 reaction see indic. refs.; for prepn. of \bar{C} from 4-chloro-3,5-diaminobenzenesulfonic acid-1 [Beil. XIV-718, XIV₁-(727)] via conv. to 3,4,5-trichlorobenzenesulfonic acid-1 and subsequently hydrolyzing the sulfonic acid group see (1).]

[For form. of \bar{C} (together with other prod.) from a mixt. of o- and p-dichlorobenzenes with Cl₂ (10), or from m-dichlorobenzene + AlCl₃ + Cl₂ (11), or from α -, β -, or γ -benzene-hexachlorides with alc. KOH (5), or from α -benzenehexachloride with pyridine or quinoline (5), see indic. refs.]

[Č with Cl₂ in pres. of Al/Hg yields (9) exclusively 1,2,3,4-tetrachlorobenzene (3:0655), m.p. 44-45° (9); Č with liq. Cl₂ in s.t. at room temp. for 7 days adds 6 atoms halogen yielding (12) 1,1',2,2',3,3',4,5,6-enneachlorocyclohexane (1,2,3-trichlorobenzene hexachloride), pr. from MeOH, m.p. 80° (12).]

[Č on hydrolysis with steam at 550-800° over cat. yields (13) pyrogallol (1:1555); for behavior of Č with NaOMe in McOH see (6) (14).]

 $\bar{\mathbf{C}}$ on mononitration, e.g., by soln. of $\bar{\mathbf{C}}$ (1 g.) in 5 ml. fumg. HNO₃ (D=1.49) (17), gives 100% yield (17) 1,2,3-trichloro-4-nitrobenzene [Beil. V-246], long colorless ndls. from alc., m.p. 56° (15) (7), 55-56° (17) (3) (note that the isomeric 1,2,3-trichloro-5-nitrobenzene [Beil. V-247, V₁-(131)] has m.p. 72°).

 \bar{C} on dinitration, e.g., \bar{C} (1 g.) refluxed 1 hr. with 5 ml. fumg. HNO₃ (D=1.49) + 5 ml. conc. H₂SO₄, then poured into aq. (17) (16), gives 100% yield 1,2,3-trichloro-4,6-dinitrobenzene, ndls. from hot alc., m.p. 92-93° (16) (17); this prod. (1 g). htd. 1 hr. at 100° with 5 g. aniline as directed (17) yields 1,3-dianilino-2-chloro-4,6-dinitrobenzene, cryst. from C₆H₆ or alc., m.p. 136-138° (17). [Note that an isomeric 1,2,3-trichloro-4,5-dinitrobenzene, cryst. from alc., m.p. 105-106° (16), has been obtd. by further nitration of 1,2,3-trichloro-5-nitrobenzene (mentioned in preceding paragraph).]

Č with chlorosulfonic acid as directed (17) gives 1,2,3-trichlorobenzenesulfonyl chloride-4, m.p. 64-65° u.c. (17), 65-66° (2); this prod. with (NH₄)₂CO₃ readily yields (17) 1,2,3-trichlorobenzenesulfonamide-4, m.p. 226-230° dec. u.c. (17).

3:0990 (1) I.G., Brit. 319,149, Oct. 10, 1929; French 661,490, July 25, 1929; Cent. 1930, I 740. (2) I.G., Brit. 287,178, May 9, 1928; Cent. 1929, II 352. (3) Beilstein, Kurbatow, Ann. 192, 234-235 (1878). (4) Dadieu, Pongratz, Kohlrausch, Monatsh. 61, 431-432 (1932). (5) van der Linden, Ber. 45, 231-247 (1912). (6) Holleman, Rec. trav. chim. 37, 196-201 (1918). (7) Körner, Contardi, Atti accad. Lincei (5) 18, I 100 (1904). (8) Zünderwerke E. Bruun, A. G., Ger. 570,460, Feb. 16, 1933; Cent. 1933, I 2770. (9) Cohen, Hartley, J. Chem. Soc. 87, 1365-1366 (1905). (10) Britton (to Dow Chem. Co.), U.S. 1,923,419, Aug. 22, 1933; Cent. 1933, II 3049; C.A. 27, 5086 (1933).

(11) Mouneyrat, Pouret, Compt. rend. 127, 1028 (1898). (12) van der Linden, Rec. trac. chim. 55, 316-317 (1936). (13) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994; C.A. 26, 2747 (1932). (14) de Crauw, Rec. trav. chim. 50, 779-780 (1931). (15) Holleman, Rec. trav. chim. 39, 449 (1920). (16) Hüffer, Rec. trav. chim. 40, 451-452 (1921). (17) Huntress, Carten, J. Am. Chem. Soc. 62, 512-514 (1940).

3:0995 1,1-Di-(p-CHLOROPHENYL)ETHANE

C₁₄H₁₂Cl₂ Beil

Beil. S.N. 479

M.P. 54-55° (1) B.P. 143-145° at 2 mm. (1)

Colorless cryst. from 90% AcOH. — Note that, when pure, neither solid \bar{C} nor its solns. snow any fluorescence either in visible or ultraviolet light. (1). — Note also that, although m.p. of \bar{C} is identical with that of its next lower homolog, viz., di-(p-chlorophenyl)methane (4,4'-dichlorodiphenylmethane) (3:1057), nevertheless the m.p. of their mixture is depressed to 40-50° (1).

[For prepn. of \tilde{C} from 1,1-di-(p-chlorophenyl)cthylene (3:2475) by cat. hydrogenation (62% yield) see (1); for formn. of \tilde{C} from chlorobenzene (3:7903) with acetylene in presence of AlCl₃ see (2), but note that by this method various undetermined impurities which show blue fluorescence are also formed (1).]

 \ddot{C} on oxidn. with $CrO_3/AcOH$ + trace of H_2SO_4 gives (1) 4,4'-dichlorobenzophenone (3:4270), m.p. 142-144°.

C does not (1) yield an addn. prod. with PkOH.

3:0995 (1) Grummitt, Buck, Becker, J. Am. Chem. Soc. 67, 2265-2266 (1945). (2) Cook, Chambers, J. Am. Chem. Soc. 43, 338 (1921).

CHAPTER IV

DIVISION A. SOLIDS

(3:1000-3:1499)

3:1000 $\gamma_1\gamma_1\gamma_2$ -TRICHLORO-n-BUTYRIC ACID $C_4H_5O_2Cl_3$ Beil. S.N. 162 $Cl_3C.CH_2.COOH$

M.P. 55° (1)

Colorless ndls. from hot aq.

[For prepn. of \bar{C} from γ, γ, γ -trichloro-*n*-butyronitrile (see below) by hydrolysis with conc. HCl at 60° for 6 hrs. see (1).]

—γ₂γ₂γ-Trichloro-n-butyronitrile: ndls. from pet. ether, m.p. 41° u.c.; b.p. 214-216° at 760 mm., 90-95° at 12 mm. (1). [From acrylonitrile with CHCl₃ in pres. of aq. trimethylbenzylammonium hydroxide at 0.5° for 24 hrs. (11% yield (1)).] [Note that this nitrile upon acid hydrolysis gives C̄, but upon alkalıne hydrolysis gives succinic acid (1:0530), m.p. 188-189° (1).]

— γ,γ,γ -Trichloro-*n*-butyramide: cryst. from toluene, m.p. 89-90° u.c. (1). [From γ,γ,γ -trichloro-*n*-butyronitrile (above) with 27% H₂O₂ + aq. NaOH at 40-45° for 5 hrs. (1).]

3:1000 (1) Bruson, Niederhauser, Riener, Hester, J. Am. Chem. Soc. 67, 601 (1945).

3:1010 3-CHLORO-2-HYDROXYBENZALDE- $C_7H_5O_2Cl$ Beil. VIII — HYDE CHO CHO CHO CHO CHO CHO CHO CHO CHO CHO

M.P. 55° (1) 54.5-55.5° (2) 54° (3) (4)

Long colorless ndls. from MeOH (1). — Readily sol. in usual org. solvents (1). — Volatile with steam [diff. from 3-chloro-4-hydroxybenzaldehyde (3:4065) (1)].

[For prepn. from o-chlorophenol (3:5980) with CHCl₃ + alk. (10-15% yield (1)) or via condensation with formalin + alk. to 3-chloro-2-hydroxybenzyl alc. and oxidn. of latter with Na m-nitrobenzenesulfonate + alk. (2) see indic. refs.; from 3-chloro-2-hydroxybenzoic acid (3-chlorosalicylic ac.) (3:4745) by reductn. with Na/Hg in pres. of H₃BO₃ see (4).]

C with satd. aq. NaHSO3 soln. yields NaHSO3 cpd. (1) (2).

C dissolves in aq. alk. with yel. color (4) (2).

C with aq. FeCl₃ yields violet-red color (2).

 \bar{C} is not nitrated by cold AcOH/HNO₃ soln. (1); but \bar{C} (2 g.) in AcOH (10 ml.) treated at 45° for 15 min. with soln. of 0.8 ml. conc. HNO₃ (D=1.42) in AcOH (4 ml.), then poured into aq., gives (1) 2.15 g. 3-chloro-5-nitro-2-hydroxybenzaldehyde, yel. ndls. from dil. alc., m.p. 129° (1).

The methyl ether of \bar{C} , viz., 3-chloro-2-methoxybenzaldehyde, is a liq., b.p. abt. 255°, f.p. 0° (1).

- 3-Chloro-2-hydroxybenzaldoxime: lfts. from dil. alc., m.p. 167-168° (2).
- --- 3-Chloro-2-hydroxybenzaldehyde phenylhydrazone: unrecorded.
- --- 3-Chloro-2-hydroxybenzaldehyde p-nitrophenylhydrazone: unrecorded.
- --- 3-Chloro-2-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.
- 3-Chloro-2-hydroxybenzaldehyde semicarbazone: cryst. from 50% AcOH, m.p. 240-243° (2).

3:1010 (1) Davies, Rubinstein, J. Chem. Soc. 123, 2850 (1923). (2) Hanus, J. prakt. Chem. (2) 158, 263-264 (1941). (3) Duff, J. Chem. Soc. 1941, 547-550. (4) Bayer and Co., Ger. 228,838, Nov. 22, 1910; Cent. 1911, I 51.

Ndls. from hot aq. or pet. ether. Spar. sol. cold but more eas. sol. hot aq.; eas. sol. alc., ether, CHCl₃, CS₂. Volatile with steam.

[For prepn. of \bar{C} from o-cresol (1:1400) with Cl_2 (7) (4) (1) in CCl_4 (61% yield (2)) in CCl_4 in pres. of Fe (8) or in pres. of PCl_5 in sunlight at elevated temp. (8), with Cl_2 in NaOH soln. at room temp. (5), or with SO_2Cl_2 (3), see indic. refs.; for formn. from 2-methylphenoldisulfonic acid-4,6 (6) in nitrobenzene with Cl_2 (other products are also formed) see (6).]

 $[\bar{C} \text{ with dry NH}_3 \text{ gas at room temp. (9) forms a cpd., } \bar{C}.2NH_3 \text{ (9); } \bar{C} \text{ on evapn. of alc. NH}_3 \text{ soln. does not give an NH}_4 \text{ salt but is recovered unchanged (dif. from 2,6-dichloro-4-methylphenol (3:0400) q.v.) (7).}$

 $[\bar{C}$ (1 pt.) in 2 pts. ice-cold HNO₃ (D=1.48) stood 24 hrs. gives (37% yield (2)) a prod. of compn. $C_7H_6O_6N_2Cl_2$, white ndls. from dry ether by pptn. with pet. ether, m.p. 109° dec. (2).

[\bar{C} with boilg. dil. HNO₃ oxidizes (7) to oxalic acid (1:0445); \bar{C} on oxidn. with $K_2Cr_2O_7$ + dil. H_2SO_4 gives (4) 6-chloro-2-methylbenzoquinone-1,4 (6-chloro-p-toluquinone) [Beil. VII-650, VII₁-(353)], yel. ndls., vol. with steam, m.p. 90° (4); \bar{C} digested with aqua regia for $1\frac{1}{2}$ hrs. at 100° gives (16% yield (5)) 3,5,6-trichloro-2-methylbenzoquinone-1,4 (trichloro-p-toluquinone) [Beil. VII-651, VII₁-(354)], yel. lfts. from alc., m.p. 233° (5); \bar{C} with CrO₃/AcOH gives a mixt. (4) of chlorinated quinones.]

[\bar{C} does not react with PCl₅ (10); \bar{C} on monosulfonation with fumg. H₂SO₄ (65% SO₃) at 50° yields (11) 4,6-dichloro-2-methylphenolsulfonic acid-3; for condensation of \bar{C} with benzaldehydesulfonic acid-4 and use as motheroofing agt. see (12).]

[C in MeOH/KOH refluxed 6½ hrs. with MeI (74% yield (3)), or C in aq. alk. with Me₂SO₄ (1) gives the corresp. methyl ether (4,6-dichloro-2-methylanisole), m.p. 33° (1), 29-30° (3), b.p. 230° (1); C in aq. alk. soln. treated with Et₂SO₄ gives (1) corresp. ethyl ether (4,6-dichloro-2-methylphenetole), m.p. 27.5° (1).]

- ① 4,6-Dichloro-2-methylphenyl acetate: m.p. 28.5°, b.p. 254° (1). [From Č with excess Ac₂O + a drop of conc. H₂SO₄ htd. 4 hrs. at 100° (1).]
- (1). [From C with benzoyl chloride (1).]
- 3:1020 (1) Bures, Chem. Listy 21, 108-114, 148-162, 221-227, 261-265 (1927); Cent. 1927, II 1344; C.A. 22, 63 (1928). (2) Zincke, Ann. 417, 199, 206-207, 221-222 (1918). (3) Martini, Gazz. chim. ital. 29, II 60-61 (1899). (4) Claus, Schweitzer, Ber. 19, 927-929 (1886). (5) Chulkov, Parini, Barshev, Org. Chem. Ind. (U.S.S.R.) 3, 410-412 (1937); Cent. 1938, II 305; C.A. 31, 7047 (1937). (6) Huston, Neeley, J. Am. Chem. Soc. 57, 2177 (1935). (7) Claus, Riemann, Ber. 16, 1601-1602 (1883). (8) Tanaka, Morikawa, Sakamoto, J. Chem. Soc. Japan 51, 275-277 (1930); C.A. 26, 706 (1932). (9) Korczynski, Cent. 1909, II 806. (10) Anschutz, Ann. 464, 108 (1927).
- (11) Weiler, Better (to I.G.), Ger. 557,450, Aug. 24, 1931; Cent. 1932, II 2371. (12) Weiler (to I.G.), Ger. 548,822, April 20, 1932; Cent. 1932, II 799.

3:1025 3-CHLORO-4-METHYLPHENOL OH C₇H₇OCl Beil. VI -402 VI₁— VI₂—

M.P. 55° (1) (2) B.P. 228° at 760 mm. (2) 229° at 735 mm. (1)

Long colorless ndls., markedly sol. in aq. and volatile with steam (1). — Eas. sol. alc., ether, or C_6H_6 .

[For prepn. (77% yield) from 3-chloro-4-methylaniline [Beil. XII-988] via diazo reaction see (1).]

Č dislvd. in 20% NaOH and shaken with (CH₃)₂SO₄ gives 95% yield of corresponding methyl ether, viz., 3-chloro-4-methylanisole, b.p. 212° (1). [Oxidn. of this ether with dil. aq. KMnO₄ yields (1) 2-chloro-4-methoxybenzoic acid [Beil. X-175], ndls. from aq., m.p. 208° (1).]

3:1025 (1) Ullmann, Wagner, Ann. **355**, 367-368 (1907). (2) Badische Anilin und Soda-fabrik, Ger. 156,333, Nov. 14, 1904; Cent. **1904**, II 1672.

3:1040 o-XYLYLENE (DI)CHLORIDE
$$(\omega,\omega'$$
-Dichloro-o-xylene) CH_2Cl $C_8H_8Cl_2$ Beil. V - 364 V_1 — CH_2Cl V_2 -(283)

Cryst. (from pet. eth.). — Sublimes. — Sol. alc., ether, CHCl₃, lgr. Powerful lachrymator.

[For prepn. from o-xylyleneglycol + boilg. conc. HCl see (3); from o-xylene (1:7430) + PCl₅ at 190° see (3) (4); from o-xylene (1:7430) + Cl₂ in sunlight see (1); for formn. of \tilde{C} (13%) during chloromethylation of benzyl chloride (3:8535) see (5).]

C on oxidn, with KMnO₄ yields phthalic ac. (1:0820).

3:1040 (1) Radziewanowski, Schramm, Cent. 1898, I 1019. (2) Quelet, Bull. soc. chim. (4) 53, 223 (1934). (3) Colson, Ann. chim. (6) 6, 108-109 (1885). (4) Colson, Gautier, Ann. chim. (6) 11, 22 (1887). (5) Kulka, Can. J. Research 23-B, 107 (1945).

Transparent cryst. (1) (2) from pet. eth. — Very spar. sol. cold aq.; pronounced phenolic odor (1).

[For prepn. from m-cresoldisulfonic acid by chlorination see (2); from 2-nitro-3-methylphenol via 2-amino-3-methylphenol see (2); from 2-chloro-3-methylanisole by boilg. with HI see (1).]

Č treated with $(CH_3)_2SO_4 + aq$. NaOH gives its methyl ether, 2-chloro-3-methylanisole, pr. from light pet. eth., m.p. 24.2°, b.p. 218.5° (1). [This methyl ether on oxidn. with dil. KMnO₄ (7½ hrs. for 5 g.) gave (1) 2-chloro-3-methoxybenzoic acid, stout colorless rectangles, m.p. 160.5° (1), 160° (3), Neut. Eq. 186.5.]

- **D** 2-Chloro-3-methylphenyl benzoate: from $\tilde{C} + BzCl + pyridine$, pr. from alc., m.p. 55-56° (2). [Note that this value is numerically the same as \tilde{C} and that the deriv. must be distinguished from orig. \tilde{C} , e.g., by mixed m.p. or behavior with alk.]
- 0 2-Chloro-3-methylphenyl benzenesulfonate: from C + benzenesulfonyl chloride + pyridine; pl. from alc., m.p. 58-58.5° (2). [See note for above deriv.]
- **D** 2-Chloro-3-methylphenyl p-toluenesulfonate: from $\bar{C}+p$ -toluenesulfonyl chloride + pyridine; pr. from alc. m.p. 96° (2). [Note that this deriv. does not distinguish \bar{C} from 6-chloro-3-methylphenol (3:0700) or 4-chloro-3-methylphenol (3:1535).]

3:1055 (1) Gibson, J. Chem. Soc. 1926, 1424-1428. (2) Huston, Chen, J. Am. Chem. Soc. 55, 4214-4218 (1933). (3) Hodgson, Beard, J. Chem. Soc. 1926, 150.

3:1057 4,4'-DICHLORODIPHENYL- C₁₃H₁₀Cl₂ Beil. V - 590 W₁— CH₂ CH₃H₁₀Cl₂ Beil. V - 590 V₁— V₂-(501) M.P. 55-56° (1) B.P. 337° at 760.5 mm. (5) 55° (2) (3) (4) (5) 186-190° at 18 mm. (1)

208-210° at 15 mm.

(3)

Colorless ndls, from MeOH.

54-55° (7)

[For prepn. of \bar{C} from 4,4'-dichlorobenzophenone (3:4270) by reduction with conc. HI + red P in boilg. AcOH (4) or as by-prod. of reduction with Zn dust + AcOH + dil. H₂SO₄ (5) see indic. refs.; from 4,4'-diaminodiphenylmethane [Beil. XII-238, XII₁-(71)] by tetrazotization and subsequent use of Cu₂Cl₂ reaction (50% yield) see (1).]

[For prepn. of \bar{C} from chlorobenzene (3:7903) by action of sym-dichloro-dimethyl ether (3:5245) in pres. of ZnCl₂ (3) or better (alm. 100% yield (3)) conc. H₂SO₄ at 40°, or by action in pres. of H₂SO₄ of various other formaldehyde derivs. (6), see indic. refs.; from p-chlorobenzyl chloride (3:0220) with chlorobenzene (3:7903) + conc. H₂SO₄ (67% yield (3)) see indic. refs.]

[For prepn. of $\bar{\mathbb{C}}$ from "DDT" (3:3298), from 1,1-dichloro-2,2-bis-(p-chlorophenyl)-ethylene (3:2438), or from di-(p-chlorophenyl)acetic acid (3:4612) by action of KOH in ethylene glycol refluxed 8-10 hrs. (alm. 100% yield) see (2).]

[For form. of \bar{C} (21% yield) from hydrazone of 4,4'-dichlorobenzophenone (3:4270) via Wolff-Kishner reduction see (7).]

C on oxidn. with CrO₃/AcOH readily gives (3) 4,4'-dichlorobenzophenone (3:4270),

m.p. 145° (3).

 \tilde{C} on dinitration by addn. to 8 pts. fumg. HNO₃ (D=1.5) with water cooling gives (1) 3,3'-dinitro-4,4'-dichlorophenylmethane, white pl. from AcOH, m.p. 198-199° (1), 196° (3); this prod. with piperidine splits out 2 moles HCl giving (1) 3,3'-dinitro-4,4'-dipiperidinodiphenylmethane, m.p. 183-184° (1). — [Note, however, that \tilde{C} dislvd. in 9-10 wt. pts. conc. HNO₃ (D=1.42) and kept at 100° for 1 hr. (3) gives some of the above dinitro derivative but is also in part oxidized and nitrated (or vice versa) with formn. of 3,3'-dinitro-4,4'-dichlorobenzophenone, ndls. from alc., m.p. 132° (3); see also text of 4,4'-dichlorobenzophenone regarding nitration.]

3:1057 (1) LeFevre, Turner, J. Chem. Soc. 1927, 1120. (2) White, Sweeney, U.S. Pub. Health Repts. 60, 66-71 (1945). (3) Stephen, Short, Gladding, J. Chem. Soc. 117, 522-523 (1920). (4) Montagne, Rec. trav. chim. 25, 390 (1906). (5) Montagne, Rec. trav. chim. 25, 412 (1906). (6) Bentley, Catlow (to W. Blythe and Co., Ltd.), Brit. 446,450, May 28, 1936; Cent. 1936, II 4050-4051; C.A. 30, 6760 (1936). (7) Grummitt, Jenkins, J. Am. Chem. Soc. 68, 914 (1946).

3:1058 β,β-DICHLOROPROPIONIC ACID

 $C_3H_4O_2Cl_2$

Beil. II -252

130

Cl₂CH.CH₂.COOH

M.P. 56° (1)

Colorless cryst., eas. sol. aq., alc., ether, C6H6, or CHCl3.

[For prepn. of \bar{C} from β -chloroacrylic acid (3:2240) by addn. of 1 HCl with 40% aq. HCl in s.t. at 80-85° for 35-40 hrs. (yield not stated) see (1).

 \bar{C} with alc. KOH splits out 1 HCl giving (1) β -chloroacrylic acid (3:2240).

 \bar{C} with SOCl₂ at 75-80° for 3-4 hrs. gives (2) β,β -dichloropropionyl chloride (3:9032-A).

- Methyl β , β -dichloropropionate: unreported.
- Ethyl β,β-dichloropropionate: b.p. 171-175° (1). [From C in EtOH with dry HCl (1).]
- \mathfrak{D} β,β -Dichloropropionamide: ndls. from CHCl₃, m.p. 140° (1). [From ethyl β,β -dichloropropionate (above) with conc. aq. NH₄OH on shaking at room temp. (1).]
- B.B-Dichloropropionanilide: unreported.
- β_{β} -Dichloropropion- β -toluidide: unreported.

3:1058 (1) Otto, Ann. 239, 266-272 (1887). (2) Leimu, Ber. 70, 1050 (1937).

3:1060 2,3,5-TRICHLOROBENZALDEHYDE

C7H3OCl3

Beil. S.N. 635

M.P. 56° (1)

Colorless and s. (from dil. alc.) with characteristic pungent odor. — Volatile with steam. — [Note that a patent abstract gives m.p. as 75-76° (2).]

[For prepn. of \bar{C} from 3-amino-2,5-dichlorobenzaldehyde (presumably by diazotization and use of Cu₂Cl₂ reaction) see {1}.]

 \tilde{C} on oxidn. with neutral KMnO₄ gives (1) 2,3,5-trichlorobenzoic acid (3:4485), m.p. 162-163°.

 \bar{C} with PCl₅ should give 2,3,5-trichlorobenzal (di)chloride, but this compd. is unreported in the literature.

- 2,3,5-Trichlorobenzaldoxime: unreported.
- 2,3,5-Trichlorobenzaldehyde phenylhydrazone: unreported.
- ---- 2,3,5-Trichlorobenzaldehyde p-nitrophenylhydrazone: unreported.
- 2,3,5-Trichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.

3:1060 (1) Hodgson, Beard, J. Chem. Soc. **1927**, 2381–2382. (2) Chem. Fabrik Griesheim-Elektron, Brit. 251,511, May 27, 1926; Cent. **1926**, II 2355; [C.A. **21**, 1361 (1927)]; French 603,-650, April 20, 1926; Cent. **1926**, II 2355; not in C.A.

M.P. 56-57° (1) (4) B.P. 118-121° (1) 55-56° (2) 96-97.5° (2)

Cryst. from C₆H₆ (3). — Eas. sol. aq. or ether; sol. CS₂.

[For prepn. of \bar{C} from dichloroacetaldehyde (3:5180) with a limited amt. of cold aq. see (2); for formn. of \bar{C} from α,β,β -trichloroethyl ethyl ether with aq. see (2); for formn. of \bar{C} as by-product of actn. of Cl_2 on paraldehyde in prepn. of butyrchloral (3:5910) see (2); for formn. of \bar{C} from chloral hydrate with Al/Hg + aq. see (5).]

C with conc. H₂SO₄ yields (3) dichloroacetaldehyde (3:5180), b.p. 89°.

3:1085 (1) Denaro, Gazz. chim. ital. 14, 119-120 (1884). (2) Oddo, Mameli, Gazz. chim. ital. 33, II 398-399 (1903). (3) Friedrich, Ann. 206, 251-254 (1880). (4) Ingold, J. Chem. Soc. 125, 1537 (1924). (5) Deodhar, J. Indian Chem. Soc. 11, 84 (1934).

[See also 2-chlorohydroquinone (3:3130).]

Pale yel. cryst.; eas. sol. aq., alc., ether, $CHCl_3$. — Volatile even at ord. tem. — Gradually dec. by light (3) (for study of photochem. decompn. in alc. see (12)). — Sol. in conc. H_2SO_4 on warming with brown black color.

[For prepn. of \tilde{C} from 2-chlorohydroquinone (3:3130) by oxidn. with NaClO₃ + H₂SO₄ + V₂O₅ in AcOH (92% yield (13)), with K₂Cr₂O₇ + H₂SO₄ (yield: 89% (14), 84% (1)) (7), with MnO₂ + dil. H₂SO₄ (56% yield (1)), or with PbO₂ in C₆H₆ (2) see indic. refs.; from 2-chloro-4-aminophenol [Beil. XIII-510, XIII₁-(181)] by oxidn. with K₂Cr₂O₇ +

H₂SO₄ (68% yield (8)) (10) (15) see indic. refs.; from benzoquinone-1,4 (1:9025) in CCl₄ with ⅓ mole HCl gas see (9); for formn. of Č (together with other prods.) from oxidn. of copper salt of quinic acid [Beil. X-535, X₁-(270)] with MnO₂, NaCl + dil. H₂SO₄ see (16).]

[For use of C as vulcanization accelerator see (17); for use as seed disinfectant see (18);

for study of bactericidal action see (19).]

 $\bar{\mathbb{C}}$ on reductn. with aq. SO₂ gives (16) (7) 2-chlorohydroquinone (3:3130) (note, however, that $\bar{\mathbb{C}}$ in dil. aq. NaOH under N₂ with SO₂ is in part reduced to 2-chlorohydroquinone and in part sulfonated (20)). [For studies on oxidn.-reductn. potential of system $\bar{\mathbb{C}}$ + 2-chlorohydroquinone (3:3130) see (1) (2) (3) (21) (22) (23) (24).] — $[\bar{\mathbb{C}}$ with 2-chlorohydroquinone (3:3130) yields (1) (16) (25) the corresp. quinhydrone, monohydrate, violet pr. with green shimmer, m.p. 70-72° (25), anhydrous form, m.p. 93-94° (25), 67° (1); $\bar{\mathbb{C}}$ with hydroquinone (1:1590) gives (25) (6) corresp. quinhydrone, dark green ndls. from alc., m.p. 132-133° (25), 130-135° (6).]

[\bar{C} in CHCl₃ with HCl gas (7) (26) or \bar{C} with hot conc. HCl (83% yield (10)) gives only 2,5-dichlorohydroquinone (3:4690), but \bar{C} in ether with HCl gas (26) or \bar{C} dislvd. in cold dil. HCl (D=1.10) (26) gives both 2,3-dichlorohydroquinone (3:4220) and 2,5-dichlorohydroquinone (3:4690); \bar{C} refluxed with conc. HBr gives (27) 2-chloro-5-bromohydroquinone [Beil. VI-853], ndls. m.p. 171-172° (28) (diacetate, m.p. 145-146° (28)); \bar{C} in alc. with KCN + H₂SO₄ gives in good yield (29) 3,6-dihydroxyphthalonitrile (2,3-dicyanohydroquinone) [Beil. X-551].]

[C with Ac₂O + trace H₂SO₄ yields (29) a chloro-hydroxyhydroquinone triacetate, ndls. from alc., m.p. 96-97° (29); C with AcCl gives (28) 2,5-dichlorohydroquinone diacetate, m.p. 141°; C with AcBr gives (28) 2-chloro-5-bromohydroquinone diacetate, m.p. 145-146° (28).]

[\tilde{C} with 2,3-dimethylbutadiene-1,3 (1:8050) gives an adduct which upon oxidn. yields (30) 2-chloro-6,7-dimethylnaphthoquinone-1,4; for reactn. of \tilde{C} with diazotized aniline see (31); for addn. prods. of \tilde{C} with hexamethylbenzene (1:7265) see (5).]

[Č in alc. or AcOH on warming with aniline gives (32) 2,5-dianilinobenzoquinone-1,4 [Beil. XIV-138, XIII₁-(413)], red-br. scales, m.p. 345° u.c.]

[C in dil. alc. with NH₂OH.HCl as directed (33) gives 2-chlorobenzoquinone-1,4-monoxime-4 (purified (with difficulty) by conv. to the mixt. of stereoisomeric oxime acetates followed by hydrolysis), m.p. 142° (34), 148° dec. (35); this prod. by special treatment yields a dioxime [Beil. VII-632].]

 \tilde{C} in cold dil. alc. with semicarbazide HCl gives (36) 2-chlorobenzoquinone-1,4-semi-carbazone-4, deep yel. cryst. from acetone + pet. ether, m.p. 185° dec. (36); this prod. on boilg. with dil. aq. NaOH yields o-chlorophenol (3:5980) + N₂ + CO₂ + NH₃ (36); \tilde{C} does not give a bis-semicarbazone (36).

Conant, Fieser, J. Am. Chem. Soc. 45, 2201-2202 (1923). (2) Hunter, Northley, J. Phys. Chem. 37, 885-886 (1933). (3) LaMer, Baker, J. Am. Chem. Soc. 44, 1956, 1960 (1922).
 Clarke, J. Ind. Eng. Chem. 10, 891-895 (1918). (5) Pfeiffer, Ann. 412, 291-292 (1916).
 Siegmund, J. prakt. Chem. (2) 92, 360-361 (1915). (7) Levy, Schultz, Ann. 210, 145-147 (1881). (8) van Erp, Ber. 58, 663-665 (1925). (9) Michael, Cobb, J. prakt. Chem. (2) 82, 304-305 (1910). (10) Eckert, Endler, J. prakt. Chem. (2) 104, 83 (1922).

(11) Kehrmann, Ber. 21, 3316 (1888). (12) Leighton, Dresia, J. Am. Chem. Soc. 52, 3557-3562 (1930). (13) Underwood, Walsh, J. Am. Chem. Soc. 58, 646-647 (1936). (14) Den Holander, Rec. trav. chim. 39, 483-484 (1920). (15) Kollrepp, Ann. 234, 14 (1886). (16) Städeler, Ann. 69, 302-309 (1849). (17) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; Cent. 1933, I 3133. (18) I.G., Brit. 275,539, Sept. 28, 1927; French 623,867, July 2, 1927; Austrian 108,914, Feb. 25, 1928; Cent. 1928, I 2292. (19) Morgan, Cooper, J. Soc. Chem. Ind. 43-T, 352-354 (1924). (20) Dodgson, J. Chem. Soc. 1930, 2498-2502.

(21) Hunter, Kvalnes, J. Am. Chem. Soc. 54, 2874-2875, 2878 (1932). (22) Kvalnes, J. Am. Chem. Soc. 56, 668 (1934). (23) Conant, Fieser, J. Am. Chem. Soc. 44, 2484-2485, 2489 (1922).

(24) Conant, J. Am. Chem. Soc. 49, 293-297 (1927). (25) Ling, Baker, J. Chem. Soc. 63, 1318-1319 (1893). (26) Peratoner, Genco, Gazz. chim. ital. 24, II 394 (1894). (27) Ref. 7, pp. 160-161.
(28) Schulz, Ber. 15, 656 (1882). (29) Thiele, Günther, Ann. 349, 48, 52 (1906). (30) I.G., Brit. 324,661, Feb. 27, 1930; French 677,296, March 6, 1930; 677,781, March 14, 1930; Cent. 1930, II 810.

(31) Günther (to I.G.), Ger. 508,395, Oct. 1, 1930; Cent. 1931, I 1676; cf. Gunther (to General Aniline Works), U.S. 1,735,432, Nov. 12, 1929; Cent. 1930, II 137. (32) Niemeyer, Ann. 228, 331 (1885). (33) Kehrmann, Ann. 279, 30-39 (1894); Ber. 21, 3316-3317 (1888). (34) Bridge, Ann. 277, 100-101 (1893). (35) Fischer, Neber, Ber. 45, 1097 (1912). (36) Heilbron, Henderson, J. Chem. Soc. 103, 1416 (1913).

Lifts. from pet. ether (5), alc. (1) (5), or ether (2); eas. sol. in org. solv. except lgr. — \bar{C} on distn. even under reduced press. loses HCl with partial conversion (2) to phenyl vinyl ketone; nevertheless in small amts. of less than 10 g. \bar{C} may be distd. below 2 mm. (3); in general, however, unnecessary htg. of \bar{C} should be avoided (4).

[For prepn. of \bar{C} from β -chloropropionyl chloride (3:5690) with $C_6H_6+AlCl_3$ (yield: 90% (1), 80–90% (6), 65% (5)) see indic. refs. (note, however, that this method is best suited for small runs (6) since with large units much ω -benzylacetophenone [Beil. VII-444, VII₁-(237)], m.p. 72°, is also formed (6) (4); furthermore that \bar{C} prepd. by this method melts at 49° even when white, unless it is treated with decolorizing carbon (3); for prepn. from benzoyl chloride (3:6240) + ethylene + $AlCl_3$ (87-92% yield) in special apparatus see (3); for prepn. of \bar{C} from phenyl vinyl ketone + HCl gas in dry ether see (2); for formn. of \bar{C} from ethyl phenyl ketone (propiophenone) (1:5525) + Cl_2 see (7).]

[\bar{C} htd. 15-30 min. in AcOH with 1½ moles NaOAc or KOAc, then poured into aq. and neutralized with K₂CO₃, gives (8) β -acetoxypropiophenone, lfts. from MeOH, m.p. 53-54° (8); \bar{C} in hot alc. treated with KOAc, then with aq. NaCN, gives (65% yield (9)) β -cyanopropiophenone, lfts. from alc., m.p. 76° (2,4-dinitrophenylhydrazone, m.p. 141°; corresp. β -benzoylpropionic acid, m.p. 116° (9)).]

[\bar{C} under certain circumstances reacts as potential phenyl vinyl ketone: e.g., \bar{C} + KOAc in hot MeOH treated with phenyl-nitromethane + NaOMe gives (82% yield (10)) (presumably by addn. to phenyl vinyl ketone) γ -nitro- γ -phenylbutyrophenone, ndls. from C_6H_6 + pet. eth. or from MeOH, m.p. 72° (10); similarly \bar{C} + KOAc in hot MeOH treated with desoxybenzoin (1:5165) + NaOMe gives (55% yield (6)) 1,2,5-triphenylpentanedione-1,5, m.p. 95° (monoxime, m.p. 131°; dioxime, m.p. 162°; 2,4-dinitrophenylhydrazone, m.p. 221°) (6).]

 \bar{C} in AcOH reduced with H_2 + Adams cat. gives (11) 3-chloro-1-phenylpropanol-1, b.p. 130-132° at 8 mm. (p-nitrobenzoate, m.p. 62-63°) (11).

[For study of rate of reactn. of \bar{C} with KI in acctone see (5); for study of \bar{C} with Na + liq. NH₃ see (12); for behavior of \bar{C} with anthrone see (13) (14) (15); for reactn. of \bar{C} with C_6H_5MgBr yielding ω -benzylacetophenone (β -phenylpropiophenone) (cf. above) see

(16) (2); for reactn. of \bar{C} with sodium benzenesulfinate giving (68% yield) β -(benzenesulfonyl)propiophenone, m.p. 98° see (17).]

 \tilde{C} htd. with aq. + aniline for 30 min. at 100° gives (4) β -anilinopropiophenone, pl. from alc., m.p. 111-112° (4); note, however, that \tilde{C} htd. with aniline + aniline HCl yields (4) 4-phenylouinoline.

[C in MeOH boiled 3 hrs. with hydrazine hydrate (87%) gives (28% yield (18)) 3-phenylpyrazoline-2, b.p. 164° at 17 mm., m.p. 44-45° (18) (1-nitroso deriv., m.p. 152.5-153.5°; 1-carbomethoxy deriv., m.p. 123-124°; 1-carbothoxy deriv., m.p. 72°) (18). — C (or phenyl vinyl ketone) with phenylhydrazine yields by ring closure (19) 1,3-diphenyl-pyrazoline-2 [Beil. XXIII-153], m.p. 152-153° (19).]

[$\bar{\mathbf{C}}$ htd. in alc. with NH₂OH.HCl + NaOH gives very small yield (8) corresp. oxime, m.p. 56-58°; from the mother liquor, however, is obtd. (8) as a result of ring closure 3-phenylisoxazoline, tbls. from lgr. m.p. 66-67°, which is the sole product starting from β -acetoxypropiophenone (above); another by-product of oximation is N,N-bis-(β -benzoylethyl)hydroxylamine dioxime, m.p. 154-155° (8).]

- β-(Phthalimido) propiophenone: cryst. from alc., m.p. 130° (1). [From C + K phthalimide in 68% yield on htg. in s.t. for 1 hr. at 130-140° (1); on hydrolysis with fumg. HCl in AcOH in s.t. at 145-150° for 1 hr. this prod. gives 95% yield (1) β-aminopropiophenone hydrochloride, cryst. from abs. alc., m.p. 128° (1).]
- ① 1-Methyl-3-carbohydrazidopyridinium p-toluenesulfonate: cryst. from alc., m.p. 171° cor. (20). [From Č + nicotinic hydrazide/methyl p-toluenesulfonate addn. prod. as directed (20).]
- 3:1115 (1) Hale, Britton, J. Am. Chem. Soc. 41, 845-847 (1919). (2) Kohler, Am. Chem. J. 42, 389 (1909). (3) Allen, Cressmann, Bell, Can. J. Research 8, 440-446 (1933). (4) Kenner, Statham, J. Chem. Soc. 1935, 301. (5) Conant, Kirner, J. Am. Chem. Soc. 46, 239-240, 251 (1924). (6) Allen, Barker, J. Am. Chem. Soc. 54, 740-742 (1932). (7) Szper, Bull. soc. chim. (4) 51, 656 (1932). (8) von Auwers, Müller, J. prakt. Chem. (2) 137, 124-127 (1937). (9) Allen, Gilbert, Young, J. Org. Chem. 2, 231 (1937). (10) Allen, Bridgess, J. Am. Chem. Soc. 51, 2153-2154 (1929).
- (11) Case, J. Am. Chem. Soc. 55, 2929 (1933). (12) Dean, Berchet, J. Am. Chem. Soc. 52, 2826 (1930). (13) Allen, Overbaugh, J. Am. Chem. Soc. 57, 1322-1325 (1935). (14) Nakanishi, Proc. Imp. Acad. Tokyo 9, 394-397 (1933); Cent. 1934, II 2218; C.A. 28, 762-763 (1934). (15) Kränzlein, Vollmann, Greune, Wolfraim, Ger. 488,608, Jan. 18, 1920; Cent. 1930, II 3860. (16) Weizmann, Bergmann, J. Chem. Soc. 1936, 402. (17) Kohler, Larsen, J. Am. Chem. Soc. 57, 1449 (1935). (18) von Auwers, Heimke, Ann. 458, 207-208 (1927). (19) von Auwers, Ber. 65, 832-833 (1932). (20) Allen, Gates, J. Org. Chem. 6, 596-601 (1941).

3:1130 p-METHYLPHENACYL CHLORIDE C_9H_9OCl Beil. VII - 309 (Chloromethyl p-tolyl ketone, CH_3 CO.CH₂Cl VII_1 -(165) ω -chloro-p-methylacetophenone)

M.P. 57-58° (1) (5) B.P. 260-263° (2) 55.5-56° (2) (3) 260-265° sl. dec. (3) 54.5-55° (4) 113° at 4 mm. (4)

Ndls. from alc.; eas. sol. alc., ether.

[For prepn. from toluene (1:7405) + chloroacetyl chloride (3:5235) + AlCl₃ see (2) (3); from toluene + chloroacetic acid anhydride (3:0730) + AlCl₃ (46-59% yield) see (4).]

C on oxidn. with alk. KMnO₄ gives terephthalic ac. (1:0910) (2).

 \bar{C} with NaI in acetone gives p-methylphenacyl iodide, ndls. from alc., m.p. 42-43° (11).

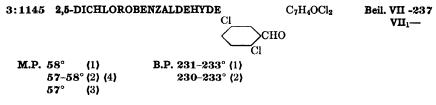
C refluxed with alc. KOAc yields (2) p-methylphenacyl acetate [Beil. VIII-113], ndls from alc., m.p. 83-83.5° (2), 85-86° (1).

 \bar{C} dislyd. in alc. warmed at 60° with Na₂S.9H₂O dislyd. in aq. gives (5) (73% yield (6)) bis-(p-methylphenacyl)sulfide, pale yel. ndls. from alc., m.p. 88° (5); 88.8-89.3° (6). [For detn. of \bar{C} by titration of residual chloride ion from this reaction see (5).]

[For reactions of \bar{C} with phenol + KOH + Cu see (7); with phenyl-p-bromophenyl-, p-nitrophenyl-, o-tolyl-, and p-tolyl-hydrazines see (5); with Br₂ see (8); with KCN or KSCN see (9); with alc. NaOEt see (10).]

3:1130 (1) von Auwers, Ber. 39, 3761 (1906). (2) Collet, Bull. soc. chim. (3) 17, 507-508 (1897). (3) Ryan, Ber. 31, 2132 (1898). (4) Noller, Adams, J. Am. Chem. Soc. 46, 1893-1894 (1924). (5) Hoogeveen, Rec. trav. chim. 50, 674-677 (1931). (6) Chrzaszc-Zewska, Chwalinski, Roczniki Chem. 8, 432-443 (1928); Cent. 1929, I 511; C. A. 23, 1629 (1929). (7) Sabetay, Bull. soc. chim. (4) 45, 537 (1929). (8) Rabcewicz-Zubkowski, Roczniki Chem. 10, 541-544 (1930); Cent. 1930, II 3273. (9) Rabcewicz-Zubkowski, Kaflinska, Roczniki Chem. 10, 555-569 (1930); Cent. 1930, II 3274. (10) Almström, Ber. 47, 848-849 (1914).

(11) Jacobs, Heidelberger, J. Biol. Chem. 21, 456 (1915).



Ndls. from alc. (4). — Very eas. sol. alc., ether, CHCl₃, C₆H₆, CS₂, AcOH (4). — Eas. volatile with steam (4). — Sol. in conc. H₂SO₄ with olive-yel. color; repptd. in cryst. form on dilution (4) (8).

[For prepn. of \bar{C} from benzaldehyde (1:0195) by chlorination in presence of SbCl₅ + I₂ see (5) (1) (9); from 2,5-dichlorotoluene (3:6245) by chlorination to 2,5-dichlorobenzal (di)chloride (3:0490) (m.p. 42°) and hydrolysis of the latter with CaCO₃ + H₂O see (1); from 5-nitro-2-chlorobenzaldehyde via reduction to 5-amino-2-chlorobenzaldehyde followed by diazotization + use of CuCl see (6).]

 \bar{C} with satd. aq. NaHSO₃ soln. yields a cpd., \bar{C} .NaHSO₃ (5), ndls. fairly eas. sol. aq. but dissociating on warming into \bar{C} + aq. (5).

 \bar{C} on oxidn. with KMnO₄ (2) (4) yields 2,5-dichlorobenzoic ac. (3:4340), m.p. 152° (2), 152-153° (4). — \bar{C} with 50% aq. KOH (5) (1) (6) undergoes Cannizzaro reactn. giving (90% yield (6)) 2,5-dichlorobenzyl alc., cryst. from C₆H₆, m.p. 80° (1) (6), and (84% yield (7)) 2,5-dichlorobenzoic ac. (3:4340), cryst. from aq., m.p. 155° (5) (7). — \bar{C} on reductn. with 4% Na/Hg in alc. yields (1) 2,5-dichlorobenzyl alc., m.p. 80° (1).

Č with PCl₅ (3) gives (78% yield (3)) 2,5-dichlorobenzal (di)chloride (3:0490), b.p. 118-120° at 14 mm., m.p. 42° (8), 43° (3).

C on mononitration as specified (5) gives (100% yield (9)) a mixt. of two isomers; by recrystallization from MeOH (9) or EtOH (5) this mixt gives (62% yield (9)) 2,5-dichloro-6-nitrobenzaldehyde, lfts. or ndls., m.p. 137° (5); the other more soluble isomer is 2,5-dichloro-3-nitrobenzaldehyde (10), m.p. 66.5-67° (5). [The latter yields a phenylhydrazone, or. ndls., m.p. 171°, a p-nitrophenylhydrazone, deep or. ndls., m.p. 290-292° dec., and on oxidn. with alk. KMnO₄ yields 2,5-dichloro-3-nitrobenzoic ac., colorless ndls. from AcOH, m.p. 220° (10).]

[For conversion of Č to 2,5-dichlorostyrene (12) (13) via reaction with MeMgX giving (83% yield (12)) 2,5-dichlorophenyl-methyl-carbinol and dehydration of latter with KHSO₄ (37% yield (12)) see indic. refs.]

Č htd. with NaOAc + Ac₂O for 8 hrs. at 180-200° gives (78% yield (11)) 2,5-dichlorocinnamic ac., colorless cryst. from dil. alc. or from AcOH, m.p. 194.5° cor. (11).

Č in alc. boiled a few minutes with aniline (1 mole) gives (5) 2,5-dichlorobenzal anil, lfts. from alc., m.p. 71.5-72° (5).

- 2.5-Dichlorobenzaldoxime: ndls. from dil. alc., m.p. 127.5-128° (5).
- 2,5-Dichlorobenzaldehyde phenylhydrazone: cryst. from alc., m.p. 104-105° (5).
- --- 2,5-Dichlorobenzaldehyde p-nitrophenylhydrazone: unrecorded.
- 2.5-Dichlorobenzaldehyde 2.4-dinitrophenylhydrazone: unrecorded.
- 2,5-Dichlorobenzaldehyde semicarbazone: unrecorded.

3:1150 TRICHLOROACETIC ACID Cl₃C—COOH

3:1145 (1) de Crauw, Rec. trav. chim. 56, 773-774 (1931). (2) Gnehm, Ber. 17, 753 (1884). (3) Asinger, Lock, Monatsh. 62, 336-337 (1933). (4) Erdmann, Schwechten, Ann. 260, 70-72 (1890). (5) Gnehm, Banziget, Ber. 29, 875-876 (1896), Ann. 296, 62-80 (1897). (6) Erdmann, Ann. 272, 154-156 (1892). (7) Lock, Ber. 66, 1531 (1933). (8) Gnehm, Schule, Ann. 299, 359-361 (1898). (9) Lock, Ber. 68, 1508-1509 (1935). (10) Hodgson, Beard, J. Chem. Soc. 1927, 2381.

(11) Bock, Lock, Schmidt, Monatsh. 64, 407 (1934). (12) Brooks, J. Am. Chem. Soc. 66, 1297 (1944). (13) Michalek, Clark, Chem. & Eng. News 22, 1559-1563 (1944).

C₂HO₂Cl₃

Beil. II - 206

```
II_{1}-(92)
                                                                                  II_{2}-(196)
M.P.
                         B.P.
                                                                 D_4^{125} = 1.5082 (9)
59.4°
               (1)
                         197.55°
                                         at 760 mm. (25) (26)
                                                                 D_4^{\tilde{1}00} = 1.5451 (9)
59.2°
               (2) (5)
                         196-197°
                                         cor.
                                                      (27)
                                                                  D_4^{75} = 1.5829 (9)
59.10°
               (3)
                         196.5°
                                                       (3)
                                                                  D_4^{\hat{6}08} = 1.6030 (31)
58.9°
               (5)
                         196°
                                         at 760 mm. (28)
58.7°
                         195.5°
                                                                      n_{\rm D}^{60.8} = 1.4603 (31)
               (5)
                                         at 765 mm. (9)
                                                                  D_4^{25} = 1.62
58.6°
               (5)
                         195.0-195.5° at 754 mm. (20)
58.5°
               (4) (5)
                         195°
                                                                 [For D_4^t over temp.
                                                      (24)
58.3°
               (5)
                         194.1-194.7°
                                                      (29)
                                                                 range 80.2°-196° see
58.1°
               (5)
                                                                 (9).]
58°
               (6)
                         141-142°
                                         at 25 mm. (30)
57.9°
              (5)(7)
                         115°
                                         at 22 mm. (19)
57.8°
               (5)
                         107°
                                         at 21 mm. (9)
57.6°
               (8)
57.5°
              (5)(9)
57.4°
             (11)
57.3°
              (7) (10)
             (11) (74)
57.2°
              (5) (12)
57°
             (13) (14)
             (15) (16) (17) (18) (19)
             (20) (78)
56.7-56.8° (21)
```

[See also chloroacetic acid (3:1370) and dichloroacetic acid (3:6208).]

56.3° cor.

55°

(22)

(23) (24)

MISCELLANEOUS PHYSICAL PROPERTIES OF C

POLYMORPHISM OF C

Note that unlike chloroacetic acid (3:1370) \bar{C} does not exhibit polymorphism [however, for a possible unstable form melting about 50° see (10)].

CRYOSCOPIC CONSTANT OF C

[Molal f.p. constant for \tilde{C} is 12.07° (for 1000 g. \tilde{C}) (32); for use of \tilde{C} as cryoscopic solvent see (17).]

Association of C

[For studies on extent of association of \tilde{C} in vapor as function of temp. (28), in C_6H_6 soln. (33) (34), in liq. HF (35) (36), in phenol (37), or in p-chlorotoluene (3:8287) (42), see indic. refs.]

HEAT OF COMBUSTION OF C

[For studies on heat of combustion of \bar{C} see (38) (39) (40) (41).]

EXCHANGE REACTIONS

[For study of behavior of \bar{C} with H_2O^{18} see (43).]

Adsorption of C by Various Adsorbents

[For studies on adsorption of \bar{C} from aqueous solns. by various forms of carbon (44) (45) (46) (47) (48) (49), by silica gel (46), by filter paper (50), by hide-powder (51), by viscose (52), by synthetic resins (53), by freshly pptd. Fe(OH)₃ (54), by metastannic acid (55), see indic. refs.]

[For studies on adsorption of C from non-aqueous solvents by wood charcoal (56), or from aq. alc. by charcoal (57), see indic. refs.]

DISTRIBUTION OF C BETWEEN SOLVENTS

[For data on distribution of \bar{C} between aq. and ether at 25° (58) (59); between aq. and amylene at 22° (60) cf. (61); between aq. and C_6H_6 (60) (61) (62) cf. (63); between aq. and toluene at 25° (64); between aq and isopropylbenzene (cumene) at 25° (64); between aq. and n-AmOH at 25° (64); between aq and iso-AmOH at 25° (64); between aq and olive oil at 25° and 37° (65), see indic refs.]

[For data on distribution of C between aq. and nitrobenzene at 25° (62) (64), between aq. and o-nitrotoluene at 25° (64) (68), see indic. refs]

[For data on distribution of \tilde{C} between aq. and $CHCl_3$ (3:5050) at 25° (62) (64); between aq. and CCl_4 (3:5100) at 25° (62) (64); between aq. and EtBr at 25° (64); between aq. and MeI at 25° (64) (69), see indic. refs.]

[For data on distribution of \bar{C} between aq. and CS_2 at 25° (62); between acetone and glycerol at 25° (66); for distribution of \bar{C} between aq. and mixtures of C_6H_6 + nitrobenzene (67); between aq. and mixtures of C_6H_6 + cH_6 + cH_6 + cH_6 (67), see indic. refs.]

BINARY SYSTEMS CONTG. C

Azeotropic Systems

[$\bar{\mathbf{C}}$ with pentachloroethane (3:5880) forms a const.-boilg. mixt., b.p. 161.8° at 760 mm., contg. 3.5 wt. % $\bar{\mathbf{C}}$ (25); $\bar{\mathbf{C}}$ with p-dichlorobenzene (3:0980) forms a const.-boilg. mixt., b.p. 174.0° at 760 mm., contg. about 12 wt. % $\bar{\mathbf{C}}$ (26); $\bar{\mathbf{C}}$ with o-bromotoluene forms a const.-boilg. mixt., b.p. 180.0° at 760 mm., contg. about 18 wt. % $\bar{\mathbf{C}}$ (26).]

Other Physical Data on Binary Systems Contg. C

 $\tilde{\mathbf{C}}$ + aq. [$\tilde{\mathbf{C}}$ is eas. sol. aq.; for study of hydration at -35° see (70) cf. (34); for f.p./compn. data see (3); for data on D_{20}^{20} (31) and D_{25}^{25} (71) of aq. solns. see indic. refs.; for n_D^{18} (8), n_D^{20} (31) cf. (73) see indic. refs.]

 $\bar{C} + H_2SO_4$. [For f p./compn. data and diagram (no compd. formed) see (10).]

 $\bar{C} + H_3PO_3$. [For f p./compn. data and diagram (no compd. formed) see (12).]

 $\tilde{\mathbf{C}}$ + AcOH (1:1010). [For f.p./compn. data (no epd.) (74), D_4^{25} (2), viscosity (2), and conductivity (1) see indic refs.]

 $\ddot{\mathbf{C}}$ + chloroacetic acid (3:1370). [For f.p./compn. data (74), eutectic, m.p. 17.5°, contg. 51.5 mole % $\ddot{\mathbf{C}}$ (75), see indic. refs.]

 \bar{C} + dichloroacetic acid (3:6208). [For f.p./compn. data (74), eutectic, m.p. -11.0°, contg. 36 mole % \bar{C} (75), see indic. refs.]

 $\ddot{\mathbf{C}}$ + miscellaneous cpds. of Order 1. [For f.p./compn. data on following systems see indic. refs.]

 \bar{C} with hydrocarbons: $\bar{C} + C_6 II_6$ (1:7400) (5); \bar{C} + camphene (76).

 \vec{C} with alcohols: \vec{C} + EtOH (1:6130) (14); \vec{C} + ter-BuOH (1:6140) (14); \vec{C} + cetyl alc. (1:5945) (14); \vec{C} + d-borneol (1:5990) (14); \vec{C} + l-menthol (1:5940) (14); \vec{C} + pinacol (1:5805) (14); \vec{C} + meso-erythritol (1:5825) (6); \vec{C} + d-manntol (1:5830) (14).

 \bar{C} with phenols: \bar{C} + phenol (1:1420) (14) (11); \bar{C} + o-cresol (1:1400) (11); \bar{C} + m-cresol (1:1730) (11); \bar{C} + p-cresol (1:1410) (11); \bar{C} + quaiacol (1:1405) (14); \bar{C} + thymol (1:1430) (11); \bar{C} + α -naphthol (1:1500) (11); \bar{C} + β -naphthol (1:1540) (11); \bar{C} + hydroquinone (1:1590) (14)

 \bar{C} with aldehydes: \bar{C} + benzaldehyde (1:0195) (7); \bar{C} + salicylaldehyde (1:0205) (7); \bar{C} + m-hydroxybenzaldehyde (1:0055) (7); \bar{C} + p-hydroxybenzaldehyde (1:0060) (7); \bar{C} + p-anisaldehyde (1:0240) (7); \bar{C} + vanillin (1:0050) (7); \bar{C} + p-peronal (1:0010) (7).

 \bar{C} with ketones: \bar{C} + acetophenone (1:5515) (7); \bar{C} + benzophenone (1.5150) (7); \bar{C} + p-methoxybenzophenone (1:5170) (7); \bar{C} + benzil (1:9015) (7); \bar{C} + dibenzalacetone (1:9024)

(7); \bar{C} + benzoquinone-1,4 (1:9025) (7). \bar{C} with acids: \bar{C} + acetrc acid (1:1010) (74); \bar{C} + benzoic acid (1:0715) (74); \bar{C} + o-toluic acid (1:0690) (74); \bar{C} + m-toluic acid (1:0705) (74); \bar{C} + p-toluic acid (1:0795) (74); \bar{C} + phenylacetic acid (1:0665) (74); \bar{C} + cinnamic acid (1:0735) (74); \bar{C} + crotonic acid (1:0425) (74).

 \bar{C} with esters: \bar{C} + EtOAc (1:3015) (5); \bar{C} + α -naphthyl acetate (1:2124) (5); \bar{C} + β -naphthyl acetate (1:2273) (5); \bar{C} + methyl benzoate (1:3586) (5); \bar{C} + ethyl benzoate (1:3721) (5); \bar{C} + benzyl benzoate (1:4422) (5); \bar{C} + phenyl benzoate (1:2257) (5); \bar{C} + methyl cinnamate (1:2090) (5); \bar{C} + phenyl salicylate ("Salol") (1:1415) (5); various others (5).

 \bar{C} with ethers: \bar{C} + duethyl ether (1:6110) (77); \bar{C} + veratrole (1:7560) (14)

 $\tilde{\mathbf{C}}$ + compounds of Order 2. $\tilde{\mathbf{C}}$ + o-nutrophenol (11); $\tilde{\mathbf{C}}$ + m-nitrophenol (11); $\tilde{\mathbf{C}}$ + p-nitrophenol (11); $\tilde{\mathbf{C}}$ + o-nutrobenzaldehyde (7); $\tilde{\mathbf{C}}$ + m-nitrobenzaldehyde (7); $\tilde{\mathbf{C}}$ + nutrophenol (7); $\tilde{\mathbf{C}}$ + azobenzene (78); $\tilde{\mathbf{C}}$ + ethyl carbamate (urethane) (16); $\tilde{\mathbf{C}}$ + urea (78A).

BIOCHEMICAL ASPECTS OF C

[For study of toxicity of \bar{C} see (79); for study of bactericidal effect see (80) (81).]

PREPARATION OF C

From chloral (anhydrous). [For prepn. of \bar{C} from chloral (3:5210) by oxidn. with fumg. HNO₃ (82) (83) (84), with HNO₂ (85), with NO₂ at 40-60° (70% yield (86)), or with aq. chlorates + cat. see (312); for formn. of \bar{C} from chloral as by prod. of oxidn. with O₂ see (23).]

From chloral hydrate. [For prepn. of \tilde{C} from chloral hydrate (3:1270) by oxidn. with fumg. HNO₃ (63% yield (82)) (85), with KMnO₄ (88), with KClO₃ (89), with Ca(OCl)₂ (15), or with an chlorates + cat. (312) see indic. refs.]

From acetic acid. [For formn. (first discovery) of \bar{C} from acetic acid (1:1010) by chlorination with Cl_2 in sunlight see (90).]

From tetrachloroethylene. [For form. of \bar{C} from tetrachloroethylene (3:5460) by stdg. in aq. in light for 4 months see (91) cf. (92); for many other methods see text of tetrachloroethylene (3:5460) under oxidation.]

From miscellaneous sources. [For form. of \bar{C} from pentachloroethyl chloroformate [Beil. III-13, III_I-(6)] with aq. on htg. (93), but yield is small (94) owing to other modes of reaction (94); from pentachloroethyl trichloroacetate [Beil. II-210] with aq. (95); from trichloroacetyl chloride (3:5420) (96) or from trichloroacetic acid anhydride (3:6575) (97) (98) with aq.; from β,β,β -trichloroethyl alcohol (3:5775) by oxidn. with fumg. HNO₃ (210), see indic. refs.]

CHEMICAL BEHAVIOR OF C

Pyrolysis of C

(See also below under decarboxylation.) Pure $\bar{\bf C}$ shows no tendency to decompose at its b.p. (99). — [However, $\bar{\bf C}$ in presence of pumice begins to decompose about 180° giving (99) HCl, COCl₂ (3:5000), CO + CO₂. — $\bar{\bf C}$ in presence of ThO₂ begins to decompose at 160–165° giving (99) the same products, although $\bar{\bf C}$ in presence of ThO₂ above 210° (100) or in presence of kaolin above 230° (100) gives CHCl₃ (3:5050), tetrachloroethylene (3:5460), hexachloroethane (3:4835), HCl, CO + CO₂. — $\bar{\bf C}$ in presence of animal charcoal at 135° gives (99) CHCl₃ (3:5050) + CO₂, but at 200–300° these are accompanied (100) by a little tetrachloroethylene (3:5460), hexachloroethane (3:4835), HCl, and CO. — $\bar{\bf C}$ at 300° in s.t. for 4 hrs. gives (101) trichloroacetyl chloride (3:5420), CO, CO₂ + HCl.

REDUCTION OF C

[\bar{C} on partial reduction with Zn + aq. (102), with Cu pwdr. in aq. (103), with Cu pwdr. in C₆H₆ + aniline (104) cf. (105), or \bar{C} on electrolytic reduction (106) gives (yields: 80% (103) (106), 75-85% (104)) dichloroacetic acid (3:6208).]

[C on complete reduction with H1 at 100° (87), or in aq. soln. with K/Hg (107) (84), or by electrolytic reduction with Pt, Cu, or Pb electrodes (108) gives acetic acid (1:1010).]

 $[\bar{C} \text{ in aq. alc. KOH with H}_2/Pd \text{ gives up all its chlorine as HCl (109) presumably yielding AcOH (1:1010).]}$

REACTIONS INVOLVING THE —COOH GROUP OF C

Decarboxulation of \bar{C}

 \bar{C} in aq., in aq. alkalies, or in aniline or other organic bases undergoes cleavage into CHCl₃ (3:5050) + CO₂; for this decompn. presence of the trichloroacetate ion appears

necessary since in relatively nonbasic solvents it does not occur [e.g., \bar{C} does not decompose at 25° in C_6H_6 (110), toluene (111), CHCl₃ (110) (111), CCl₄ (110), CS₂ (110), isoamyl alc. (117), acetone (110), ether (110), ethyl acetate (117), ethyl benzoate (110), acetic acid (117), nitrobenzene (110), or 6 N H₂SO₄ (117); in MeOH (111) and in EtOH (111) (112) the only reaction is esterification (see below)].

The decompn. of \bar{C} into CHCl₃ + CO₂ by boiling with aq. or aq. alk. has long been known (90) (113) (114) (115), and KCN behaves similarly (116). — [For studies on kinetics of decompn. of \bar{C} in aq. at various temps. see (4) (118) (119) (103) cf. (120); note that rate of decompn. is catalyzed by light (111) (119) (121) (122). — For studies of decompn. of aq. solns. of various salts (117) (123) (124) (125) and influence of light (126) (127) or of presence of various other inorganic salts (128) see indic. refs. — For studies of decompn. of \bar{C} in aqueous dioxane see (129). — Note that \bar{C} with Ca(OH)₂ on htg. gives CHCl₃ and that this reaction has been patented (134).]

[For study of decompn. of \bar{C} in aniline (117) (111) (130) (131) including influence of supersonic waves (132) see indic. refs.; for decompn. of \bar{C} in tertiary bases such as dimethylaniline see (133) but note in \bar{C} does not decompose in pyridine (111).]

[\overline{C} on htg. in resorcinol or cresol gives (135) CHCl₃ + CO₂, but \overline{C} on htg. in phenol or thymol decomposes differently yielding (135) (136) phosgene (3:5000) + HCl + CO.]

[Note that, as a consequence of the decompn. of \bar{C} into CHCl₃ + CO₂, it has been employed in Reimer-Tiemann types of condensation: e.g., \bar{C} with phenol + aq. NaOH gives o-hydroxybenzaldehyde (1:0205) + p-hydroxybenzaldehyde (1:0060) (137) (138); many other phenols have also been studied (137) (138).]

Acid Strength of C

 \bar{C} in aq. soln. behaves as an exceedingly strong monobasic acid; Neut. Eq. = 163.4 (found 164.6 (91)). — [Ionization constant of \bar{C} in aq. soln. at 25° is about 1.2 (139) cf. (140), but because of strength of \bar{C} and its tendency to decompn. (see above) no accurate value is available (143). — For discussion of resonance and acid strength of \bar{C} see (141) (142) (143). — For studies of electrical conductivity of \bar{C} in aq. solns. at various temps. see (144) (145) (146) (147) (30).]

[Studies of acid strength of \tilde{C} in nonaqueous solvents include the following: in EtOH (148) (149), in n-BuOH (150) (13), in ether (151), in CHCl₃ (151), in formamide (152), in C₆H₆ (153), in chlorobenzene (154), or in dioxane (155). — For study of electrometric titration of \tilde{C} in C₆H₆ (156), in ethylene glycol monomethyl ether ("methylcellosolve") (157), in anisole-n butyl alc. (157), see indic. refs. — For titration of \tilde{C} in Ac₂O soln. with NaOAc see (158) cf. (310). — For study of behavior of \tilde{C} with indicators in C₆H₆ soln. see (159) (160).]

Catalytic Effect of C on Various Reactions

The catalytic influence of \tilde{C} upon diversified types of chem. reactions has been extensively examined; although this matter cannot be recorded exhaustively, the following examples are cited.

[For studies on catalytic effect of \bar{C} upon the inversion of *l*-menthone to *d*-isomenthone in C_6H_6 (161) (162) or in chlorobenzene (163); upon racemization of methyl-phenyl-acetophenone and of isobutyl-phenyl-acetophenone in various solvents (164); of isopulegone to pulegone in nonaqueous solvents (165); or on hydrogen disproportionation of *d*-limonene (311), see indic. refs.]

[For studies of catalytic effect of \bar{C} upon the hydrolysis of EtOAc (144) or of sucrose (166) (167) see indic. refs.]

[For studies of catalytic effect of C upon forms. of ether from EtOH (168); upon rate

of esterification of various org. acids in MeOH (169) or in EtOH (170); upon nitration of toluene (171) cf. (172); upon decompn. of ethyl diazoacetate in C_6H_6 (162) or other solvents (173) (174) (175); upon decompn. of nitramide in 180-AmOH (176); upon rearr. of N-chloroacetanilide (177); upon rearr. of N-bromoacetanilide in chlorobenzene (178) (179) or in other solvents (179); upon rearr. of N-bromobenzanilide in chlorobenzene (180); upon chromate or perchlorate oxidn. of EtOH (181); upon addition of HBr to 3-methylbutene-1 (182), see indic. refs.

Salts of C

This topic cannot here be treated exhaustively but the following examples are cited. Salts with inorganic bases. [NH₄Ā, prepn. (183); NH₄Ā.Ĉ (184) (185); 2NH₄Ā.5H₂O (186) — Hydroxylamine salt, HONH₃Ā, cryst. from dry ether by pptn. with lgr., m.p. 133-134° (187).]

[Li \bar{A} , n_D^{18} of aq. solns. (8), nonhygroscopic cpds. with betaine or pyridine betaine (188); Li \bar{A} .2H₂O (189), conductivity of aq. solns. (190). — Na \bar{A} (198), effect of dry distillation (191), conductivity in aq. (190) (192), in dry MeOH (193), in dry EtOH (194); n_D^{18} of aq. solns. (8); Na \bar{A} .3H₂O (196). — K \bar{A} .H₂O (189) (198), solubility and decompn. (197); K \bar{A} .C (184) (185).

[AgĀ, spar. sol. aq., darkens in air; on dry htg. decomposes above 80° (199) yielding (198) AgCl, CO, CO₂, and trichloroacetic acid anhydride (3:6575); with boilg. aq. AgĀ yields (198) AgCl, CO, CO₂, CHCl₃ (3:5050), and \bar{C} ; for behavior of AgĀ with I₂ in C₆H₆ see (200). — HgĀ, ndls. from aq. in which it is spar. sol. (201) (202) (203) (209) (note that it soluble in C₆H₆ (202)). — HgĀ₂, attempts to prepare this mercuric salt have been unsuccessful (201) (204); aq. solns. of \bar{C} react with HgO long after theoretical amt. has been used (201), and CO, CO₂, and CHCl₃ are also formed (205).]

[Mg $\bar{A}_2.4H_2O$ (189). — Ca $\bar{A}_2.6H_2O$ (196); Ca $\bar{A}_2.3I_2H_2O$, cas. sol. (198). — Sr $\bar{A}_2.6H_2O$ (196). — Ba $\bar{A}_2.6H_2O$ (196); Ba $\bar{A}_2.2H_2O$ (206). — Pe $\bar{A}_2.2H_2O$ (207) (206) — Cd \bar{A}_2 (208); Cd $\bar{A}_2.1I_2H_2O$ (217). — Zn $\bar{A}_2.6H_2O$ (209). — Pb $\bar{A}_2.I_2H_2O$ (210); Pb $\bar{A}_2.H_2O$ (83). — Cu $\bar{A}_2.6H_2O$ (83) (could not be confirmed (201) (211)); Cu $\bar{A}_2.4H_2O$ (211); Cu $\bar{A}_2.3H_2O$ (201) (complexes with benzylamine (212)); Cu $\bar{A}_2.2H_2O$ (complexes with various amines (213)); Cu \bar{A}_2 (201) (complexes with various amines (213)); electrolysis (215), electrometric titration (216).]

[Mn \bar{A}_2 .3½ H₂O (217). — Co \bar{A}_2 .4H₂O (218) (complexes with various amines (218) (219)); Co \bar{A}_2 .3½H₂O (217). — Ni \bar{A}_2 .4H₂O (189) (218) (complexes with NH₃ (211) and various amines (220)).]

Salts with organic bases. [Antline trichloroacetate, from $\bar{\mathbb{C}}$ (1 mole) + aniline (1 mole) in C_6H_6 (223) (224), or without solvent (225), or in aq. (226); this salt has no true m.p. (224) although various values ranging from 145° (226) to 163° (225) have been reported. — Note that, although action of heat would be expected to cause loss of H_2O giving ω,ω,ω -trichloroacetanilide (see below), no actual study has been reported. — Note that $\bar{\mathbb{C}}$ + aniline + Cu powder in C_6H_6 soln. gives dichloroacetic acid (3:6208) (75–85% yield (223) cf. (227)). — Note finally the existence of an acid salt of $\bar{\mathbb{C}}$ with aniline, m.p. 107–108° (224), from $\bar{\mathbb{C}}$ (2 moles) with aniline (1 mole). — o-Toluidine trichloroacetate; the prepn. of this salt, m.p. 167–168° dec. (225), has been claimed (225) but could not be confirmed (224) (228); no other record of it can be found. — p-Toluidine trichloroacetate; the prepn. of this salt, m.p. 135° dec. (225), has been claimed (225) but could not be confirmed (224) (228); no other record of it can be found. — N-Methylandine trichloroacetate: m.p. 97° (228).]

 α -Phenylethylamine trichloroacetate: unreported. — Benzylamine trichloroacetate: from $\ddot{\mathbf{C}}$ + benzylamine in EtOAc, m.p. 118.8-119.8° u.c., 120.3-121.3° cor. (229) (note that this

m.p. is practically identical with corresp. benzylamine salt of chloroacetic acid (3:1370) q.v.). — Piperazine bis-(trichloroacetate), m.p. 121.0-121.5° cor. (230). — Semicarbazide trichloroacetate: m.p. 154° dec. (231).

[Phenylhydrazine trichloroacetate from \bar{C} with phenylhydrazine in C_6H_6 , mp. 123° (232). (Note that this product is definitely the salt since on titration with alk it gives Neut. Eq. 204.7 as against a calcd value of 202 6 (232); this salt upon htg. would be expected to lose H_2O giving trichloroacetophenylhydrazide, but this product is unreported.)]

[For salts of \bar{C} with o-, m-, and p-phenylenediamines see (233).]

Behavior of \bar{C} with Metals

[\bar{C} with aq. + Zn wool (102), or \bar{C} with Cu powder in aq. or C₆H₆ (223) (103) (227), gives dichloroacetic acid (3:6208) q v — \bar{C} in conc. NH₄OH dissolves Cu, Zn, or Cd with strong evoln, of ht. but does not attack Ag (234)]

Esterification of \bar{C}

This book includes the following esters of C under their own individual numbers, q.v.: methyl trichloroacetate (3:5800), ethyl trichloroacetate (3:5950), n-propyl trichloroacetate (3:5975), n-butyl trichloroacetate (3:6315), isobutyl trichloroacetate (3:6140), sec-butyl trichloroacetate (3:9372), ter-butyl trichloroacetate (3:0138), n-amyl trichloroacetate (3:6560), isoamyl trichloroacetate (3:6490), ter-amyl trichloroacetate (3:6510), and β -methoxyethyl trichloroacetate (3:9250).

[For studies on esterification of \bar{C} under various conditions with MeOH (1:6120) (235) (236), with EtOH (1:6130) (235) (237) (238) (239) (240) (241) (242) (243) (244) (20), with n-propyl alc. (1:6150) (245), with isopropyl alc. (1:6135) (245) (246) (238), with n-butyl alc. (1:6180) (247) (248), with isobutyl alc. (1:6165) (247) (248) (83), with sec -butyl alc. (1:6155) (247), with ter-butyl alc. (1:6140) (238), with n-amyl alc. (1:6205) (248), with pentanol-2 (1:6185) (248), with pentanol-3 (1:6175) (248), with ter-amyl alc. (1:6160) (248), with neopentyl alc. (1:5812) (249), with methyl-vinyl-carbinol (250), with benzyl alc. (1:6480) (238) (251), with diphenylcarbinol (1:5960) (238), with triphenylcarbinol (1:5985) (238), see indic. refs [

[For study of equilibrium of transesterification with MeOAc (1:3005) or with EtOAc (1:3015) at 30° see (21).]

Addition Reactions of \bar{C} with Organic Compounds

Addition to unsaturated linkages. \bar{C} in pres. of suitable catalysts adds to unsatd, linkages giving the corresp. esters [e.g., \bar{C} with propylene + BF₃ gives (48.8% yield (246)) isopropyl trichloroacetate (3:5975); \bar{C} with trimethylethylene (2-methylbutene-2) (1:8220) gives both *ter*-amyl trichloroacetate (3:6185) and methyl-isopropyl-carbinyl trichloroacetate (for extensive studies of this reaction see (252) (253) (254) (255) (256) (257) (258) (259) (260))].

[\bar{C} with acetylene + HgSO₄ at 60-80° gives (261) vinyl trichloroacetate [Beil. II₁-(94)], b.p. 149° at 760 mm.]

Addition to epoxy compounds. [\bar{C} with ethylene oxide (1:6105) in cold gives (28% yield (262)) (263) (264) ethylene glycol (mono)trichloroacetate (β -hydroxyethyl trichloroacetate) (3:9099). — For behavior of \bar{C} with 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358) see (264).]

Conversion of C to Corresponding Acid Halides

[The corresponding trichloroacetyl fluoride is unreported.]

[\bar{C} with PCl₃ (266) (268) (269), with PCl₃ + ZnCl₂ (25% yield (270)), with SOCl₂ (yield 12% (270), 30% (271)) in C₆H₆ (60% yield (272)) or in pyridine (90% yield (273)), with P₂O₅ + HCl gas (274), with benzotrichloride (3·6540) + ZnCl₂ at 100° (77% yield (275)), or with benzoyl chloride (3:6240) (51-56% yield (276)) gives trichloroacetyl chloride (3:5420). — Note also that \bar{C} on pyrolysis at 300° decomposes (100) with formn. of CO₂ + CO₂ + trichloroacetyl chloride (3:5420) + HCl.]

[\bar{C} with PBr₃ gives (265) (266) trichloroacetyl bromide, b.p. 143° (266), 139.5-140° (265); this product is also obtd. from trichloroacetyl chloride (3:5420) with HBr gas at -5° (70% yield (267)).]

[\bar{C} with PI₃ (266) (or better trichloroacetyl chloride (3:5420) with HI at -5° (277)) gives (71.5% yield (277)) trichloroacetyl todide, b.p. 74 0-74 2° at 30 mm. (277).]

Conversion of \bar{C} to Corresponding Auhydride

[\bar{C} with P₂O₅ at 200–215° (278) (279), or Na \bar{A} with SO₂Cl₂ (or SO₂ + Cl₂) in EtOAc (280), or \bar{C} with trichloroacetyl chloride (3·5420) and PCl₃ (281), P₂O₅ (282), or AlCl₃ (283) gives (yields. 90–95% (280), 80% (278)) trichloroacetic acid anhydride (3:6575).]

- P Color test with NH₄OH/Cu₂Cl₂ reagent. \bar{C} on shaking in filled stoppered bottle with conc. aq. NH₄OH cont₅ Cu₂Cl₂ gives dark blue color instantly (284); note, however, that very similar behavior is shown by dichloroacetic acid (3:6208).
- Methyl trichloroacetate: oil, b p 153° (see 3.5800).
- Ethyl trichloroacetate: oil, b p. 167° (see 3:5950).
- Phenyl trichloroacetate: oil, b.p. 254-255° dec. (135). [From trichloroacetyl chloride (3:5420) with sodium phenolate in pet other (135).] [Note that the isomeric 4-(trichloroacetyl)phenol, m.p. 99-0-99-5° has been prepd. indirectly from trichloroacetonitile ¬- phenol + AlCl₃ (285)]
- --- o-Tolyl trichloroacetate: unreported. [Note, however, that the isomeric 4-(tri-chloroacetyl)-2-methylphenol, mp. 90-91°, has been obtd. indirectly (285).]
- —— m-Tolyl trichloroacetate: unreported. [Note, however, that both the isomers, viz., 4-(trichloroacetyl)-3-methylphenol, mp. 83-87°, and 6-(trichloroacetyl)-3-methylphenol, oil, have been obtd. indirectly (285)]
- p-Tolyl trichloroacetate: mp 68 69° (285) [Obtd only by indirect means (285).] Benzyl trichloroacetate: oil, b p 178 5° at 50 mm (286), 448-149° at 15 mm. (264), $D_4^4 = 1.3887$ (286), $n_5^{18.8} = 1.5288$ (286). [From $\bar{\text{C}}$ with benzyl alc. (1:6480) + HCl gas at 100° (286), or from trichloroacetyl chloride (3:5420) with benzyl alc
- (1.6480)] p-Nitrobenzyl trichloroacetate. mp about 80° cf. (287). [Unsuitable as ① (287).]
- Phenacyl trichloroacetate: unreported.
- --- p-Chlorophenacyl trichloroacetate: unreported.
- --- p-Bromophenacyl trichloroacetate: unreported.
- —— p-Iodophenacyl trichloroacetate: unreported.
- --- p-Phenylphenacyl trichloroacetate: unreported.
- ⑤ S-Benzylthiuronium trichloroacetate: mp 148-149° (288). [Note that for corresp. salts from chloroacetic acid (3:1370) and from dichloroacetic acid (3:6208) m.p. values are respectively 159-160° and 178-179° (288)]
- S-(p-Chlorobenzyl)thiuronium trichloroacetate: m.p. 148° cor. (289). [From C
 (as NaA) with S-(p-chlorobenzyl)thiuronium chloride (289) (m.p. 197°) in alc. (289);
 note that corresp. deriv. of chloroacetic acid (3:1370) has m.p. 158° cor. (289).]

- S-(p-Bromobenzyl)thiuronium trichloroacetate: m.p. 146° cor. (290). [From C (as NaA) with S-(p-bromobenzyl)thiuronium bromide (290) (m.p. 213°) in alc. (290); note that corresp. deriv. of chloroacetic acid (3:1370) has m.p. 154° cor. (290).]
- Φ ω,ω,ω-Trichloroacetamide: m p. 142° (291), 141° (91) (235) (292), 140.5° (293), 137° (294), 136° (300). [From ethyl trichloroacetate (3.5950) with conc. aq. NH₄OH in cold (293) (295) (299) (300), from trichloroacetyl chloride (3.5420) with dry NH₃ gas in C₆H₆ (293), from trichloroacetonitrile with alk H₂O₂ (294), and also from other sources] [For studies on taste of this amide see (296); note also that trichloroacetamide with P₂O₅ on htg gives (85% yield (297)) trichloroacetonitrile, b.p. 83-84° (300).]
- Φ ω,ω,ω-Trichloroacetanilide: m p. 95-97° (302), 94-95° (304), 94° (301) (303) (305).
 [From C by conversion to trichloroacetyl chloride (3:5420) and reaction with aniline directly (301) or in dry ether (83), C₆H₆ (302), or pyridine (303).]
- ω,ω,ω-Trichloroaceto-o-toluidide: m.p. 96° (305). [From ethyl trichloroacetate (3:5950) with o-CH₃.C₆H₄.NH-MgI (305).]
- \mathfrak{D} ω, ω, ω -Trichloroaceto-p-toluidide: m.p. 113° (306). [From $\overline{\mathbf{C}}$ via conversion to trichloroacetyl chloride (3:5420) and reaction with p-toluidine (306).]
- ω,ω,ω-Trichloroacet-N-benzylamide: m p. 92.8-93.6° u.c. (307), 93-6-94 4° cor. (307), 90-91° (308). [From \(\tilde{\Color}\) by conversion to ethyl trichloroacetate (3:3950) and reaction with aq. benzylamine on shaking in cold (307) of (309); note, however, that the corresp. derives from chloroacetic acid (3:1370) have m p's of 93-0-93.6° cor. and 94.8-95.6° cor., respectively (307); also that simple salt of \(\tilde{\Color}\) with benzylamine has m.p. 120-3-121.3° cor. (229).]
- Kendall, Gross, J. Am Chem Soc. 43, 1429-1436 (1921) (2) Kendull, Brakeley, J. Am. Chem. Soc. 43, 1826 1834 (1921). (3) Pickering, J. Chem. Soc. 67, 675-684 (1895).
 Johnson, Moelwyn-Hughes, Proc. Roy. Soc. London A-175, 118-131 (1940). (5) Kendall, Booge, J. Am. Chem. Soc. 38, 1719-1733 (1916). (6) Puschin, Dezelic, Monatsh 60, 432 (1932).
 Kendall, Gibbons, J. Am. Chem. Soc. 37, 152-159 (1915). (8) Schremet, Z. physik Chem. 133, 423-424 (1928). (9) Jaeger, Z. anory. allyem. Chem. 101, 65 (1917) (10) Kendall, Carpenter, J. Am. Chem. Soc. 36, 2505 (1914).
- (11) Kendall, J. Am. Chem. Soc. 38, 1312-1316 (1916) (12) Redfield, King, J. Phys. Chem. 40, 921-922 (1936). (13) Wooten, Hammett, J. Am. Chem. Soc. 57, 2289-2296 (1935). (14) Puschin, Rikovski, Ann. 516, 286-295 (1935); Bull. soc. chim roy Youyoslav. 5, 123–134 (1934); Cent. 1936, I 2737; C.A. 29, 3650-3651 (1935). (15) Ssuknewitsch, Tschilingarjan, Ber. 68, 1215 (1935). (16) Puschin, Rikovsky, Monatsh. 60, 446 (1932). (17) Walden, Ric trav chim. 48, 880-884 (1929). (18) Rabinowitsch, Z. physik. Chem. 119, 65 (1926) (19) Walden, Z. physik. Chem. 70, 577 (1910). (20) Sudborough, Lloyd, J. Chem. Soc. 75, 476 (1899). (21) Sudborough, Karve, J. Indian Inst. Sci. 5, 1-21 (1922), Cent. 1923, I 295, C.A. 17, 665
- (21) Sudborough, Karve, J. Indian Inst. Sci. 5, 1-21 (1922), Cent. 1923, 1 295, CA. 17, 665 (1923). (22) Winkler, Arch. Pharm. 266, 49 (1928). (23) Moureu, Dufraisse, Berchet, Bull. soc. chim. (4) 43, 949 (1928). (24) Clermont, Ann. chim. (6) 6, 135-139 (1885). (25) Lecat, Rec. trav. chim. 47, 17 (1928). (26) Lecat, Ann. soc. sci. Bruxelles 47, I 24, 154 (1927). (27) Perkin, J. Chem. Soc. 65, 422 (1894). (28) Landee, Johns, J. Am. Chem. Soc 63, 2892 (1941). (29) Kohrausch, Koppl, Pongratz, Z. physik. Chem. B-21, 255 (1933). (30) Mameli, Gazz. chim. ital. 41, I 309-311 (1911).
- (31) Hantzsch, Durigen, Z. physik. Chem. 136, 14 (1928). (32) Brand, Wirsing, Ber. 45, 1768 (1912). (33) LeFevre, Vine, J. Chem. Soc. 1938, 1795-1801. (34) Bell, Arnold, J. Chem. Soc. 1935, 1432-1435. (35) Fredenhagen, Cadenbach, Z. physik. Chem. A-164, 206 (1933). (36) Klatt, Z. anorg. allgem. Chem. 222, 294 (1935). (37) Robertson, J. Chem. Soc. 83, 1428 (1903). (38) Berthelot, Ann. chim. (6) 28, 136-137 (1893). (39) Berthelot, Matignon, Ann. chim. (6) 28, 567-571 (1893). (40) Schjamberg, Svensk. Kem. Tid. 44, 227-231 (1932), Cent. 1932, II 3685, C.A. 27, 3133 (1933).
- (41) Kharasch, J. Research Natl Bur. Standards 2, 418 (1929).
 (42) Bell, Baughan, Vaughan-Jackson, J. Chem. Soc. 1934, 1969-1972.
 (43) Cohn, Urey, J. Am. Chem. Soc. 69, 679-687 (1938).
 (44) Ockrent, J. Chem. Soc. 1932, 613-630.
 (45) Ockrent, J. Chem. Soc. 1932, 1864-1875.
 (46) Swearingen, Dickinson, J. Phys. Chem. 36, 534-545 (1932).
 (47) Sabaltschka, Pharm. Zig. 74, 382-384 (1929); Cent. 1929, I 2288, C.A. 23, 2627 (1929).
 (48) Namasivayan, J. Indian.

- Chem. Soc. 4, 449-458 (1927). (49) Kolthoff, Rec. trav. chim. 46, 557-558 (1927). (50) Makruschin, Kryloff, Kolloid-Z. 43, 388 (1927).
- (51) Kubelka, Taussig, Kollord-Berhefte 22, 150-190 (1926). (52) Brass, Frei, Kollord-Z. 45, 248 249 (1928). (53) S. S. Bhatnagar, A. N. Kapur, M. S. Bhatnagar, J. Indian Chem. Soc. 17, 367 (1940). (54) Sen, J. Phys. Chem. 31, 526 (1927). (55) Ghosh, J. Chem. Soc. 1928, 3035. (56) Bimolenko, Ginzburg, Collord J. (U.S.S.R.) 5, 263-270 (1939); Cent. 1939, II 3556; C.A. 33, 8469 (1939). (57) Griffin, Richardson, Robertson, J. Chem. Soc. 1928, 2705-2709. (58) Dermer, Markham, Trimble, J. Am. Chem. Soc. 63, 3524-3525 (1941). (59) Smith, J. Phys. Chem. 25, 610, 616, 624 (1921). (60) Nernst, Hohmann, Z. physik. Chem. 11, 370 (1893).
- (61) Schilow, Lepin, Z. physik. Chem. 101, 377-378 (1922). (62) Andreasov, Ukrainskii Khem. Zhur. 3, Sci. Pt., 463-465 (1928), Cent. 1929, II 550; C.A. 23, 3145 (1929). (63) von Georgievics, Monatsh. 36, 400-401 (1915), Z. physik. Chem. 90, 55 (1915). (64) Kolosovskii, Kulikov, Z. physik. Chem. A-169, 459-471 (1934). (65) Bodansky, Meigs, J. Phys. Chem. 36, 816 (1932). (66) Smith, J. Phys. Chem. 25, 734 (1921). (67) Andreasov, Trans. Inst. Chem. Kharkov Univ. 4, No. 13, 107-130 (1938); C.A. 34, 3156 (1940). (68) Kolosovskii, Kulikov, J. Gen. Chem. (U.S.S.R.) 4, 1370-1377 (1934), Cent. 1936, II 1511; C.A. 29, 3898 (1935). (69) Kolosovskii, Kulikov, J. Gen. Chem. (U.S.S.R.) 5, 63-68 (1935); Cent. 1936, II 2880; C.A. 29, 4652 (1935). (70) Colles, J. Chem. Soc. 89, 1253 (1906).
- (71) Drucker, Z. physik. Chem. 52, 652 (1905). (72) Zeechini, Gazz. chim. ital. 35, II 73-74 (1905). (73) Frivold, Ruud, Avhandl. Norske Videnskaps-Akad. Oslo Mat.-Naturv. Klasse 1932, No. 12, 1-19, Cent. 1933, I 1747; C.A. 27, 5619 (1933). (74) Kendall, J. Am. Chem. Soc. 36, 1722-1734 (1914). (75) "International Critical Tables," IV, 101 (1928). (76) Brooks, Humphrey, J. Am. Chem. Soc. 40, 845 (1918). (77) Tsakalotos, Guye, J. chim. phys. 8, 348 (1910). (78) Kiemann, Zechnei, Monatsh 46, 175-176 (1925). (78A) Puschin, Konig, Monatsh. 49, 75-76 (1928). (79) Woodward, Lange, Nelson, Calvery, J. Ind. Hyg. Toxicol. 23, 78-82 (1941). (80) Tetsumoto, J. Agr. Chem. Soc. Japan 12, 22-26 (1936), Cent. 1936, II 817; Japan. J. Expll Med. 15, 1-8 (1937), C.A. 31, 5010 (1937).
- (81) Sabalitschka, Durmann, Pharm. Ztg. 81, 335-337 (1936), Cent. 1936, II 504; C.A. 36, 3942 (1936).
 (82) Clermont, Ann. 161, 128 (1872); Compt. rend. 73, 113 (1871).
 (83) Judson, Ber. 3, 782-784 (1870).
 (84) Kolbe, Ann. 54, 183-185 (1845).
 (85) Wallach, Ber. 5, 256 (1872).
 (86) Khotinskn, Aleksandrova, Proc. Kharkov State Univ. 4, 59-61 (1936), C.A. 31, 6615 (1937).
 (87) Clermont, Ann. clam. (6) 6, 135-139 (1885).
 (88) Clermont, Ann. 166, 64 (1873); Compt. rand. 74, 1492 (1872).
 (89) Seubert, Ber. 18, 3336-3339 (1885).
 (90) Dumas, Ann. chim. (2) 73, 77-90 (1840); Ann. 32, 106-113 (1839).
- (91) Bailey, Hickson, J. Chem. Soc. 1941, 145.
 (92) Kolbe, Ann. 54, 182 (1845).
 (93) Cloez, Ann. chim. (3) 17, 300 (1846); Ann. 60, 260 (1846).
 (94) Muller, Ann. 258, 63-64 (1890).
 (95) Leblanc, Ann. chim. (3) 10, 205 (1844).
 (96) Malaguti, Ann. chim. (3) 16, 10 (1846); Ann. 56, 270 (1845).
 (97) Buckney, Thomsen, Ber. 10, 698-699 (1877).
 (98) Fichter, Fritsch, Muller, Helv. Chim. Acta. 6, 503-504 (1923).
 (99) Senderens, Compt. rend. 172, 155-157 (1921).
- (101) Engler, Steude, Ber. 26, 1444-1145 (1893). (102) Doughty, Lacoss, J. Am. Chem. Soc. 51, 852-855 (1929). (103) Doughty, Derge, J. Am. Chem. Soc. 53, 1594-1596 (1931). (104) Doughty, Black, J. Am. Chem. Soc. 47, 1091-1094 (1925). (105) Doughty, Freeman, J. Am. Chem. Soc. 44, 640-645 (1922). (106) Brand, Ger. 246,661, May 6, 1912, Cent. 1912, I 1742, C.A. 6, 2496 (1912). (107) Melsens, Ann. 42, 111-112 (1842). (108) Sandonnini, Borghello, Att. accad. Lancer 21, 30-35 (1935), C.A. 29, 4679 (1935). (109) Busch, Stove, Ber. 49, 1063-1071 (1916). (110) Timofeev, J. chim. Ukraine 1, 102-106 (1925), Cent. 1925, II 1651-1652; C.A. 20, 2820 (1926).
- (111) Pearce, Nelson, Proc. Iowa Acad. Sci. 36, 251-260 (1929); C.A. 25, 1147 (1931). (112) Lichty, Am. Chem. J. 18, 597 (1896). (113) Beckurts, Otto, Ber. 14, 589-590 (1881). (114) Seubert, Ber. 18, 339-3343 (1885). (115) Lossen, Ann. 342, 122-123 (1905). (116) Bourgoin, Bull. soc. chim. (2) 37, 403 (1882). (117) Verhoek, J. Am. Chem. 56, 571-577 (1934). (118) Kappanna, Z. physik. Chem. A-158, 355-364 (1932). (119) Banei ii, Dhar, Z. auorg. allgem. Chem. 134, 172-174 (1924). (120) Petrenko-Kritschenko, Opotzky, Ber. 59, 2137 (1926).
- (121) Bhattacharya, Dhar, Z. anory allycm. Chem. 209, 123-125 (1932). (122) Kailan, Kunze, Monatsh. 71, 373-423 (1938). (123) Benrath, Ann. 382, 224 (1911). (124) Fairclough, J. Chem. Soc. 1938, 1186-1190. (125) Drushel, Simpson, J. Am. Chem. Soc. 39, 2459 (1917). (126) Jaeger, J. Chem. Soc. 119, 2072-2073 (1921). (127) Jaeger, Berger, Rec. trav. chim. 41, 73-74 (1921). (128) Jander, Immig, Ber. 69, 1291-1292 (1936). (129) Salmi, Korte, Ann. Acad. Sci. Fennicae A-54, No. 10, 22 pp. (1940); Cent. 1942, I 328; C.A. 37, 2642 (1943). (130) Patwardham, Kappanna, Z. physik. Chem. A-166, 51-58 (1933).

(131) Goldschmidt, Brauer, Ber. 39, 109-112 (1906). (132) Urazovskii, Polotskii, J. Gen. Chem. (U.S.S.R.) 10, 812-818 (1940), Cent. 1940, II 3583, C.A. 35, 1298 (1941). (133) Silberstein, Ber. 17, 2663-2664 (1884). (134) Strosacker (to Dow Chemical Co.) U.S. 1,801,887, April 21, 1931, Cent. 1931, II 120, C.A. 25, 3362 (1931). (135) Anselmino, Ber. deut. pharm. Ges. 16, 390-393 (1906), Cent. 1907, I 339. (136) Bistizycki, von Siemiradzki, Ber. 41, 1671 (1908). (137) Armstrong, Richardson, J. Chem Soc 1933, 496-500. (138) van Alphen, Rec. trav. chim. 46, 144-149 (1927). (139) Ostwald, Z. physik. Chem. 3, 177-178 (1889). (140) Bhagwat, J. Indian Chem. Soc. 16, 236 (1939).

(141) Jenkins, Nature 145, 625 (1940). (142) Bell, Nature 146, 166-167 (1940). (143) Banghan, Nature 146, 461 (1940). (144) Kendall, King, J. Chem Soc. 127, 1784-1789 (1925). (145) Schreiner, Z. physik. Chem. 133, 427 (1928). (146) Wightman, Jones, Am. Chem. J. 46, 71-72 (1910), 48, 327 (1912). (147) Dawson, Crann, J. Chem. Soc. 109, 1265 (1916). (148) Devrup, J. Am. Chem. Soc. 56, 60-64 (1934). (149) Welcher, Briscoe, Proc. Indiana Acad. Sci. 43, 142-153 (1934), C.A. 28, 7116 (1934). (150) Mason, Kilpatrick, J. Am. Chem. Soc. 59, 572-578 (1937). w (151) Hantzsch, Voigt, Bcr. 62, 975-984 (1929). (152) Verhoek, J. Am. Chem. Soc. 58, 2577-

2584 (1936). (153) Bronsted, Ber. 61, 2062 (1928). (154) Griffiths, J. Chem. Soc. 1938, 818-823. (155) Gemant, J. Chem. Phys 12, 83-84 (1944) (156) Rabinovich, Trav. inst. chim. Kharkov 1, 99-107 (1935); CA. 32, 4085 (1938) (157) Ruehle, Ind. Eng. Chem., Anal. Ed. 10, 130-131 (1938). (158) Usanovich, Vatsimirskii, J. Gen. Chem. (U S S R) 11, 957-958 (1941), C.A. 36, 6444 (1942). (159) LaMer, Downes, J. Am. Chem. Soc. 55, 1840–1864 (1933) (160) Weissberger, Fasold, Z. physik. Chem. A-157, 6595 (1931)

(161) Weissberger, J. Am. Chem. Soc. 65, 242–245 (1943). (162) Weissberger, J. Am. Chem. Soc. 65, 245-246 (1943). (163) Bell, Caldin, J. Chem Soc. 1938, 382-389. (164) Bell, Lidwell, Wright, J. Chem. Soc. 1938, 1861-1865. (165) Kon, Naigund, J. Chem. Soc. 1934, 624. (166) Ostwald, J. prakt. Chem. (2) 29, 396 (1884) (167) Hantzsch, Weissberger, Z. physik. Chem. 125, 254-255 (1927). (168) van Alphen, Rec. trav. chim. 49, 754-761 (1930) (169) Goldschmidt, Marum, Thomas, Z. physik. Chem. 129, 233-240 (1927) (170) Goldschmidt, Z. physik. Chem. 94, 237 (1920).

(171) Usanovich, Glukhov, J. Gen. Chem. (U.S.S.R.) 10, 227-229 (1940), C.A. 34, 7285 (1940). (172) Usanovich, J. Gen. Chem. (U.S.S.R.) 10, 219-222 (1940), C.A. 34, 7285 (1940). (173) Weissberger, Högen, Z. physik Chem. A-156, 321-351 (1931). (174) Braune, Z. physik. Chem. 85, 170-210 (1913). (175) Bredig, Z. Elektrochem 18, 536 (1912). (176) Bronsted, Vance, Z. physik. Chem. A-163, 240-256 (1933). (177) Rivett, Z. physik. Chem. 82, 211 (1913). (178) Bell, Levinge, Proc. Roy. Soc. (London) A-151, 211-219 (1935). (179) Bell, Proc. Roy. Soc. (London) A-143, 377-399 (1934). (180) Bell, Lidwell, J. Chem. Soc. 1939, 1096-1099.

(181) Bobtolsky, Cohn, Z. anorg. allgem. Chem. 210, 227-231 (1933). (182) Michael, Weiner, J. Org. Chem. 5, 396, 399 (1940). (183) Bateman, Hoel, J. Am. Chem. Soc. 36, 2518 (1914). (184) Jaeger, Cent. 1911, II 1852-1854, not in C.A. (185) Jaeger, Z. Krist. 50, 242-256 (1912), C.A. 6, 1870 (1912). (186) Rivals, Ann. chim. (7) 12, 508-510 (1897). (187) Jones, Werner, J. Am. Chem. Soc. 39, 418-419 (1917). (188) Jungmann (to Kali-chemie), Ger 647,057, June 1937; Cent. 1937, II 1895; CA. 31, 6833 (1937). (189) Clermont, Compt. rend. 74, 942-944

(1872). (190) Ostwald, Z. physik. Chem. 1, 103-104 (1887).

(191) Henry, Ber. 12, 1844-1848 (1879). (192) Wightman, Jones, Am. Chem. J. 46, 66 (1911). (193) Goldschmidt, Aarflot, Z. physik. Chem. 117, 317-319 (1925) (194) Lloyd, Pardee, Carnege Inst. Wash. Pub. 260, 110 (1918). (195) Gold-chmudt, Z. physik. Chem. 91, 54-57 (1916). (196) Clermont, Compt. rend. 73, 501-502 (1871). (197) Scubert, Ber. 18, 3339 3342 (1885). (198) Beckurts, Otto, Ber. 14, 588-591 (1881). (199) Wieland, Fischer, Ann. 446, 63 (1926). (200) Birckenbach, Mcisenheimer, Ber. 69, 723-729 (1936).

(201) Bateman, Conrad, J. Am. Chem. Soc. 37, 2553-2559 (1915). (202) Davidson, Sutton, J. Chem. Soc. 1942, 565-567. (203) Rosenthaler, Mikrochemie 12, 101 (1933). (204) Kharasch. Staveley, J. Am. Chem. Soc. 45, 2963 (1923). (205) Braud, J. prakt. Chem. (2) 88, 342-357 (1913). (206) Sirucek, Collection Czechoslov. Chem. Commun 10, 117-128 (1938). (207) Parsons, Sargent, J. Am. Chem. Soc. 31, 1205-1206 (1909). (208) Kertesz, J. chim. phys. 35, 371 (1938). (209) Clermont, Compt. rend. 76, 774-775 (1873). (210) Garzarolli-Thurnlackh, Ann. 210,

(211) Grossmann, Jaeger, Z. anorg. allgem. Chem. 73, 51-52 (1911). (212) Ablov, Bull. soc. chim. (5) 3, 1915 (1936). (213) King, J. Chem. Soc. 1930, 2307-2319. (214) Costachescu. Ablov, Ann. sci univ Jassy 17, 149-172 (1933); Cent. 1933, I 3038; C.A. 27, 2647 (1933). (215) Kravtzoff, Compt. rend. 197, 137-140 (1933) (216) Beebe, J. Phys. Chem. 35, 3677-3683 (1931). (217) Fogel, Rubinsztein, Taumann, Roczniki Chem. 9, 348-353 (1929); Cent. 1930, II 227; C.A. 23, 3900 (1929). (218) Reitzenstein, Z. anorg. allgem. Chem. 32, 302-303, 307-308 (1902).

(219) Ablov, Bull. soc. chim. (5) 3, 1673-1678 (1936). (220) Ablov, Bull. soc. chim. (5) 1, 731-738 (1934).

(221) Ablov, Bull. soc. chim. (5) 1, 1489-1494 (1934). (222) Ablov, Bull. soc. chim. (5) 2, 1724-1736 (1935). (223) Doughty, Black, J. Am. Chem. Soc. 47, 1091-1092 (1925). (224) Doughty, J. Am. Chem. Soc. 47, 1096 (1925). (225) Wheeler, Smith, J. Am. Chem. Soc. 48, 1994-1998 (1923). (226) Beamer, Clarke, Ber. 12, 1067 (1879). (227) Doughty, Freeman, J. Am. Chem. Soc. 44, 639-645 (1922). (228) Wheeler, Jennings, J. Am. Chem. Soc. 49, 1091-1093 (1927). (229) Buehler, Carson, Edds, J. Am. Chem. Soc. 57, 2181-2182 (1935). (230) Pollard, Adelson, Bain, J. Am. Chem. Soc. 56, 1759-1760 (1934).

(231) Michael, J. Am. Chem. Soc. 41, 415 (1919).
(232) Stempel, Schaffel, J. Am. Chem. Soc. 64, 470-471 (1942).
(233) Feigl, Popp-Halpern, Monatsh. 59, 137, 140-141 (1932).
(234) Doughty, Freeman, J. Am. Chem. Soc. 43, 702 (1921).
(235) Toole, Sowa, J. Am. Chem. Soc. 59, 1971-1973 (1937).
(236) Sudborough, Turner, J. Chem. Soc. 101, 237-240 (1912).
(237) Hinshelwood, Legard, J. Chem. Soc. 1935, 1588-1591.
(238) Petrenko-Kritschenko, Bogatsky, Lubman, Z. physik. Chem. 115, 289 302 (1925).
(239) Prager, J. Ann. Chem. Soc. 30, 1911-1912
(1008) J. Zabard, Chem. 68, 207 (1908).
(1008) J. Market, Chem. 68, 207 (1908).
(1008) J. Market, Chem. 68, 207 (1908).

(1908); Z. physik. Chem. 66, 297 (1909). (240) Kailan, Monatsh 29, 799-844 (1908).

(241) Goldschmidt, Udby, Z. physik. Chem. 60, 748-749 (1907) (242) Goldschmidt, Sunde, Ber. 39, 714-715 (1906). (243) Lichty, Am. Chem. J. 18, 590-600 (1896). (244) Clermont, Ann. chem. (6) 6, 241-249 (1885). (245) Gayler, Waddle, J. Am. Chem. Soc. 63, 3358-3359 (1941). (246) Dorris, Sowa, Nieuwland, J. Am. Chem. Soc. 56, 2689-2690 (1934). (247) Waddle, Adkins, J. Am. Chem. Soc. 61, 3361-3364 (1940) (248) Liston, Dehn, J. Am. Chem. Soc. 60, 1264-1265 (1938). (249) Quayle, Norton, J. Am. Chem. Soc. 62, 1170-1171 (1940). (250) Burton, J. Chem. Soc. 1930, 250-251.

(251) Hanshelwood, Legard, J. Chem Soc 1935, 587 596. (252) Clark, Univ. Microfilms (Ann Arbor, Mich), Pub. 138, 78 pp.; Microfilm Abstracts 2, No. 1, 1–2 (1939), [C.A. 35, 2060 (1941)]. (253) Andreasov, Ukrainskii Khem Zhur, Sci. Pt. 4, 143–148 (1929), Cent. 1929, II 2875, C.A. 24, 1014 (1930); 4, 89 92 (1929), Cent. 1929, II 2433; C.A. 23, 4439 (1929); 3, 467–470 (1928); Cent. 1929, I 3084, C.A. 23, 322 (1929). (254) Timofeev, Israilevich, Chaskes, J. chim. Ukraine 1, 576–580 (1925); Cent. 1926, I 565, C.A. 20, 2820 (1926). (255) Timofeev, Andreasov, J. chim. Ukraine 1, 107–110 (1925); Cent. 1925, II 1652, C.A. 20, 2820 (1926). (255) Timofeev, Kravizov, J. Russ. Phys.-Chem. Soc. 48, 985–993 (1916), Cent. 1923, III 831, C.A. 11, 788 (1917). (257) Timofeev, Andreasov, J. Russ. Phys.-Chem. Soc. 47, 838–818 (1915), Cent. 1916, I 1015, C.A. 9, 2896–2897 (1915). (258) Konowalov, J. Russ. Phys.-Chem. Soc. 39, 825–841 (1907), Cent. 1908, I 98 100, not in C.A. (259) Konowalov, Z. physik. Chem. 2, 380–389 (1888). (260) Nernst, Hokmann, Z. physik. Chem. 11, 357–362 (1893)

(261) Chem Fabrik Grieshem-Elektron, Ger. 271,381, March 13, 1914; Cent. 1914, I 1316, [C A. 9, 356 (1915)] (262) Meerwein, Hinz, Ann. 484, 16 (1930). (263) Meerwein, Sonke, J. prakt. Chem. (2) 137, 308 (1933). (264) Hibbert, Greig, Can. J. Research 4, 254-263 (1931). (265) Hofferiehter, J. piakt. Chem. (2) 20, 196 (1870). (266) Gal, Compt. rend. 76, 1020 (1873); Bill. soc. chim. (2) 20, 11-13 (1873). (267) Simons, Sloat, Meumer, J. Am. Chem. Soc 61, 436 (1939). (268) Delacre, Bull. acad. roy. Bill. 1902, 189 202; Cent. 1902, I 1197. (269) Thorpe, J. Chem. Soc. 37, 189-190 (1880). (270) Clark, Bell. Trans. Roy. soc. Can. (3) 27, HI 97-103 (1933).

(271) Boeseken, Rec. trav. chrm. 29, 100, 112 (1910). (272) Leimu, Ber. 70, 1049 (1937). (273) Carré, Libermann, Compt. rend. 199, 1422-1423 (1934). (274) Friederica, Ber. 11, 1971 (1878). (275) Rabcewicz-Zubkowski, Roczinki Chem. 9, 528 (1929), Cent. 1929, II 2677, C.A. 24, 61 (1930). (276) Brown, J. Am. Chem. Soc. 60, 1325-1328 (1938). (277) Gustus, Stevens, J. Am. Chem. Soc. 55, 374-377 (1933). (278) Swaitz, Bull soc. chim. (3) 13, 992 (1895). (279) Fichter, Fritsch, Muller, Helv. Chim. Acta 6, 503-504 (1923). (280) I.G., French 703,816, May 6, 1931; Cent. 1931, II 1347, [C.A. 25, 4559 (1931)].

(281) Buckney, Thomsen, Ber 10, 698-699 (1877). (282) Cleimont, Compt. rend. 86, 337 (1878); Bull. soc. chim. (2) 30, 505 (1878). (283) Strosacker, Schwegler (to Dow Chem. Co.), U.S. 1,713,104, May 14, 1929, Cent. 1929, II 1215, C A. 23, 3234 (1929). (284) Doughty, J. Am. Chem. Soc. 41, 1130-1131 (1919). (285) Houben, Fischer, J. makt Chem. (2) 123, 266-275 (1929). (286) Seubert, Ber. 21, 283-281 (1888). (287) Lyons, Reid, J. Am. Chem. Soc. 39, 1742 (1917). (288) Veibel, Ottung, Bull. soc. chim (5) 6, 1434-1435 (1939). (289) Dewey, Sperry, J. Am. Chem. Soc. 61, 3251-3252 (1939). (290) Dewey, Shasky, J. Am. Chem. Soc. 63, 3256-3257 (1941).

(291) Wittek, Z. physik. Chem. B-51, 106 (1942). (292) Zincke, Kegel, Ber. 23, 241 (1890).
(293) Calvet, J. chim. phys. 30, 159 (1933) (294) McMaster, Langreck, J. Am. Chem. Soc. 39, 108 (1917). (295) Cleimont, Compt. rend. 133, 737-739 (1901). (296) Giacolone, Collesano, Gazz. chim. ital. 65, 129-131 (1935). (297) Houben, Fischer, Ber. 60, 1765 (1927). (298)

Steinkopf. Ber. 41, 2541 (1908). (299) Bauer, Ann. 229, 165-167 (1885). (300) Bisschopinck, Ber. 6, 731-734 (1873).

(301) Tommasi, Meldola, Bull. soc. chim. (2) 21, 398-399 (1874). (302) Votocek, Burda, Ber. 48, 1006-1007 (1915). (303) Shah, Deshpande, J. Univ. Bombay 2, No. 2, 125-127 (1933); Cent. 1934, II 3110; C.A. 28, 6127 (1934). (304) Anschutz, Haslam, Ann. 253, 129 (1889). (305) Bodroux, Compt. rend. 140, 1598 (1905); Bull soc. chim. (3) 33, 834 (1905). (306) Heller, Ann. 332, 264-265 (1904). (307) Buehler, Mackenzie, J. Am. Chem. Soc. 59, 421-422 (1937). (308) von Braun, Jostes, Munch, Ann. 453, 143 (1927). (309) Dermer, King, J. Org. Chem. 8, 168-173 (1943). (310) Usanovich, Vatsimirskii, J. Gen. Chem. (U.S.S.R.) 11, 954-956 (1941); C.A. 39, 4540 (1945).

(311) Ipatieff, Pines, Olberg, J. Am. Chem. Soc. 67, 694-695 (1945). (312) Plump (to Pennsylvania Salt Mfg. Co.), U.S. 2,370,577, Feb. 27, 1945, C.A. 39, 4085 (1945).

3: 1160 2,3,6-TRICHLOROPHENOL OH
$$C_6H_3OCl_3$$
 Beil. VI - 190 VI_1 — VI_2 -(180) M.P. 58° (1) (2) B.P. 252-253° u.c. (5)

55° (4) 248.5-249.5° (6) 53-54° (5) (6)

Ndls. (from alc.) with intense and persistent phenolic odor. - Somewhat sol. in hot aq.; volatile with steam. - Eas. sol. alc., ether, lgr, AcOH; sol. hot C6H6 but ppts. on cooling.

[For prepn. from 2,3,6-trichloro-4-aminophenol via diazo reactn. sec (3).]

 \bar{C} is strongly acidic; ionization const. at 25° is 7.3 \times 10⁻⁷ (2); \bar{C} dissolves in Na₂CO₃ or NaOH (5); \bar{C} can be titrated with N/10 alk.; Neut Eq. = 197.5 (1) (4)

C in AcOH, treated with 1.4 moles Br2, poured into aq. yields 4-bromo-2,3,6-trichlorophenol, ndls. from AcOH, m.p. 80° (3). [The methyl ether of this prod has m p. 69-70°; the benzoate, m.p. 110° (3).]

C treated with 1.5 moles Br2 without solvent yields (3) 4,5-dibromo-2,3,6-trichlorophenol, ndls. from dil. AcOH, m.p. 205° (3). [The methyl ether of this prod. has m.p. 130°; the benzoate, m.p. 153° (3).1

 \bar{C} treated with $(CH_3)_2SO_4 + 20\%$ KOH at 100° for an hour yields its own methyl ether. 2,3,6-trichloroanisole, b.p. 227-229° at 756 mm.; pr. from alc., m.p. 45° (3).

D 2,3,6-Trichlorophenyl benzoate: from \bar{C} + BzCl + 10% KOH; cryst. from pet. ether/lgr., m.p. 92-93° (3); from alc., m.p. 90° (4).

3:1160 (1) Tiessens, Rec. trav. chim. 50, 113-114 (1931). (2) Tiessens, Rec. trav. chim. 48, 1066-1068 (1929). (3) Kohn, Fink, Monatsh. 56, 139-141 (1930). (4) Holleman, Rec. trav. chim. 39, 742-743 (1920). (5) Lampert, J. prakt. Chem. (2) 33, 376-378 (1886). (6) Hirsch, Ber. 13, 1908 (1880).

Cryst. (from pet. eth. (3)). — C mixed with 2,5-dichlorophenol (3:1190), m.p. 57°,

56-57° (2) (3)

depresses m.p. (2). — C is extraordinarily volatile; if dried in vac. this leads to substantial

losses; the volatility and intense odor of \tilde{C} differentiate this dichlorophenol from its isomerides (2). — Odor resembles that of o-chlorophenol and iodoform (3). — \tilde{C} is volatile with steam (3).

[For prepn. from 3-amino-2-chlorophenol via Sandmeyer method see (2) (4); from 2,3-dichloroanline via diazo reaction see (3); from barium 2,3-dichlorophenol-4,6-disulfonate by hydrolysis of sulfonic acid groups with steam (70% yield) see (1).]

[For data on dissociation constant see (5).]

C on direct bromination (1) yields 4,6-dibromo-2,3-dichlorophenol, colorless ndls. (rapidly becoming opaque) from AcOH (1), or colorless feathery ndls. from alc. (4), m.p. 90° (1) (4). [The methyl ether of this product, 4,6-dibromo-2,3-dichloroanisole, long needle-like pr. from alc., has m.p 82° (1).]

 \bar{C} dislyd. in aq. NaOH and shaken with (CH₃)₂SO₄ yields (3) the methyl ether, 2,3-dichloroanisole, m.p. 31° (3).

3:1175 (1) Hodgson, Kershaw, J. Chem. Soc. 1930, 1423. (2) Henley, Turner, J. Chem. Soc. 1930, 940 (3) Holleman, Rec trav. chim. 37, 101 104 (1918) (4) Hodgson, Smith, J. Chem. Soc. 1931, 2271. (5) Murray, Gordon, J. Am. Chem. Soc. 57, 110-111 (1935).

3:1190 2,5-DICHLOROPHENOL

Cryst with strong and persistent phenolic odor. — Spar. sol. aq., eas. sol. alc., ether, C_6H_6 . — Volatile with steam.

[For prepn. from 2,5-dichloroaniline [Beil. XII-625] via diazo reaction (90% yield (1); 86% yield (6); 70% yield (5)) see (1) (6) (5) (2); from 1,2,4-trichlorobenzene + NaOCH₃ in MeOH at 180° see (7)]

C in dil. alc. reddens blue litmus, dec. on boilg, with Na₂CO₃ Gives only faint color with FeCl₃ (1). [For study of ionization const see (11).]

Č dislyd. in 3 pts. CHCl₃ and shaken with conc. HNO₃ gives on cooling CHCl₃ 80% yield of 2,5-dichloro-4-nitrophenol [Beil. VI-241], colorless ndls. from pet ether, m.p. 117° (8). [Further nitration yields 2,5-dichloro-4,6-dinitrophenol, yel. pr, mp. 146° (8).]—
Č htd. with conc. H₂SO₄ + fumg. H₂SO₄, then nitrated as specified (9), yields 2,5-dichloro-6-nitrophenol, volatile with steam, yel pr. from pet. eth, mp. 70° (9).

 \bar{C} in AcOH treated with 2 moles Br₂, poured into aq., gives (100% yield (6)) 2,5-di-chloro-4,6-dibromophenol, ndls. from dil. AcOH, m.p. 100.5° (6), 99-100° (10). [This dibromo compd. results also from \bar{C} in AcOH + NaOAc + 1 mole Br₂ on htg. at 100° (10).] $[\bar{C}$ with Fe + excess Br₂ gives (100% yield (6)) 2,5-dichloro-3,4,5-tribromophenol, ndls. from AcOH, m.p. 206° (6).]

 \ddot{C} dislyd in KOH and shaken with $(CH_3)_2SO_4$ yields the methyl ether, 2,5-dichloroanisole, b.p. 225-227° u.c. at 752 mm. (6), b.p. 140° at 40 mm. (2), m.p. 24° (5) (2).

② 2,5-Dichlorophenyl benzoate: from C + aq. KOH + BzCl, ndls. from 96% alc.,
m.p. 69° (6).

3:1190 (1) Noelting, Kopp, Ber. 38, 3510 (1905). (2) Holleman, Rec. trav. chim. 37, 101-104 (1918). (3) Kohlrausch, Stockmair, Ypsilanti, Monatsh. 67, 90 (1936). (4) Ger. 349,794, March 9, 1922; Cent. 1922, IV 45. (5) de Crauw, Rec. trav. chim. 50, 770 (1931). (6) Kohn, Fink, Monatsh. 58, 78-83 (1931). (7) Holleman, Rec. trav. chim. 37, 201 (1918). (8) Fries, Ann. 454,

247 (1927). (9) Hodgson, Kershaw, J. Chem. Soc. 1929, 2922-2923. (10) Fox, Turner, J. Chem. Soc. 1930, 1860.

(11) Murray, Gordon, J. Am. Chem. Soc. 57, 110-111 (1935).

3:1200 2,4,6-TRICHLOROBENZALDEHYDE Cl
$$C_7H_3OCl_3$$
 Beil. VII -238 Cl Cl Cl Cl

M.P. 58-59° (1) (2)

Cryst. from lgr.

[For prepn. of \bar{C} from 2,4,6-trichlorobenzal (di)chloride (3:0142) by hydrolysis with fumg. H₂SO₄ (94% yield) see (1), for prepn. of \bar{C} from 4-amino-2,6-dichlorobenzaldehyde by diazotization and use of Cu₂Cl₂ reaction see (1).]

[C on oxidn. with KMnO₄ should yield 2,4,6-trichlorobenzoic acid (3:4545), m.p. 164°, but this reaction is not actually reported in the literature.]

 \bar{C} with 50% aq. KOH or 50% aq. NaOH at 100° undergoes cleavage of the aldehyde group giving (yields: 89% and 74% respectively) 1,3,5-trichlorobenzene (3:1400), m.p. 63°, accompanied by the corresp potassium formate (1)

[Č with McMgI in dry ether, followed by usual hydrolysis, gives (93% yield (3)) methyl-2,4,6-trichlorophenyl-carbinol, ndls. from lgr., m p. 76.5°, b.p. 158-163° cor. at 17 nm.]

- ---- 2,4,6-Trichlorobenzaldoxime: unreported.
- --- 2,4,6-Trichlorobenzaldehyde phenylhydrazone: unreported.
- --- 2,4,6-Trichlorobenzaldehyde p-nitrophenylhydrazone: unreported.
- 2,4,6-Trichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.

3:1200 (1) Lock, Ber **66**, 1532 (1933). (2) Geigy & Co. Ger. 199,943, July 4, 1908; Cent. **1908**, II 363-364, [C.A. **2**, 3000 (1908)]. (3) Lock, Bock, Ber. **70**, 924 (1937).

3:1205 2,4-DICHLORO-3-METHYLPHENOL OH
$$C_7H_6OCl_2$$
 Beil. VI — Cl_2 VI_1 — VI_2 — VI_2 — VI_2 — VI_2 — VI_2 — VI_2 — VI_3 — VI_3 — VI_4 —

Note that the products of m.p. 44° (3), 45° (4), and 46° (5) formerly supposed to have been \tilde{C} are now regarded (1) as 2,4,6-truchloro-3-methylphenol (3:0618).

[For prepn. of $\bar{\mathbb{C}}$ from 2-chloro-3-methylphenol (3.1055) or from 4-chloro-3-methylphenol (3:1535) in cold CHCl₃ with Cl₂ see (1), from 3-methylphenol (m-cresol) (1:1730) in CHCl₃ with 2 moles Cl₂ (other isomers are also formed) see (1); from 3-methylphenol-sulfonic acid-4 (2) in nitrobenzene solution with Cl₂ (other products are also formed) see (2).

 $\bar{\mathbb{C}}$ in CHCl₃ gives with Cl₂ (1 mole) alm. quant. yield (1) 2,4,6-trichloro-3-methylphenol (3:0618), m.p. 46° (1).

 \bar{C} in CHCl₃ gives with Br₂ (1 mole) (1) 2,4-dichloro-6-bromo-3-methylphenol, m.p. 58-59° (1).

D 2,4-dichloro-3-methylphenyl benzoate: fine plates from alc., m.p. 78-78.5° (1) [From $\ddot{\mathbf{C}}$ with BzCl in pyridine (1).]

- ② 2,4-Dichloro-3-methylphenyl benzenesulfonate: fine ndl.-like pl. from alc., m.p. 69.5° (1). [From C with benzenesulfonyl chloride in pyridine (1).] [Note the proximity of the m.p. of this deriv. to that of the corresp. deriv. of 2,6-dichloro-3-methylphenol (3:0618).]
- 2,4-Dichloro-3-methylphenyl p-toluenesulfonate: shiny pl. from alc., m.p. 100-101°
 (1). [From C with p-toluenesulfonyl chloride in pyridine (1).]

3:1205 (1) Huston, Chen, J. Am Chem Soc. 55, 4216-4218 (1933).
(2) Huston, Neely, J. Am Chem. Soc. 57, 2178 (1935).
(3) Tanaka, Morekawa, Sakamoto, J. Chem. Soc. Japan 51, 275-277 (1930); C.A 26, 706-707 (1932).
(4) Datta, Mitter, J. Am. Chem. Soc. 41, 2033 (1919).
(5) Claus, Schweitzer, Ber. 19, 930 (1886).

3:1212 PHENACYL CHLORIDE C—C—CH₂ C₈H₇OCl Beil. VII - 282 (
$$\alpha$$
-Chloroacetophenone, Cl VII₁-(151) chloromethyl phenyl ketone)

M.P.	[60° 59°	(1)] (2)	B.P.	244-245° 244°	u.c.	(6) (37)
	58-59°	(3) (4) (5) (6)		241-242°		(36)
	58.8°	(7)		140°	at 15 mm.	(1)
	58.5°	(8)		139-141°	at 14 mm.	(3)
	57-58°	(9) (71)		120.0-120.2°	at 10 mm.	(12)
	57°	(10) (11)		120-125°	at 4 mm.	(15)
	56.5-56.8°	(12)				m -
	56.5°	(13) (14)				
	56-57°	(15) (64)				
	56°	(16) (36)				
	55-55.5°	(17)				
	55°	(37)		، برگر برگری		
	54.5°	(18) (154)		,54°		
	54°	(31)				

Colorless tbls. from dil. alc. or lgr. — Vapors of $\bar{\mathbf{C}}$ are very strongly lachrymatory (see also below). — $\bar{\mathbf{C}}$ is insol. aq. but volatile with steam; $\bar{\mathbf{C}}$ is eas sol. alc., ether, or $\mathbf{C_6H_6}$.

[For study of soly. of $\bar{\mathbf{C}}$ in EtOH, C_6H_6 , CCl_4 , or acctophenone over range -23.5° to 53.5° see (19): note that $\bar{\mathbf{C}}$ with C_6H_6 (1·7400) gives (19) a eutectic, m.p. -1.6° , contg. 76 wt. % $\bar{\mathbf{C}}$; $\bar{\mathbf{C}}$ with acetophenone (1:5515) gives a eutectic, m.p. $+5.9^\circ$, contg. 70 wt. % $\bar{\mathbf{C}}$ (19).]

USES OF C

In addn. to its uses as a chem. intermediate, \bar{C} because of its irritant and lachrymatory properties has been much studied as a chemical warfare agent and tear gas under the arbitrary designation "CN."

[For general surveys from this viewpoint see (20) (21). — \bar{C} is sol. in many org. solvents and is frequently loaded into grenades and shells in such solutions of which three common examples are "CNB" (consisting of $\bar{C} + C_6H_6 + CCl_4$), "CND" (consisting of $\bar{C} + Chylene dichloride (3:5130)), and "CNS" (consisting of <math>\bar{C} + Chylene + Chylene$

[For dispensing apparatus for \tilde{C} (29) or for mill for disintegration of \tilde{C} (30) see indic. refs.]

[For m.p. /compn. diagram of system \bar{C} + "Adamsite" (10-chloro-9,10-dihydrophenars-azine), eutectic, m.p. 50°, contg. 90 mole % \bar{C} , see (31).]

[For studies of effect of \bar{C} on skin see (32) (33) (34); for contamination of food by \bar{C} see (35).]

PREPARATION OF C

From chloroacetyl chloride with benzene. [For prepn. of \bar{C} from chloroacetyl chloride (3:5235) with $C_6H_6 + AlCl_3$ (yield 85-88% (15) (64)) (2) (14) (36) (71) see indic. refs.]

From acetophenone. [For prepn. of \bar{C} from acetophenone (1:5515) with Cl_2 in AcOH (4) (18), in CS_2 (85% yield (37)), in lgr. (38) or directly without solvent (yields 65% (6) (37)) (39) see indic. refs.; from acetophenone (1:5515) by electrolysis of its soln. in HCl (40), or by chlorination with aq. N-chlorourea (41), see indic. refs.]

From benzoyl chloride with diazomethane. [For formn. of \bar{C} from benzoyl chloride (3:6240) with diazomethane in ether (72% yield) see (3); note, however, that this procedure has subsequently been much disputed, and for discussion see also (42) (43) (44) (45) (46) (47) (48).]

From miscellaneous sources. [For prepn. of $\bar{\mathbb{C}}$ from N- $(\alpha,\beta$ -dichlorovinyl)diethylamine (yield 92.6% (49)), from chloroacetonitrile (50), or for possible forms. from chloroacetic acid (3:1370) (51), all with C_6H_5MgBr , see indic. refs.; for forms. of $\bar{\mathbb{C}}$ from phenyl copper (52), from phenyldichloroarsine (yields: 58.5% (53), 55% (54)) (55), all with chloroacetyl chloride (3:5235), see indic. refs.; for forms. of $\bar{\mathbb{C}}$ from 1-chloro-2-phenylpropanol-2 (styrene chlorohydrin) (3:9570) by oxidn. with $K_2Cr_2O_7/H_2SO_4$ (1) or from diphenacyltelluride dichloride by oxidn with KMnO₄ (5) see indic. refs; for forms. of $\bar{\mathbb{C}}$ from benzalacetophenone (chalcone) (1:5155) by acts. of Cl_2 in ter-butyl alc. (other prods. are also formed) see (17).]

CHEMICAL BEHAVIOR OF C

REDUCTION

No authentic studies on reduction of C appear to be reported.

OXIDATION

 \tilde{C} on oxidn. with CrO₃ (39), or $K_2Cr_2O_7 + H_2SO_4$ (58) (13) gives benzoic acid (1:0715). — \tilde{C} also reduces NH₄OH/AgNO₃ (13) [perhaps because of some hydrolysis to ω -hydroxy-acetophenone (1:5180)].

HALOGENATION

Chlorination. [\bar{C} on further chlorination under conditions favoring side-chain substitution would be expected to yield ω, ω -dichloroacetophenone (3:6835) and ultimately ω, ω, ω -trichloroacetophenone (3:6874), but no authentic record that this has actually been achieved can be found.]

Bromination. [\bar{C} with Br₂ under suitable conditions gives (56) ω -bromo- ω -chloroaceto-phenone, m.p. 37-37.5°, b.p. 133-134° at 7.5 mm. (56). — \bar{C} in AcOH + NaOAc with Br₂ as directed (57) gives a mixt. consisting of 30% ω , ω -dibromo- ω -chloroacetophenone + 70% ω , ω , ω -tribromoacetophenone.]

Nitration. \bar{C} in conc. H_2SO_4 at -20° treated as directed (9) with a mixt. of fumg. HNO₃ (D=1.50) + conc. H_2SO_4 gives (77% yield (9)) m-nitrophenacyl chloride, m.p. 103° (59), $102-103^\circ$ (16), $100.5-102^\circ$ (9). — [Note that the other two isomeric mononitrophenacyl chlorides, viz., o-nitrophenacyl chloride, m.p. $66-67^\circ$ (60) (61), and p-nitrophenacyl chloride, m.p. 107° (62), are also known, but prepd. indirectly; note also that no dinitration prods. of \bar{C} are known.]

BEHAVIOR OF Č WITH OTHER INORGANIC REACTANTS

With water. [\bar{C} does not readily hydrolyze with aq. but on protracted boilg. (e.g., 20 hrs. (63)) with a large vol. of aq. gives ω -hydroxyacetophenone (1:5180).]

With nitrous acid. \bar{C} with $\bar{H}NO_2$ (from *n*-butyl nitrite + HCl gas) in dry ether gives (yields: 85.6% (64), 82-86% (15)) ω -chloro- ω -isonitrosoacetophenone (phenylglyoxylohydroxamyl chloride) [Beil. X-662, X₁-(315)], white ndls. from CCl₄ (64) or from CCl₄ + C₆H₆ (3:1) (15), m.p. 132-133° (15) (64).

With PCl₅. [\tilde{C} with PCl₅ on distn. gives (65) α,β -dichlorovinylbenzene (α,β -dichlorostyrene) [Beil. V-477, V₂-(367)], b.p. 221°.]

With various salts of inorganic acids. [\bar{C} with KI (66) (67) or better NaI (38) in alc. gives ω -iodoacetophenone (phenacyl iodide) [Beil. VII-286], m.p. 30°; for study of rate of reactn. of \bar{C} with KI in acetone at 0° (11) or with NaI or LiI in acetone at 0° or -10° (10) see indic. refs.]

 \bar{C} does not add NaHSO₃ (37). — \bar{C} in alc. with Na₂S₂O₃ (2 moles) in aq. refluxed 20 hrs. gives sodium phenacylthiosulfate which with HCl gives (73% yield (69)) ω -mercaptoacetophenone (phenacyl mercaptan). — \bar{C} with Na₂S in alc. at 60° gives (70) diphenacyl sulfide [Beil. VIII-94, VIII₁-(541)], m.p. 76.5-77.2° (70), 76° (147); for use of this reactn. in detn. of \bar{C} see (14).

With ammonia. [\bar{C} with NH₃ (1 mole) would be expected to give ω -aminoacetophenone (phenacylamine) [Beil. XIV-49, XIV₁-(368)], but such direct result has never been reported; note, however, that \bar{C} (1 mole) with hexamethylenetetramine (1 mole) in CHCl₃ at room temp. for 12 hrs. gives (60% yield (68)) a 1:1 addn. cpd., m.p. 145°, which upon alcoholysis with conc. HCl in alc. 3 days in cold gives (63-74% yield (68)) phenacylamine hydrochloride.

[Č with alc. NH₃ in s.t. at 100° as directed (2) gives a mixt. contg. diphenacylamine hydrochloride [Beil. XIV-53, XIV₁-(371)], m.p. 235°, together with the hydrochlorides of 2,5-diphenylpyrazine and 2,6-diphenylpyrazine; for discussion of mechanism see (2).]

BEHAVIOR OF C WITH ORGANIC REACTANTS

With Hydrocarbons (+ AlCl₃)

 \tilde{C} with $C_6H_6+AlCl_3$ in s.t. at 100° failed to react (71). — \tilde{C} with toluene (1:7405) + $AlCl_3$ under reflux gives (71) a prod., m.p. 84–85°, which is presumably ω -(p-tolyl)acetophenone [Beil. VII-448], although this prod. obtd. by other methods has different consts.

With Organic Hydroxy (or Mercapto) Compounds

With alcohols. [C with NaOMe might be expected to yield ω-methoxyacetophenone, b.p. 228–230° at 760 mm. (72) (73), b.p. 118–120° at 15 mm. (72) (73), m.p. 7-7.5° (73) (corresp. semicarbazone, m.p. 85° (72), 129° (73) (note disagreement); corresp. 2,4-dinitrophenylhydrazone, m.p. 191–192° (73)); note, however, that no record of this reaction has been reported and the ω-methoxyacetophenone is best prepd. (71–78% yield (74)) from methoxyacetonitrile with C₆H₅MgBr; note also that C with alk. reagts. such as NaOMe reacts in an unexpectedly complex manner yielding (153) cyclic "halogen-diphenacyls."]

[\bar{C} with NaOEt would be expected to yield ω -ethoxyacetophenone [Beil. VIII-90], b.p. 134-136° at 21 mm. (75), 130° at 15 mm. (76), 120-122° at 15 mm. (77), $D_1^{20} = 1.0552$ (77), $D_2^{20} = 1.5250$ (77) (corresp. oxime, m.p. 55° (75); corresp. semicarbazone, m.p. 128° (75)); note, however, that no record of this reactn. has been reported and the ω -ethoxyacetophenone is best prepd. (68% yield (77)) cf. (75) (76) from ethoxyacetonitrile with

C₆H₅MgBr; note also that C with alk. reagts. such as NaOEt reacts in an unexpectedly complex manner yielding (153) cyclic "halogen diphenacyls."

[\bar{C} (1 mole) with ethylene glycol (1:6465) (1 mole) in C_6H_6 contg. trace of benzenesulfonic acid gives on htg (95% yield (81)) the corresp. cyclic ketal, viz., 2-(chloromethyl)-2-phenyl-1,3-dioxolane, mp. 67°, b.p. 144-146° at 15 mm. (81).]

With phenois. [\bar{C} with dry sodium phenolate (78) gives ω -phenoxyacetophenone [Beil. VIII-91], m.p. 74° cor. (79), b.p. 255-257° (78), 187° cor. at 9 mm. (79) (corresp. semi-carbazone, m.p. 187.0-187.5° cor. (79)); note, however, that this prod. is best prepd. (45% yield (79)) from phenoxyacetonitrile with C_6H_5MgBr , or from phenoxyacetyl chloride + C_6H_6 + AlCl₃ cf. (80).]

With mercaptans. [C with *n*-BuSH in alc. NaOH gives (82) phenacyl *n*-butyl sulfide, b.p. 140° at 3 mm., $D_{25}^{25} = 1.0589$, $n_{10}^{20} = 1.5050$.]

[$\bar{\mathbf{C}}$ with sodium p-nitrothiophenate in aq. alc. on htg. gives (98% yield (83)) phenacyl p-nitrophenyl sulfide, yel. pl. from 50–80% AcOH, m.p. 118°. — $\bar{\mathbf{C}}$ (1 mole) with sodium p-thiocresolate (1 mole) in MeOH boiled several hrs. does not give the expected phenacyl p-tolyl sulfide, m.p. 37° cf. (101); distillation of the reaction prod. gives (58 5% yield (84)) phenacyl p-tolyl sulfoxide, b p. 182–184° at 5 mm., m.p. 46° accompanied by acetophenone; note that with $\mathbf{H}_2\mathbf{O}_2$ this sulfoxide oxidizes to phenacyl p-tolyl sulfone, m.p. 110° (see also below).]

Behavior with Carbonyl Compounds

With aromatic aldehydes. [\bar{C} (1 mole) with benzaldehyde (1½ moles) in alc. with alc. NaOEt (1 mole) in cold condenses with loss of HCl giving (80% yield (85)) α -benzoyl- α -phenyl-othylene oxide (benzalacetophenone oxide) [Bul. XVII₁-(196)], colorless cryst. from alc. (85) or from cold acctone by addn. of pct. ether (86), mp. 89-90° (85) (86); note that this prod. can also be obtd. in other ways, notably from benzalacetophenone (chalcone) (1:5155) with Na₂O₂ + HCl in cold (85% yield (86)) or with H₂O₂ in alk. soln. (90% yield (88)) (87) (89); although *cis* and *trans* stereoisomers are possible, only one form is known.]

[\bar{C} with o-nitrobenzaldehyde in alc. NaOEt (although this particular pair has not actually been reported) should yield similarly α -benzoyl- α' -(o-nitrophenyl)ethylene oxide [Beil. XVII₁-(197)] since phenacyl bromide behaves (90) in this fashion; note that for this prod. the two expected geom. stereoisomers are both formed, one with m.p. 175°, the other with m.p. 110°.]

 $[\bar{C}]$ with m-nitrobenzaldehyde ir alc. NaOEt (although this particular pair has not actually been reported) should give similarly α -benzoyl- α' -(m-nitrophenyl)ethylene oxide [Beil. XVII₁-(197)] since phenacyl bromide behaves in this manner (80% yield (91)); one stereoisomer is known, m.p. 118° (91). — Note, however, that \bar{C} (1 mole) with m-nitrobenzaldehyde (1 mole) in AcOH satd. with HCl gas and stood 24 hrs. reacts differently giving (92) m-nitrobenzalacetophenone dichloride [Beil. VII₁-(238)], m.p. 148°,

[$\bar{\mathbb{C}}$ (1 mole) with p-methoxybenzaldehyde (anisaldehyde) (1:0240) (1 mole) in alc. NaOEt gives (93) α -benzoyl- α' -(p-methoxyphenyl)ethylene oxide, m p. 87° (93) (89); also obtd. from p-methoxybenzalacetophenone (1:9011) with alk. H₂O₂ (89).]

[\bar{C} (1 mole) + o-nitrobenzalacetophenone (1 mole) in acetone/diovane with alg. NaOEt (1 mole) gives in 15 min. but yield not stated (93) 1,2-dibenzoyl-3-(o-nitrophenyl)cyclopropane, m.p. 177° (93).]

Behavior of C with Salts of Organic Acids

Č with salts of organic acids gives in general the corresp. phenacyl esters although when the latter are to be prepd. as means of identification of the acids the more reactive phenacyl bromide is usually employed; for m.p.'s of the phenacyl esters of various acids of Order I see Vol. I, p. 650.

[\bar{C} with KCN in dil. alc. on htg. gives (47% yield (94)) ω -cyanoacetophenone (benzoylacetonitrile) [Beil. X-680, X₁-(322)], m.p. 83° (94), 80-81° (95) (96); this prod. may also be prepd. by other means, e.g., from phenacyl bromide with dil. alc. KCN (60% yield (97)), or from ethyl benzoate with acetonitrile + NaOEt (yields: 60% (96), 56% (95)).]

[Č with KSCN in MeOH (98) or EtOH (65) gives ω -thiocyanoacetophenone (phenacyl thiocyanate) [Beil. VIII-94], m.p. 74.1-76.6° cor. (98), 74° (99).]

[\tilde{C} with sodium *p*-toluenesulfinate in boilg, alc. gives (100) cf. (101) phenacyl *p*-tolyl sulfone (ω -(*p*-toluenesulfonyl)acetophenone), m.p. 110° (100) (see also above for formn. of this prod. from \tilde{C} + sodium thio-*p*-cresolate).]

Behavior of \bar{C} with RMgX Compounds

[$\bar{\mathbf{C}}$ (1 mole) with EtMgBr (1 mole) in dry ether gives an addn. prod. which after evapn. of ether, htg. at 130–140°, and hydrolysis gives (yield not stated {102}) benzyl ethyl ketone (1-phenylbutanone-2) [Beil VII-314, VII₁-(167)], b.p. 222–227° (103), 221–223° (102), 110° at 13 mm. (104) (corresp. semicarbazone, m.p. 156–156.5° cor. (105), 150–153° (103), 153° (106), β -form 152°, α -form 146° (104), 146° (102); corresp. 2,4-dimtrophenylhydrazone, m.p. 140–141° (103)); not rearr. in formn of this prod. by this method.]

[Č with n-hexyn-1-yl MgBr in dry ether adds normally and on hydrolysis gives (107) the expected 1-chloro-2-phenylnonyn-3-ol-2.

Behavior of C with Amines

With primary aliphatic amines. [C (1 mole) with MeNII₂ (2.5 moles) in alc. for 5-6 hrs. in cold gives (108) ω -(methylamino)acetopherone [Beil. XIV-50, XIV₁-(369)] (corresp. B.HCl (23% yield (108)), m.p. 219° (108)). — C with n-BuNH₂ similarly gives (35% yield (108)) ω -(n-butylamino)acetopherone hydrochloride, m.p. 214-215° (108).]

[\bar{C} with β -ammoethanol (ethanolamine) readily gives (109) N-(β -hydroxyethyl)phenacylamine, m.p. 144° (109).]

With primary aromatic amines. [C with aniline should yield N-(phenacyl)aniline [Beil. XIV-51, XIV₁-(369)], m.p. 98-99° (110) (corresp. oxime, m.p. 105-106° (111); corresp. semicarbazone, m.p. 171° (110)); however, although the rate of this reaction in abs. alc. at 40° (38) and in 90% alc. at 30.5° (16) cf. (112) has been studied, the usual method of prepn. of N-(phenacyl)aniline is from phenacyl bromide + amline. — Pure N-(phenacyl)aniline, contrary to earlier statements, is remarkably stable and can be exposed to air at room temp. for 18 months or distilled under reduced press. (b.p. 208-210° at 12 mm.) without change (113); for important study of mechanism of conversion of N-(phenacyl)aniline to 2-phenylindole see (113) (114).]

[The behavior of \bar{C} with the three toluidines has not itself been studied but should be similar to that of phenacyl bromide which with o-toluidine gives (115) (116) N-(phenacyl)o-toluidine [Beil. XIV-52, XIV₁-(370)], m.p. 91° (116), 89° (115) (corresp. oxime, m.p. 92° (116)); with m-toluidine gives N-(phenacyl)-m-toluidine, m.p. 110° (117); with p-toluidine gives N-(phenacyl)-p-toluidine [Beil. XIV-52, XIV₁-(370)], m.p. 134° (118), 127° (115) (corresp. oxime in two geom. stereoisomers of m.p. 97° and 92°, resp. (111)).]

With secondary aliphatic amines. [\bar{C} with Me₂NH should yield ω -(dimethylamino)-acetophenone (phenacyl dimethylamine) [Bell. XIV-50], b.p. 126-128° at 18 mm. (119), 122-123° at 14 mm. (120) (corresp. \bar{B} .HCl, m.p. 174° (120), corresp. \bar{B} .HBr, m.p. 184-186° (121), corresp. \bar{B} .PkOH, m.p. 150° (119), 143° (122), 141° (123)); note, however,

that this particular combination of reactants has not actually been reported and that the ω -(dimethylamino)acetophenone is usually obtd. from phenacyl bromide with Me₂NH (119) (121), or from dimethylaminoacet-N,N-dimethylamide with C₆H₅MgBr (80% yield (120) (125)).]

[\bar{C} (1 mole) with Et₂NH (2 moles) in C₆H₆ stood 2 days at room temp. ppts. Et₂NH.HCl and gives (65% yield {125}) ω -(diethylamino)acetophenone, b.p. 148-152° at 30 mm. {125}, $n_{13}^{25} = 1.5180$ (125).]

 $[\bar{C} + bis-(\beta-hydroxyethyl)amine (diethanolamine) in C₆H₆ on long boilg. gives (109) N-phenacyl-N,N-bis-(\beta-hydroxyethyl)amine, m.p. 44° (109).]$

With secondary heterocyclic amines. [Č with piperidine in dry ether splits out HCl and yields (126) ω -(piperidine)acetophenone (N-(phenacyl)piperidine) [Beil. XX-42], b.p. 180-181° cor. at 26 mm. (127), 157° at 15 mm. (128), 163-164° at 13 mm. (126), $D_2^{21.2} = 1.0430$ (126), $n_D^{22.4} = 1.5408$ (126) (corresp. B.HCl, mp 226-227° (129), corresp. B.HBr, m.p. 227-228° (135), corresp. oxime, m.p. 112-115° (130)).]

[Č with morpholine in dry ether ppts. morpholine HCl and yields (131) ω -(morpholino)-acetophenone (N-(phenacyl)morpholine), m.p. 50-52° (132) (corresp. B.HCl, m.p. 222-223° cor. (133), 219-223° (134), 213-214° dec. (131), 212-214° (132); corresp. B.PkOH, m.p. 156-157° (132)).]

[\bar{C} (1 mole) with N'-phenylpiperazine (2 moles) in dry ether at room temp. for several hrs. (136) or \bar{C} (1 mole) with N'-phenylpiperazine (1 mole) + slight excess anhydr. Na₂CO₃ in alc. refluxed ½ hr. (136) gives 80-85% yield N-phenacyl-N'-phenylpiperazine, m.p. 106-108° cor. (136) (corresp. B.HCl, m.p. 210-212° cor.; corresp. oxime, m.p. 157-158° cor. (136)).]

[Note, however, that \bar{C} with 3-carbethoxy-2-methylpyrrole + AlCl₃ in CS₂ does not acylate the nitrogen but gives Friedel-Crafts type reaction yielding (137) 3-carbethoxy-2-methyl-5-phenacylpyrrole, m.p. 205°.]

With tertiary aliphatic amines. [Direct addn. of \ddot{C} to Me₃N appears not to have been reported; the quaternary salt to be expected, viz, phenacyl-trimethyl-ammonium chloride, m.p. 204° dec. (138), 202° (121), has been prepd. indirectly.]

With tertiary aromatic amines. [The quaternary salt, viz., dimethyl-phenyl-phenacyl-ammonium chloride, to be expected from C + dimethylaniline is unreported.]

With tertiary heterocyclic amines. (See also below under O's.)

[\bar{C} (1 mole) with pyridine (1+ moles) in dry C_6H_6 on warming gives (25% yield (139)) phenacyl-pyridinium chloride, mp. 109-110° (139), 113° (140); note that this prod. with aq. 20% NaOH at room temp. undergoes cleavage giving (96% yield (141)) benzoic acid (1:0715) and (30% yield (141)) N-methylpyridone-2 [Beil. XXI-268, XXI₁-(278)], b.p. 127° at 12 mm. (141). — For study of rate of addn. of \bar{C} to pyridine in alc. soln. at 55.6° (142) or in 90% alc. at 30.5° (16) cf. (112) see indic. refs.]

Behavior of C with Arylhydrazines

(See also below under \mathbb{O} 's.) — $\overline{\mathbb{C}}$ with many arylhydrazines does *not* yield the corresp. arylhydrazones because the reaction takes a different course.

Č (2 g.) with phenylhydrazine (1.4 g.) in warm EtOH (20 ml.) contg. NaOAc.3H₂O in aq. (10 ml.) ppts. (14) a yellow solid, m.p. 137° dec. (14), regarded as 1,3-diphenyl-(1,2-diazacyclobutene-2). — Similarly, Č with o-tolylhydrazine gives (14) 1-(o-tolyl)-3-phenyl-(1,2-diazacyclobutene-2), m.p. 147.2° (14); Č with p-tolylhydrazine gives (14) 1-(p-tolyl)-3-phenyl-(1,2-diazacyclobutene-2), m.p. 159.8° dec. (14); Č with p-nitrophenyl-hydrazine gives (14) 1-(p-nitrophenyl)-3-phenyl-(1,2-diazacyclobutene-2), m.p. 173° dec. (14). — [For further discussion of structures of these prods. see also (143).]

Behavior of C with Other Miscellaneous Nitrogeneous Reactants

Č with diazomethane in dry ether + MeOH for 12 hrs. gives (88% yield (144)) 3-chloro-2-phenyl-1.2-epoxypropane (α -chloromethyl- α -phenyl-ethylene oxide), b.p. 135-137° at 17 mm. (144).

- © Chloromethyl phenyl ketoxime: cryst. from CS₂, m.p. 88.5-89° (4), 88-89° (17). [From C (1 mole) + hydroxylamine hydrochloride (3 moles) in dil. MeOH stood overnight, prod. pptd. by addn. of aq. (4); note that this oxime on Beckmann rearr. with PCl₅ gives (4) ω-chloroacetanilide, m.p. 134.5° (5).]
- © Chloromethyl phenyl ketone 2,4-dinitrophenylhydrazone: orange cryst., m.p. 212° cor. (145). [See above for behavior of \tilde{C} with various other arythydrazines.]
- © Chloromethyl phenyl ketone semicarbazone: m.p. 160° on "Maquenne bloc" (1), 156° (146), 149° (147). [From Č (3.1 g.) in alc. (25 ml.) with semicarbazide hydrochloride (2.2 g.) in aq. (12.5 ml.) at 40° on addn. of NaHCO₃ (1.7 g.) in small increments; yield 71% (147); for study of chem. behavior of this prod. see (147).]
- N-(Phenacyl)phthalimide (ω-phthalimidoacetophenone) [Beil. XXI-479]: m.p. 167° u.c. (148), 166° (149). [This prod. has never been reported from C + K phthalimide but has been prepd. indirectly. However, for its prepn. from phenacyl bromide with K phthalimide see (150).]
- N-(Phenacyl)tetrachlorophthalimide (ω -(tetrachlorophthalimido)acetophenone): pl. from CHCl₃ on pouring into MeOH, m.p. 258-259° (151). [From \bar{C} (?) or phenacyl bromide with K tetrachlorophthalimide (151).]
- © Condensation prod. from \tilde{C} with N-methyl- β -(carbohydrazido)pyridinium p-toluenesulfonate: cryst. from EtOH/ether 1:1, m.p. 120° cor. (152). [From \tilde{C} + the quatsalt of nicotinic acid hydrazide with methyl p-toluenesulfonate (152).]
- 3:1212 (1) Detoeuf, Bull. soc. chim. (4) 31, 177 (1922). (2) Tutin, J. Chem. Soc. 97, 2495-2503 (1910). (3) Clibbens, Nierenstein, J. Chem. Soc. 107, 1491-1492 (1915). (4) Korten, Scholl, Ber. 34, 1902-1907 (1901). (5) Rust, Ber. 30, 2833 (1897). (6) Staedel, Ber. 10, 1830-1835 (1877). (7) Mohler, Sorge, Helv. Chim. Acta 21, 70 (1938). (8) Mohler, Polya, Helv. Chim. Acta 19, 1238 (1936). (9) Barkenbus, Clements, J. Am. Chem. Soc. 56, 1369-1370 (1934). (10) Conant, Hussey, J. Am. Chem. Soc. 47, 486 (1925).
- (11) Conant, Kirner, J. Am. Chem. Soc. 46, 239, 250 (1924). (12) Kohlrausch, Pongratz, Monatsh. 64, 379 (1934). (13) Dijkstra, Chem. Weekblad 34, 354-355 (1937). (14) Hoogeveen, Rec. trav. chim. 50, 669-678 (1931). (15) Levin, Hartung, Org. Syntheses 24, 25-28 (1944). (16) Baker, J. Chem. Soc. 1932, 1148-1157. (17) Jackson, Pasiut, J. Am. Chem. Soc. 49, 2078-2079 (1927). (18) Nathan, Watson, J. Chem. Soc. 1933, 895. (13) Kireev, Kaplan, Vasneva, J. Phys. Chem. (U.S.S.R.) 5, 739-741 (1934); Cent. 1935, II 2043 [C.A. 29, 2424 (1935)]. (20) Prentiss, "Chemicals in War," McGraw-Hill Book Co. N.Y., 1st ed., pp. 142-144 (1937).
- (21) Sadtler, Chem. Industries 40, 584-586 (1937). (22) Barker, Danner (to Secretary of War, U.S.A.), U.S. 2,146,715, Feb. 14, 1939; Cent. 1939, I 5100; C.A. 33, 3920 (1939). (23) von Frantzius (to Hercules Gas Munitions Corp), U.S. 2,068,159, Jan. 19, 1937; Cent. 1937, I 3442; C.A. 31, 2010 (1937). (24) Kobe, U.S. 1,993,610, March 5, 1935; Cent. 1935, I 3750; C.A. 29, 2631 (1935). (25) Oglesby, Ehrenfeld (to Federal Laboratories, Inc.), U.S. 1,864,754, June 28, 1932; Cent. 1932, II 2912; C.A. 26, 4393 (1932). (26) Bradner, U.S. 1,805,755, May 19, 1931; Cent. 1931, II 3076; C.A. 25, 3745 (1931). (27) Goss (to Lake Erie Chem Co), U.S. 1,792,010, Feb. 10, 1931; Cent. 1932, I 168; C.A. 25, 2000 (1931). (28) I.G., Ger. 494,463, March 24, 1930; Cent. 1930, II 1430; C.A. 24, 2849 (1930). (29) Anthony, Chem. Warfare Bull. 28, 187 (1942); C.A. 37, 196 (1943). (30) McBride, U.S. 2,269,466, Jan. 13, 1942; C.A. 36, 2765 (1942).
- (31) Pusin, Hrustanovic, Ber. 71, 802-803 (1938). (32) Linton, J. Franklin Inst. 235, 642-643 (1943). (33) Dietel, Med. Klin. 29, 1208 (1933); Cent. 1933, II 2026; not in C.A. (34) Hanzlik, Tarr, et al., J. Pharmacol. 14, 221-229 (1919); Cent. 1920, I 510; C.A. 14, 1161 (1920). (35) Plücker, Z. Untersuch. Lebensm. 68, 313-320 (1934). (36) Friedel, Crafts, Ann. chim. (6) 1, 507-508 (1884). (37) Gautier, Ann. chim. (6) 14, 377-381 (1888). (38) Matheson, Humphries, J. Chem. Soc. 1931, 2514-2516. (39) Graebe, Ber. 4, 34-35 (1871). (40) Szper, Bull. soc. chim. (4) 51, 655-656 (1932).

(41) Behal, Detoeuf, Compt. rend. 153, 1231 (1911).
(42) Bradley, Robinson, J. Chem. Soc. 1928, 1310-1318.
(43) Bradley, Schwarzenbach, J. Chem. Soc. 1928, 2904-2912.
(44) Nierenstein, Nature 121, 940-941 (1928).
(45) Bradley, Robinson, Nature 122, 130-131 (1928).
(46) Nierenstein, Nature 122, 313 (1928).
(47) Malkin, Nierenstein, J. Am. Chem. Soc. 52, 1504-1508 (1930).
(48) Bradley, Robinson, J. Am. Chem. Soc. 52, 1558-1565 (1930).
(49) Ott, Dittus, Weissenburger, Ber. 76, 86 (1943).
(50) Mathus, Bull. soc. chim. Belg. 34, 285-289 (1925).

(51) Peters, Griffith, Briggs, French, J. Am. Chem. Soc. 47, 453-454 (1925). (52) Bolth, Whaley, Starkey, J. Am. Chem. Soc. 65, 1457 (1943). (53) Malinovskii, J. Gen. Chem. (U.S.S.R.) 5, 1355-1358 (1935); Cent. 1936, II 1528; C.A. 30, 2182 (1936). (54) Malinovskii, Sci. Records Gorky State Univ. 7, 34-47 (1939); C.A. 35, 444 (1941). (55) Gibson, Johnson, Vining, Rectrav. chim. 49, 1035 (1930). (56) Rabcewicz-Zubkowski, Roczniki Chem. 9, 532-537 (1929); Cent. 1929, II 2773; C.A. 24, 92 (1930). (57) Aston, Newkirk, Dorsky, Jenkins, J. Am. Chem. Soc. 64, 1415-1416 (1942). (58) Hoogeveen, Chemistry & Industry 59, 550 (1940). (59) Baker,

J. Chem. Soc. 1931, 2420. (60) Arndt, Eistert, Partale, Ber. 60, 1369 (1927).

(61) Ruggli, Reichwein, Helv. Chim. Acta 20, 917 (1937). (62) Dale, Nierenstein, Ber. 60, 1027 (1927). (63) Weidenhagen, Herrmann, Ber. 68, 1955 (1935). (64) Levin, Hartung, J. Org. Chem. 7, 411-412 (1942). (65) Dyckerhoff, Ber. 10, 119-121 (1877). (66) Collet, Compt. rend. 128, 312 (1899). (67) Paal, Stern, Ber. 32, 532-533 (1899). (68) Mannich, Hahn, Ber. 44, 1544-1546 (1911). (69) Kretov, Panchenko, Konovalchk, J. Gen. Chem. (U.S.S.R.) 1, 396-400 (1931); Cent. 1932, I 2835; C.A. 26, 2442 (1932). (70) Chrzasczewska, Chwalinski, Roczniki Chem. 7, 67-73 (1927); Cent. 1927, II 415, C.A. 22, 1339 (1928).

(71) Collet, Bull. soc. chim. (3) 17, 506-507 (1897).
(72) Pratt, Robinson, J. Chem. Soc. 123, 748 (1923).
(73) Allen, Scarrow, Can. J. Rescarch 11, 400 (1934).
(74) Moffett, Shriner, Org. Syntheses 21, 79-80 (1941).
(75) Sommelet, Ann. chim. (8) 9, 521-522 (1906); Bull. soc. chim.
(4) 1, 389-390 (1907), Compt. rend. 138, 91 (1904).
(76) Pratt, Robinson, J. Chem. Soc. 121, 1580 (1922).
(77) Rigler, Henze, J. Am. Chem. Soc. 58, 475 (1936).
(78) Vandevelde, Bull. acad. roy. Belg. 1899, 204-211; Cent. 1899, II 91-92.
(79) Whitney, Henze, J. Am. Chem. Soc. 60, 1149-1150 (1938).
(80) Ramart-Lucas, Hoch, Bull. soc. chim. (4) 51, 826, 835-836 (1932).

(81) Kuhn, J. prakt. Chem. (2) 156, 119-121 (1940). (82) Whitner, Reid, J. Am. Chem. Soc. 43, 639 (1921). (83) Waldron, Reid, J. Am. Chem. Soc. 45, 2401-2402 (1923). (84) Kohler, Potter, J. Am. Chem. Soc. 58, 2168 (1936). (85) Widman, Ber. 49, 478 (1916). (86) Kohler, Richtmyer, Hester, J. Am. Chem. Soc. 53, 213 (1931). (87) Weitz, Ger. 395,435, May 19, 1924; Cent. 1924, II 1404, not in C.A. (88) Moureu, Ann. chim. (10) 14, 339-340 (1930). (89) Weitz, Scheffer, Ber. 54, 2338-2340 (1921). (90) Bodforss, Ber. 51, 195 (1918).

(91) Bodforss, Ber. 49, 2796–2797 (1916). (92) Bodforss, Ber. 55, 144 (1919); Ber. 55, 3581 (1922). (93) Bodforss, Ann. 534, 227–229, 241–243 (1938). (94) Arndt, Loewe, Ber. 71, 1630 (1938). (95) Dorsch, McElvain, J. Am. Chem. Soc. 54, 2962 (1932). (96) Rehberg, Henze, J. Am. Chem. Soc. 63, 2787, Note 10 (1941). (97) Gabriel, Eschenbach, Ber. 30, 1127–1128 (1897). (98) Rabeewicz-Zubkowski, Kaflinska, Roczniki Chem. 10, 555–569 (1930); Cent. 1930, 11 3274; not in C.A. (99) Arapides, Ann. 249, 10–12 (1888). (100) Arndt, Martius, Ann. 499, 281 (1932).

(101) Gilman, King, J. Am. Chem. Soc. 37, 1140 (1925). (102) Tiffeneau, Ann. chim. (8) 10, 368-369 (1907). (103) Thomson, Stevens, J. Chem. Soc. 1932, 2611. (104) Levy, Dvoleitzka-Gombinska, Bull. soc. chim. (4) 49, 1770 (1931). (105) Tiffeneau, Cahnmann, Bull. soc. chim. (5) 2, 1882 (1935). (106) Tiffeneau, Fourneau, Compt. rend. 146, 699 (1908). (107) Tiffeneau, Deux, Compt. rend. 213, 753-758 (1941); Cent. 1942, II 1558, C.A. 37, 4049 (1943). (108) Hyde, Browning, Adams, J. Am. Chem. Soc. 50, 2290-2291 (1928). (109) Brighton, Reid, J. Am. Chem. Soc. 65, 479 (1943). (110) Busch, Hefele, J. prakt. Chem. (2) 83, 431-432 (1911).

(111) Busch, Kammerer, Ber. 63, 652-653, 658 (1930). (112) Baker, J. Chem. Soc. 1933, 1128-1133. (113) Crowther, Mann, Purdie, J. Chem. Soc. 1943, 58-68. (114) Verkade, Janetzky, Rec. trav. chim. 62, 763-774 (1943); C.A. 38, 6284 (1944). (115) Bischler, Ber. 25, 2865-2867 (1892). (116) Busch, Stratz, J. prakt. Chem. (2) 150, 27 (1937). (117) Cooper, Campbell, J. Chem. Soc. 1935, 1210. (118) Lellmann, Donner, Ber. 23, 167-168 (1890). (119) von Braun, Weissbach, Ber. 62, 2425 (1929). (120) Eidebenz, Arch. Pharm. 280, 49-63 (1942); Cent. 1942, II 1227; C.A. 38, 4927 (1944).

(121) Rumpel, Arch. Pharm. 237, 223, 234-235 (1899). (122) Thomson, Stevens, J. Chem. Soc. 1932, 2610. (123) Stevens, Cowan, MacKinnon, J. Chem. Soc. 1931, 2572. (124) Eidebenz (to Chem. Werke Albert), Ger. 681,849, Oct. 3, 1939; Cent. 1939, II 4281; C.A. 37, 2376 (1942); Ger. 651,543, Oct. 16, 1937; Cent. 1938, I 658; C.A. 32, 588 (1938). (125) Marvel, du Vigneaud, J. Am. Chem. Soc. 46, 2098 (1924). (126) DuFraisse, Moureu, Bull. soc. chim. (4) 41, 472-473 (1927). (127) Rabe, Schneider, Ber. 41, 874-875 (1908). (128) Wegler, Frank, Ber. 79.

1283 (1937). {129} Cromwell, J. Am. Chem. Soc. 63, 838 (1941). {130} Cromwell, Caughlan, Gilbert, J. Am. Chem. Soc. 66, 403 (1944).

(131) Eidebenz (Chem. Werke Albert), Ger. 667,356, Nov. 9, 1938; Cent. 1939, I 1410; C.A. 33, 2287 (1939). (132) Mason, Ross, J. Am. Chem. Soc. 62, 2883 (1940). (133) Rubin, Day, J. Org. Chem. 5, 57 (1940). (134) Cromwell, J. Am. Chem. Soc. 62, 2899 (1940). (135) Dunn, Stevens, J. Chem. Soc. 1934, 281. (136) Hampton, Pollard, J. Am. Chem. Soc. 59, 2446-2447 (1937). (137) Fischer, Barat, Ann. 512, 238 (1934). (138) Algar, Hickey, Sherry, Proc. Roy. Irish Acad. 49-B, 109-119 (1943); C.A. 37, 6659 (1943). (139) Babcock, Nakamura, Fuson, J. Am. Chem. Soc. 54, 4408-4409 (1932). (140) Marvel, Scott, Amstutz, J. Am. Chem. Soc. 51, 3639 (1929).

(141) Babcock, Fuson, J. Am. Chem. Soc. 55, 2946-2947 (1933). (142) Clarke, J. Chem. Soc. 97, 427 (1910). (143) Bodforss, Ber. 72, 468-482 (1939). (144) Adamson, Kenner, J. Chem. Soc. 1939, 185. (145) Allen, Richmond, J. Ory Chem. 2, 224 (1937). (146) Knopfer, Monatsh. 31, 108 (1910). (147) Hoogeveen, van Hoogstraten, Rec. trav. chim. 52, 378-384 (1933). (148) Gabriel, Ber. 41, 242, Note 1 (1908). (149) Wanag, Veinbergs, Ber. 75, 1562 (1942). (150) Gabriel, Ber. 41, 1132 (1908).

(151) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934). (152) Allen, Gates, J. Org. Chem. 6, 596-601 (1941). (153) Widman, Ann. 400, 86-130 (1913).

3:1220 1,2,3,4,5,6-HEXACHLOROHEXENE-3

Beil. S.N. 11

M.P. 58-59° (1) B.P. 110-112° at 2 mm. (1)

Colorless cryst. from pet. ether.

[For prepn. from hexadiene-2,5-yne-3 (divinylacetylene) (2) with excess Cl₂ in CCl₄ for 12 hrs. (10% yield (1)) see (1)]

C fails to react with Cl₂ even at elevated temperatures in light, and is unaffected by hot HNO₃ or by O₃; alk. KMnO₄ causes complete decomposition (1).

3:1220 (1) Coffman, Carothers, J. Am. Chem. Soc. **55**, 2040-2047 (1933). (2) Nieuwland, Calcott, Downing, Carter, J. Am. Chem. Soc. **53**, 4200-4202 (1931).

3: 1265 1,1,1,2,3-PENTACHLORO-2- CH_3 $C_4H_5Cl_5$ Beil. S.N. 10 $CICH_2$ —C— CCl_3

M.P. 59.5° (1)

[For prepn. of \bar{C} from 1,1,3-trichloro-2-methylpropene-1 (3:5025) with Cl_2 see (1).] 3:1265 (1) Jacob, Bull. soc. chim. (5) 7, 581-586 (1940).

46-47°

46°

(12)

(13)

[See also anhydrous chloral (3:5210) and chloral ethylalcoholate (3:0860)]

The m.p. of \bar{C} is profoundly affected by mode of heating and by pressure (1) (2) but when taken in test tube in ord. m.p. apparatus is claimed to be consistently $59-60^{\circ}$ (2). — [For especially extensive studies on the m p. of \bar{C} see (1) (2) (6) (10)]

 \bar{C} undergoes a transition point at 32° detectable by dilatometric methods (15). Furthermore, \bar{C} on heating dissociates into anhydrous chloral and H_2O ; the temperature at which dissocn. begins is unknown, but dissocn. is complete at 78° (15).

Ordinary, definitely the monohydrate, but other hydrates of chloral (3:5210) have been claimed (6). However, the suggestion (16) that C may exist in two modifications appears to be discredited (6) (10).

[For study of crystal structure of \bar{C} see (18); for density and refractive index of various solns. of \bar{C} in aq., EtOH, or toluene see (12); for study of toxicity of \bar{C} see (19)]

Note that \tilde{C} on htg. does *not* give inflammable vapor (diff. from chloral ethylalcoholate (3:0860).

 \bar{C} is eas. sol. in aq. or alc.; much less sol. in CHCl₃ or toluene. [E.g., 1 pt. aq. dissolves following parts \bar{C} at indic. temps.: at 0°, 2.4; at 5°, 2.9; at 10°, 3.8; at 15°, 4.9; at 20°, 6.6; at 25°, 8.3; at 30°, 10.1; at 35°, 12.1; at 40°, 14.3 pts. \bar{C} (20).] — Aq. solns. of \bar{C} are frequently designated as chloral sirup; for study of stability of such solns. see (21).

CHEMICAL BEHAVIOR OF Č

Important note. The chemistry of chloral hydrate ($\bar{\mathbb{C}}$) on one hand and that of anhydrous chloral (3:5210) on the other is so closely interwoven that the division of material between them in this book is necessarily arbitrary. Most of the definite chemical reactions of chloral hydrate have been associated with the text of anhydrous chloral (3:5210), which should always be consulted. Certain methods for the detection and for determination of chloral and chloral hydrate, however, are brought together here under the latter.

DETERMINATION OF C

For the quantitative detn. of $\tilde{\mathbf{C}}$ several different principles have been employed as further explained below.

By behavior with alkali. This method is based upon the fact that \bar{C} with aq. alkali undergoes hydrolytic cleavage to CHCl₃ (3:5050) and formic acid (1:1005); since the

latter is neutralized 1 equivalent of alkali is used up for each mole of formic acid produced and therefore for each mole of \tilde{C} originally present. Since on the one hand the CHCl₃ produced is readily volatile and since on the other it is itself attacked by the excess alkali, some standardization of conditions is required. The process usually involves use of a known amount (excess) of standard alkali followed by back titration with standard acid.

[For especially valuable summaries and discussion of this method see (22) (23); for additional material on characteristics of this method see (24) (25) (26) (27) (28) (29) (31) (32) (33) (34) (35) (41); for discussion of detn. of the formate produced see (22).]

If the sample contains other substances which independently react with alkali and thus interfere with the above method, \bar{C} may be determined by reduction to acetaldehyde (1:0100) and characterization of the latter. E.g., \bar{C} with Zn + strong HCl (36) (37), or with Zn + dil. H₂SO₄ (37) (38) (27) cf. (42), gives acetaldehyde (1:0100); this may be detd. as p-nitrophenylhydrazone (36) (or otherwise) or if H₂SO₄ was used total chloride ion may be determined (42). This reduction to acetaldehyde is of value in detn. of \bar{C} in presence of CHCl₃ (3:5050) or of α,α,β -trichloro-n-butyraldehyde ("butyrchloral") (3:5910) (38).

By determination of total chlorine as chloride ion. In addition to the reduction methods (mentioned in the preceding paragraph) for conversion of all the chlorine of C to chloride ion, this may also be effected by complete hydrolysis with alkali (usually alcoholic alkali best in pressure bottle (39)) (40) (41); for extensive review of methods based on this principle see (22); the total chloride ion is afterward detd. by conventional methods.

By oxidation methods. By appropriate reagents \bar{C} can be oxidized to trichloroacetic acid (3:1150); by use of a known amount (excess) of standard soln. of oxidant followed by back titration to determine residual oxidant, the amount corresp. to oxidn. of \bar{C} can be detd. For studies of this method using I_2 (22) (42) (34) (43), Br₂ (42), KMnO₄ (42), or (NH₄)₂S₂O₈ (44) see indic. refs.

DETECTION OF C BY VARIOUS COLOR REACTIONS

With various phenols. [For color tests with resorcinol (1:1530) + aq. alk. (45), with pyrogallol (1:1555) + 66% H₂SO₄ (use in distinction from "butyrchloral" (3:5910) (46)), with phloroglucinol (1:1620) + aq. alkali (47) (49) see indic. refs.]

[For behavior of \bar{C} with resorcinol (1:1530) + KBr + conc. H₂SO₄ see (52).]

With pyridine + aq. alk. Since \bar{C} with aq. alk. on warming gives CHCl₃ (3:5050), detection of the latter by means of the pink to red color produced with pyridine in pres. of conc. aq. alkali (Fujiwara reaction) may be used as indirect test for \bar{C} (48) (51). Note, however, that the test is not specific since it is given by various other-trihalogen compounds. [For further information on the Fujiwara reaction see also under trichloroethylene (3:5170).]

With fuchsin-aldehyde reagent. Note that \bar{C} (unlike chloral (3:5210)) does not give color with fuchsin-aldehyde reagent (50).

① 1,1,1-Trichloro-2-methylpropanol-2 ("Chloretone"): M.p. 96°. Convert Č with aq. alk. to CHCl₃ (3:5050) and derivatize the latter by combination with acetone to "chloretone" (3:2662).

3:1270 (1) Banchetti, Ann. chim. applicata 31, 422-429 (1941); Cent. 1942, II 1779; C.A. 38, 2313 (1944). (2) Banchetti, Ann. chim. applicata 31, 463-466 (1941); Cent. 1942, II 2577; C.A. 38, 2314 (1944). (3) Ingold, J. Chem. Soc. 125, 1536-1537 (1924). (4) Meyer, Dulk, Ann. 171, 74-76 (1874). (5) Petrikaln, Hochberg, Z. physik. Chem. B-4, 306 (1929). (6) van Rossem, Z. physik. Chem. 62, 681-712 (1908). (7) Tsakalotos, Bull. soc. chim. (4) 13, 282-283 (1913). (8) Bellucci, Gazz. chim. ital. 43, I 527 (1913). (9) Ramsay, Young, Phil. Trans. 177, I 77 (1886). (10) Wolf, J. Phys. Chem. 4, 21-32 (1900).

(11) Jacobsen, Ann. 157, 243-248 (1871). (12) Rudolfi, Z. physik. Chem. 37, 426-447 (1901).

(13) Personne, Compt. rend. 69, 1363 (1869). (14) Berthelot, Ann. chim. (5) 12, 536 (1877). (15) Mounfield, Wood, J. Chem. Soc. 1926, 498-499. (16) Pope, J. Chem. Soc. 75, 455-460 (1899). (17) Kurnakow, Efremov, Z. physik. Chem. 85, 401-418 (1913). (18) Elliott, Z. Krist. 98, 180 (1937); Cent. 1938, I 1104; C.A. 32, 1998 (1938). (19) Adams, J. Pharmacol. 78, 340-345 (1943); C.A. 37, 6035 (1943). (20) Speyers, Am. J. Sci. (4) 14, 294 (1902).

(21) Danckworth, Arch. Pharm. 280, 197-205 (1942); C.A. 37, 2516 (1943). (22) Watson, Am. J. Pharm. 102, 506-525 (1930). (23) Weston, Ellis, Chem. News 95, 210-211 (1907). (24) Meyer, Haffter, Ber. 6, 600-601 (1873). (25) Khait, Ukraın Gosudarst. Inst. Eksptl. Farm. (Kharkov) 1939, No. 3, 80-81; C.A. 36, 2812 (1942). (26) Goretskii, Farmatsiya 1949, No. 6, 31-33; C.A. 35, 2678 (1941). (27) Meillere, J. pharm. chim. (8) 11, 145-147 (1930); Cent. 1930, I 3221; C.A. 24, 4586 (1930). (28) Andron, J. pharm. chim. (8) 8, 453-455 (1928); Cent. 1929, I 1845; C.A. 23, 3775 (1929). (29) Andron, Bull. soc. pharm. Bordeaux 64, 199-201 (1926): Cent. 1927, I 1874; C.A. 21, 2045-2046 (1927). (30) Fleury, Malmy, J. pharm. chim. (8) 8, 537-542 (1928), Cent. 1929, I 2092; C.A. 23, 3775 (1929).

(31) Francois, J. pharm. chim. (8) 7, 54-57 (1928); Cent. 1928, I 1898, C.A. 22, 1652 (1928). (32) Brugeas, Bull. soc. pharm. Bordeaux 66, 12-17 (1928), Cent. 1928, I 1986; CA. 23, 4014 (1929). (33) Self, Pharm. J. (4) 25, 4-7 (1907); Cent. 1907, II 1019; C.A. 2, 448 (1908). (34) Kolthoff, Pharm. Weekblad 60, 2 (1923), cf. Z. anal. Chem. 64, 454 (1924). (35) Garnier, Bull. sci. pharmacol. 15, 77-82 (1908); Cent. 1908, I 1492; C.A. 4, 234 (1910), cf. Z. anal. Chem. 49, 249 (1910). (36) Griebel, Weiss, Z. Untersuch. Lebensm. **56**, 163 (1928) (37) Personne, Ann. **157**, 113-115 (1871). (38) Jona, Giorn. farm. chim. **61**, 57-59 (1912); Cent. **1912**, 1 1148, C.A. **6**, 1337-1338 (1912). (39) Wallis, Pharm. J. (4) 22, 162-163 (1906); Cent. 1906, I 1053. (40) Lormand, J. pharm. chim.

(8) 9, 151-153 (1929), Cent. 1929, I 2909; C.A. 23, 3775 (1929).

(41) Brugeas, Bull. soc. pharm. Bordeaux 66, 78-83 (1928), Cent. 1928, II 591; not in C.A. (42) Schwicker, Z. anal. Chem. 110, 161-165 (1937). (43) Rupp, Arch. Pharm. 241, 326-328 (1903); see also correction Pharm. Zentralhalle 64, 151, Cent. 1923, IV 483. (44) Rogers, Trans. Roy. Soc. Canada (3) 17, III 164 (1923), Cent. 1924, II 515, not in CA. (45) Ware, Chemist and Druggist, 123, 282 (1935), Cent. 1936, I 1667. (46) Gabutti, Boll. chim farm. 42, 777-778 (1903); Cent. 1904, I 480-481. (47) Jaworowski, Z. anal. chem. 37, 60 61 (1898) (48) Ross, J. Biol. Chem. **58**, 641–642 (1923/24). (49) Kul'berg, Presman, Farm. Zhur. **13**, No. 3, 12–14 (1940); Cent. **1942**, I 1531–1532, C A. **37**, 2883 (1943) (50) Schmidt, Ber. **13**, 2343, Note (1880). (51) Adams, J. Pharmacol. **74**, 11–17 (1942); C.A. **36**, 1343 (1942). (52) Pesez, J. pharm. chim.

(8) 22, 68-69 (1935); Cent. 1936, I 1050, C.A. 30, 1517-1518 (1936).

3: 1275
$$\alpha_1\alpha_2\beta$$
-TRICHLOROPROPIONIC ACID $C_3H_3O_2Cl_3$ Beil. II — Cl II_1 — II_2 —(228)

M.P. [65-66° (4)] 60° (1) 50-52° (2)

Colorless very hygroscopic cryst.; note that m.p. is rapidly lowered by exposure to moist air (1). — Eas. sol. aq., alc., C₆H₆; best crystd. from CS₂.

[For prepn. of \tilde{C} from α, α, β -trichloropropional dehyde (3:9033) by oxidn, with fumg. HNO₃ (2) (1) or by aq. acid solns. of chlorates + cat. (4) see indic. refs.; from 1,2,2,3tetrachlorobutene-3 (3:9060) by oxidn. with excess aq. KMnO₄ see (3).]

C titrates readily as monobasic acid; Neut. Eq., calcd. 177.5; found, 176.6 (2).

[C in abs. alc. contg. a little H2SO4, refluxed 1 hr. gives (2) ethyl 1,1,2-trichloropropionate, b.p. 121° at 55 mm., $D_{-}^{25} = 1.36$, $n_{-}^{25} = 1.458$ (2).]

[For conversion of \tilde{C} to acid chloride with SOCl₂ or S₂O₂ + Cl₂ + cat. see (5).]

3:1275 (1) Muskat, Becker, J. Am. Chem. Soc. 52, 817-818 (1930). (2) Berlande, Bull. soc. chim. (4) 37, 1392 (1925). (3) Berchet, Carothers, J. Am. Chem. Soc. 55, 2008 (1933). (4) Plump (to Pennsylvania Salt Mfg. Co.), U.S. 2,370,577, Feb. 27, 1945; C.A. 39, 4085 (1945). (5) Lichty (to Wingfoot Corp.), U.S. 2,361,552, Oct. 31, 1944; C.A. 39, 2297 (1945).

M.P. 60° (1) B.P. 236-238° (3) 57.9° (2)

Colorless hygroscopic lfts. or ndls. from pet. ether; deliquesces in moist air to yield an oil sol. in 20-25 pts. aq. (4). [New comml. prod. (1942) in U.S A.]

[For prepn. (100% yield (5)) from α,α,β -trichloro-n-butyraldehyde hydrate (n-butyr-chloral hydrate) (3:1905) via actn. of 2 pts. fumg. HNO₃ (D=1.504) at 30° (5) (6) or with aq. acid solns. of chlorates + cat. (8) see indic. refs.; for prepn. from α -chloro-crotonic acid (3:2760) or α -chloro-isocrotonic acid (3:1615) by addn. of Cl₂ see (4).

 \bar{C} with Zn dust and aq. gives excellent yield (5) of α -chlorocrotome acid (3:2760), m.p. 99-100° (5).

Na \overline{A} on warming (4) or boilg. (3) with aq. dec. into CO₂ and 1,1-dichloropropene-1 (3:5120), b.p. 78°. — Pb \overline{A}_2 (7) or Pb \overline{A}_2 .2H₂O (3) is insol. cold aq., spar. sol. hot aq., but eas. sol. in alc. or ether.

 \tilde{C} with PCl₃ (3) yields α, α, β -trichloro-n-butyryl chloride, b.p. 162-166° (3).

- Methyl α, α, β -trichloro-n-butyrate: unreported.
- Ethyl α,α,β -trichloro-n-butyrate: b.p. 212° (see 3:6380).
- α,α,β-Trichloro-n-butyramide: scales from alc., m.p. 96° (3). [From α,α,β-trichloro-n-butyryl chloride (above) with conc. aq. NH₄OH (3).]
- ---- α,α,β -Trichloro-n-butyranilide: unreported

3:1285 2-CHLORONAPHTHALENE

 α,α,β -Trichloro-n-butyr- α -naphthalide: unreported.

3:1280 (1) Kahlbaum, Ber 12, 2337 (1879). (2) Kendall, J. Am Chem Soc. 36, 1231 (1914). (3) Judson, Ber. 3, 785-788 (1870). (4) Valentin, Ber. 28, 2661-2663 (1895). (5) Roberts, J. Chem. Soc. 1938, 779. (6) Knamer, Pinner, Ber. 3, 389 (1870). (7) Garzarolli-Thurnlack, Ann. 182, 184 (1876). (8) Plump (to Pennsylvania Salt Mfg. Co.), U.S. 2,370,577, Feb. 27, 1945; C.A. 39, 4085 (1945).

C₁₀H₇Cl

Beil. V - 541

V1-(262) V₂-(445) M.P. B.P. 61° 256.5° cor. $n_{\rm D}^{70.7} = 1.60787 (12)$ (20) (1) 60° (2) 256° (2) $(D_4^{20} = 1.178)$ (12) 59.5-60° (3) 255.6° cor. at 752 mm. (10) 58.6-59.8° (4) 264-266° cor. at 751 mm. (13) $(n_D^{20} = 1.631)$ (12) 59° (5) 251-252° (18)58.6° (6) 121-122° at 12 mm. (12) 58.5° 119.6-119.8° at 11 mm. (4) (7) 58-59° (8) 58° (9) 57.4-57.8° (10)56.7° (11) 56.5° (18)56° (12) (13) (14) (21) (27) 55° (15)

[For 1-chloronaphthalene see 3:6878.]

Colorless lfts. from alc.; eas. sol. alc., ether, C₆H₆, CHCl₃, CS₂. — Volatile with steam.

[For prepn. from β -naphthylamine [Beil. XII-1265, XIII₁-(532)] via diazotization and use of Cu₂Cl₂ reaction (yields: 90-95% (17), 82% (15), 75-80% (16)) (3) or even on boilg. diazonium salt soln. with conc. HCl (1) (18), or from diazonium/ZnCl₂ cpd. on addn. to phenol at 60° (44% \bar{C} + 35% hydroxybiphenyl + 13% diphenyl ether (39)), see indic. refs.; from β -naphthol (1:1540) with PCl₅ at 135-140° for 24 hrs. as directed (30% yield (19)) (20) (13) cf. (16) or from trs-(β -naphthyl)phosphoric acid dichloride by htg. at 310° (21) or from sodium β -naphtholate with PCl₃ in toluene (55% yield (22)) see indic. refs.; from sodium β -naphthalenesulfonate with PCl₅ via conv. to β -naphthalenesulfonyl chloride and distn. of latter with a second mole of PCl₅ see (13); from mercury bis-(β -naphthyl) with SOCl₂ see (2); from di- β -naphthyl sulfone with PCl₅ see (23); from β -chloronaphthole acid-1 (3:4845) by decarboxylation in quinoline at 225° in pres. of copper chromite cat. see (8); for formn. of \bar{C} ir small proportion from 1-chloronaphthalene (3:6878) by htg. with AlCl₃ (9) or from naphthalene dichloride by actn. of alkali (24) see indic. refs.]

[For sepn. of \bar{C} from 1-chloronaphthalene (3:6878) by fractional freezing of appropriate solutions see (25).]

[For thermal anal. of systems of \bar{C} with SbCl₃ (14) (26) or SbBr₃ (14) see indic. refs.; with β -naphthol (1:1540), with β -naphthylamine, or with 2-methylnaphthalene (1:7605) see (5), with PkOH see (11).]

[Č with even twice calcd. amt. 5% Na/Hg in alc. for 22 hrs. is not reduced but can be recovered almost quant. (27).]

[Č with Li in dry ether subsequently treated with Me₂SO₄ gives (43% yield (28)) 2-methylnaphthalene (1:7605). — Č with chlorobenzene + Na in xylene refluxed 12 hrs. gives small yield (38) 2-phenylnaphthalene [Beil. V-687], m.p. 101.5° (38).]

[\bar{C} with strong alc. KOH in s.t. at 220° is unchanged (13), but \bar{C} with 5 moles 3-25% aq. NaOH htd. under press. 1 hr. at 350-360° in pres. of Cu gives (29) a mixt. of β -naphthol (1:1540) + α -naphthol (1:1500) cf. (30)]

[Č on mononitration as directed (31) gives 2-chloro-8-nitronaphthalene [Beil. V-556], yel. ndls. from alc., m.p. 116° (31) (of the other theoretically possible mononitro Č isomers only the following are known, and these have been prepd. indirectly: viz, 1-nitro-2-chloronaphthalene, m.p. 99-100° (32), 3-nitro-2-chloronaphthalene, m.p. 105° (33), 4-nitro-2-chloronaphthalene, m.p. 79° (34), 5-nitro-2-chloronaphthalene, m.p. 100.5° (37).]

[C on dinitration with fumg. HNO₃ (17) is claimed to yield 2-chloro-1,6(?)dinitronaphthalene, pale yel. ndls. from alc., m.p. 174° (17); in the pres. of H₂SO₄, however, the same author (17) regards the prod. as 2-chloro-1,8-dinitronaphthalene, pale yel. ndls. from AcOH, m.p. 175° (17), and no later work appears to be recorded as to whether these are the same and if so which.]

[$\bar{\mathbf{C}}$ on trinitration, e.g., by soln. in 8 pts. abs. HNO₃ at 0°, or better (38% yield (15)) by addn. of $\bar{\mathbf{C}}$ (2 g.) to a mixt. of abs. HNO₃ (16 ml.) + conc. H₂SO₄ (8 ml.) at 0°, followed by warming as directed, gives 2-chloro-1,6,8-trinitronaphthalene, pale yel. cryst. from AcOH, m.p. 193°, white ndls. from C₆H₆, m.p. 194° (15).]

[\tilde{C} on cat. oxidn. with air at 250-300° gives (35) 53% phthalic anhydride (1:0725) + 47% 4-chlorophthalic anhydride (3:2725).]

[For chloromethylation of \bar{C} with paraformaldehyde + HCl gas in AcOH see (40).]

- D 2-Chloronaphthalenesulfonamide-8 (7-chloronaphthalenesulfonamide-1): cryst. from dil. alc., m.p. 231-232° u.c. (36). [From \(\bar{C}\) with chlorosulfonic acid as directed, followed by conversion of the intermediate 2-chloronaphthalenesulfonyl chloride-8, m.p. 124-126° u.c., with (NH₄)₂CO₃ to desired sulfonamide (36).]
- --- 2-Chloronaphthalene picrate: m.p. 81.5° (by thermal anal. (11)).

Liebermann, Palm, Ann. 183, 270 (1876). (2) Heumann, Köchlin, Ber. 16, 1627 (1883). (3) Hampson, Weissberger, J. Chem. Soc. 1936, 394. (4) Gockel, Z. physik. Chem. B-29, 86 (1935). (5) Grimm, Ganther, Titus, Z. physik. Chem. B-14, 195, 199, 202 (1931). (6) Parts, Z. physik. Chem. B-10, 265 (1930). (7) L. Klemm, W. Klemm, Schiemann, Z. physik. Chem. A-165, 384 (1933). (8) Price, Chapin, Goldman, Krebs, Shafer, J. Am. Chem. Soc. 63, 1861 (1941). (9) Roux, Ann. chim. (6) 12, 349 (1888). (10) Zil'berman, Rashevskaya, Martyntseva, J. Applied Chem. (U.S.S.R.) 9, 1832-1840 (1936), Cent. 1937, I 4786; C.A. 31, 2597 (1937).

(11) Jefremov, J. Russ. Phys.-Chem. Soc. 50, 381 (1918); Cent. 1923, III 380. (12) von Auwers, Frthling, Ann. 422, 194, 200, 202 (1921). (13) Rimarenko, J. Russ. Phys.-Chem. Soc. 8, 139 (1876), Ber. 9, 663-666 (1876). (14) Menschutkin, J. Russ. Phys.-Chem. Soc. 44, 1084 (1912); Cent. 1912, II 1436. (15) van der Kam, Rec. trav. chim. 45, 568-569 (1926). (16) Chattaway, Lewis, J. Chem. Soc. 65, 875-877 (1894). (17) Scheid, Ber. 34, 1813-1815 (1901). (18) Gasiorowski, Wayss, Ber. 18, 1940 (1885). (19) Berger, Bull. soc. chim. (3) 35, 30-32 (1906). (20)

Cleve, Juhlin-Dannfelt, Bull. soc. chim. (2) 25, 258-259 (1876).

(21) Autemieth, Geyer, Ber. 41, 158 (1908). (22) Darzens, Berger, Bull. soc. chim. (4) 5, 785-787 (1909). (23) Cleve, Bull. soc. chim. (2) 25, 257 (1876). (24) Armstrong, Wynne, Chem. News 61, 284 (1890); Ber. 24, Referate, 713 (1891). (25) Britton, Reed (to Dow Chem. Co.), U.S. 1,917,822, July 11, 1933; Cent. 1933, II 2194; C.A. 27, 4547 (1933). (26) Vasil'ev, J. Russ. Phys.-Chem. Soc. 49, 428-431 (1917); Cent. 1923, III 668; C.A. 18, 1418 (1924). (27) Franzen, Stauble, J. prakt. Chem. (2) 103, 389 (1921/22). (28) Vesely, Stursa, Collection Czechoslov. Chem. Commun. 4, 142 (1932); Cent. 1932, I 3060 (29) Britton, Stearns (to Dow Chem. Co.), U.S. 1,996,745, April 9, 1935; Cent. 1935, II 2126; C.A. 29, 3354 (1935). (30) Hale, Britton (to Dow Chem. Co.), U.S. 1,882,824, 1,882,825, 1,882,826, Oct. 18, 1932; Cent. 1933, I 309; C.A. 27, 731 (1933).

(31) Armstrong, Wynne, Chem. News 59, 225 (1889). (32) Hodgson, Leigh, J. Chem. Soc. 1937, 1352-1353. (33) Hodgson, Elliott, J. Chem. Soc. 1934, 1705-1706. (34) Hodgson, Elliott, J. Chem. Soc. 1936, 1153. (35) Pongratz, Bassi, Fuchs, Suss, Wustner, Schober, Angew. Chem. 54, 22-26 (1941); C.A. 35, 3248 (1941). (36) Huntress, Carten, J. Am. Chem. Soc. 62, 511-514 (1940). (37) Hodgson, Turner, J. Chem. Soc. 1942, 723-725; C.A. 37, 879 (1943). (38) Chattaway, Lewis, J. Chem. Soc. 65, 871-872 (1894). (39) Hodgson, Foster, J. Chem. Soc. 1942, 582-583. (40) Horn, Warren, J. Chem. Soc. 1946, 144.

[See also p-chlorocarvacrol (3:0480).]

Note that \tilde{C} is also known as 4-chlorothymol (Beilstein) and as 6-chlorothymol (C.A.) according to differing methods of numbering the thymol nucleus.

PREPARATION OF C

From thymol. [For prepn. of \tilde{C} from thymol (1:1430) by chlorination with Cl_2 in aq. Na_2CO_3 (80% yield (10)), with Cl_2 in AcOH (50% yield (8)), or with SO_2Cl_2 (1) (9) in CHCl₃ (5) see indic. refs.]

From 4-chloro-3-methylphenol (4-chloro-m-cresol). [For prepn. of C from 4-chloro-3-methylphenol (3:1535) by conversion with isopropyl alcohol or isopropyl chloride

(3:7025) (11) or with propylene (3) to 4-chloro-3-methylphenyl isopropyl ether and subsequent rearr. (11) (3), e.g., with H₂SO₄/AcOH (6), to C, see indic. refs.]

From other sources. [For prepn. of C from 4-amino-2-isopropyl-5-methylphenol via diazotization and use of CuCl₂/ZnSO₄ see (4).]

BIOCHEMICAL ASPECTS AND USES OF C

 \bar{C} as a halogenated phenol has been widely considered as an antiseptic, bactericide, disinfectant, germicide, fungicide, etc.; while this aspect cannot here be recorded in detail, the following examples may serve as leading references.

[For general and technical articles on bactericidal (12) (13) (14) (15) (16) (17) (18), fungicidal (12) (19) (20) (21), or anthelmintic (22) action of \bar{C} see indic. refs.; for patents on various means of improving the aqueous solubility of \bar{C} for use as germicide see (23) (24) (25) (26) (27) (28) (2) (29); for patent on use of \bar{C} in mouthwash see (30); for use as disinfectant of a mixt. of \bar{C} (2 pt.) with camphor (1 pt.) (which mixt. is *liquid* above 5°) see (31).]

CHEMICAL BEHAVIOR OF C

Reduction. [\bar{C} in aq. alk. with H_2 + cat. at 180° and 30 atm. (32), or \bar{C} in aq. alk. with Fe filings at 170° or at 200° under pressure (33) gives (100% yield (32)) thymol (1:1430), m.p. 51.5°.]

Oxidation. \bar{C} on oxidation with CrO₃ (8) or with MnO₂ in ice-cold conc. H₂SO₄ (1) gives thymoquinone (1:9003), m p. 45.5°.

Reactions Involving Nuclear Substitution of C

Bromination. [C with Br2 in AcOH gives (8) a mixt. of products]

Nitration. [\bar{C} in lt. pet. floated on an aqueous soln. of nitrous acid (from NaNO₂ + HCl) for a week gave (8) 4-chloro-2-isopropyl-5-methyl-6-nitrophenol [Beil. VI-542, VI₁-(267)], pale yel. ndls. from alc., m.p. 116° (8) (34). — Note that attempts to effect direct nitration of \bar{C} with HNO₃ in AcOH below 20° (8) give a mixt. of products; also that \bar{C} in dry CHCl₃ at — 20° with NO₂ (from htg. dry Pb(NO₃)₂) gives (8) 4-chloro-3,4,6-trinitro-2-isopropyl-5 methyl-cyclohexadien-2,5-one-1 [Beil. VII₁-(100)], yel. cryst., m.p. about 105° dec. (8).]

Mercuration. [For patents on mercuration of \bar{C} see (35) (36).]

Miscellaneous nuclear substitutions. [Note that NaĀ with benzyl chloride (3:8535) in toluene at 110° for 4 hrs. gives (by nuclear benzylation) (37) 4-chloro-6-benzyl-2-iso-propyl-3-methylphenol, b.p. 180° at 3 mm. (37).]

[C with SCl₂ in CS₂ gives (65% yield (5)) a sulfide, C₂₀H₂₄O₂Cl₂S, m.p. 110-111°, of undetermined structure.]

Reactions Involving the Phenolic Group of \bar{C}

(See also below under @'s.)

[\bar{C} with PCl₅ at 180–200° for 2 hrs. gives (9) 2,5-dichloro-p-cymene [Beil. V-423, V₂-(326)], b.p. 240–243°; this prod. on oxidn. with dil. HNO₃ (D=1.15) in s.t. at 180° for 10 hrs. gives (38) 2,5-dichloroterephthalic acid [Beil. IX-847], m.p. 305° (38) (corresp. dimethyl ester, m.p. 136° (38)).]

[For behavior of \bar{C} with POCl₃ giving compds, of types ROPOCl₂ and (RO)₂POCl (R = p-chlorothymyl) see (39); for clinical tests of sodium salt of p-chlorothymylphosphoric acid "thymophogen") with tuberculosis see (40), for prepn. of such salt see (41),

— p-Chlorothymyl methyl ether: oil, b.p. 251° cor. at 760 mm. (1). [From Č with MeI + KOH (1) or from thymyl methyl ether with SO₂Cl₂ (42).]

- --- p-Chlorothymyl ethyl ether: unreported.
- p-Chlorothymyl acetate: oil, b.p. 112-114° at 2 mm. (43). [From C with Ac₂O (9) or AcCl (44); for Fries rearr. to the corresp. acetophenone deriv. see (44) cf. (43).]
- p-Chlorothymyl benzoate: m.p. 71-73° (9). [From C with BzCl in aq. KOH (9).]
- D p-Chlorothymyl benzyl ether: m.p. 55° (7).
- D p-Chlorothymyl o-nitrobenzyl ether: m.p. 117° (7).
- --- p-Chlorothymyl p-nitrobenzyl ether; unreported.
- p-Chlorothymoxyacetic acid: unreported.

3:1293 (1) Peratoner, Condorelli, Gazz. chim. ital. 28, I 214-215 (1898). (2) Raschig, Ger. 579,897, July 4, 1933; Cent. 1933, II 1553; C.A. 28, 1142 (1934): U.S. 1,816,297, July 28, 1931; Cent. 1931, II 3638; C.A. 25, 5514 (1931). (3) Schöllkopf (to Rheinisches Kampfer Fabrik) U.S. 2,115,884, May 3, 1938; Cent. 1938, II 2180; C.A. 32, 4606 (1938). Brit. 319,205, Aug. 8, 1929; Cent. 1930, I 736; C.A. 24, 2468: Ger. 638,756, Nov. 21, 1936; not in Cent.; C.A. 31, 3064 (1937). French 681,049, May 8, 1930, Cent. 1930, II 1132; C.A. 24, 4051 (1930). (4) Skraup, Steinruck (to Rheinische Kampfer Fabrik) Ger. 431,513, July 10, 1926; Cent. 1926, II 1462; not in C.A. (5) Lesser, Gad, Ber. 56, 977 (1923). (6) Niederl, Natelson, J. Am. Chem. Soc. 54, 1068-1069 (1932). (7) Jones, J. Chem. Soc. 1941, 364. (8) Robertson, Briscoe, J. Chem. Soc. 101, 1968-1971 (1912). (9) Bocchi, Gazz. chim. ital 26, II 403-406 (1896). (10) Tischenko, J. Russ. Phys.-Chem. Soc. 60, 153-162 (1928), Cent. 1928, II 767; C.A. 22, 3397 (1928).

(11) Raschig, U.S. 1,769,648, July 1, 1930, Cent. 1930, II 3462; C.A. 24, 4524 (1930): Brit. 270,283, June 22, 1928, Cent. 1929, I 439; C.A. 22, 1366 (1928). Ger. 555,904, July 30, 1932; Cent. 1932, II 1693; C.A. 26, 5972 (1932): Ger. 531,774, April 30, 1926, not in Cent.; C.A. 26, 157 (1932): French 633,067, Jan. 20, 1928; Cent. 1929, I 439; [C.A. 22, 3418 (1928)]: Swiss 127,035, Aug. 16, 1928; Cent. 1929, I 439, C.A. 23, 1142 (1929). (12) Law, J. Soc. Chem. Ind. 60, No. 3, 66-67 (1941). (13) Alchin, Chem. Products 2, 93 95 (1939); C.A. 33, 7961 (1939). (14) Roeg, Am. J. Pharm. 110, 72-75 (1938). (15) Heading, Pharm. J. 138, 321-322 (1937); Chemist and Druggist 126, 392-393 (1937), Cent. 1937, II 2208; C.A. 31, 8119 (1937). (16) Etinger-Tulczynska, Ulrich, Z. Hyg. Infektionskrankh. 113, 437-444 (1932); Cent. 1932, II 77; C.A. 26, 2551 (1932). (17) Lockemann, Ulrich, Z. Hyg. Infektionskrankh. 113, 475-481 (1932), Cent. 1932, II 99; C.A. 26, 2551 (1932). (18) Malcolm, J. Bact. 22, 403-425 (1931); Cent. 1932, I. 2974; C.A. 26, 1932). (19) Eastwood, Scance 100, 10-11 (1044). (20) Woodward, Kingery, Williams, J. Lab. Clin. Med. 20, 950-953 (1935); Cent. 1936, I. 93, C.A. 29, 5025 (1935).

(21) Woodward, Kingery, Williams, J. Lab. Clnn. Med. 19, 1216-1223 (1934), Cent. 1935, I 256; C.A. 28, 6849 (1934). (22) Oclkers, Rathje, Arch. exptl. Path. Pharmakol. 198, 317-337 (1941); Trop. Discases Bull. 39, 767-768 (1942); C.A. 37, 1507 (1943). (23) Hueter, Engelbrecht (to Unichem.), U.S. 2,267,101, Dec. 23, 1941; C.A. 36, 2376 (1942). (24) Schering, A.G., French 870,574, March 16, 1942; Cent. 1942, II 1374; not in C.A. (25) Deutsche Hydrierwerke, A.G., French 823,289, Jan. 18, 1938; Cent. 1938, I 2587; C.A. 32, 5582 (1938). (26) Gelinsky, Ger. 649,126, Aug. 16, 1937; Cent. 1937, II 3627; C.A. 31, 8838 (1937). (27) Goedrich, U.S. 2,073,057, March 9, 1937; Cent. 1937, I 4830; C.A. 31, 3214 (1937). (28) Goedrich (to Goedrich Chem. Co.) U.S. 1,930,474, Nov. 17, 1935; Cent. 1934, I 2314, C.A. 28, 263 (1934). (29) Raschig, Ger. 580,880, July 17, 1933; Cent. 1933, II 2294; C.A. 28, 1142 (1934). (30) Pepsodent Co., French 693,083, Nov. 14, 1930; Cent. 1931, I 1481; C.A. 25, 1640 (1931).

(31) Raschig, Ger. 433,293, Aug. 23, 1926; Cent. 1926, II 2205, not in C.A. (32) Schöllkopf (to Rheinisches Kampfer Fabrik), Ger. 432,802, Aug. 11, 1926; Cent. 1926, II 1693; not in C.A. (33) Raschig, Ger. 396,454, June 6, 1924, Cent. 1924, II 1275; not in C.A. (34) Kehrmann. Schön, Ann. 310, 106-107 (1900). (35) Christiansen (to Squibb and Sons), U.S. 2,252,705, Aug. 19, 1941; C.A. 35, 7657 (1941). (36) Christiansen, Moness (to Squibb and Sons), U.S. 2,137,236, Nov. 22, 1938; C.A. 33, 1886 (1939). (37) Klarmann, Gates (to Lehn, Fink, Inc.), U.S. 1,926,874, Sept. 12, 1933; Cent. 1934, 1 83, [C.A. 27, 5896 (1933)]. (38) Wheeler, Giles, J. Am. Chem. Soc. 44, 2611 (1922). (39) Rosenmund, Vogt, Arch. Pharm. 281, 317-327 (1943); C.A. 38, 5804-5805 (1944). (40) Hisasi, Bettr. Klin. Tuberk. 92, 52-57 (1938); C.A. 33, 8794 (1939).

(41) Ayukawa, Japanese 93,182, Oct. 9, 1931; C.A. 27, 1452 (1933). (42) Peratoner, Ortoleva, Gazz. chim. ital. 28, I 228 (1898). (43) Klarmann, Shternov, Gates, J. Am. Chem. Soc. 55, 2586–2587 (1933). (44) Klarmann, Gates (to Lehn, Fink, Inc.), U.S. 1,938,912, Dec. 12, 1935; Cent. 1934, I 2006; C.A. 28, 1472 (1934): Brit. 432,955, Sept. 5, 1935; Cent. 1936, I 809–810; [C.A. 39, 575 (1936)].

3:1300
$$\beta$$
-CHLOROISOCROTONIC ACID $C_4H_5O_2Cl$ $C_4H_5O_$

[See also β-chlorocrotonic acid (3:2625).]

(11) (17)

59.5°

Cryst. from aq. or pet. ether. — \bar{C} is somewhat less sol. in aq. than its stereoisomer (3:2625); e.g., \bar{C} is sol. in 52.4 pts. aq. at 19° (12), in 79 pts. aq. at 7° (11). — \bar{C} is very easily volatile with steam (11) (dif. from β -chlorocrotonic acid (3:2625). — \bar{C} in either cis- α,β -dichloroethylene (3:5028) is very much more sol. than the stereoisomeric β -chlorocrotonic acid (3:2625) (13). — \bar{C} sublimes even at room temp. (11).

For f.p./compn. data and diagram of system \bar{C} + the stereoisomeric β -chlorocrotonic acid (3:2625) (eutectic, m.p. 38.9° contg. 66.8 mole % \bar{C}) see (14).

Preparation. [The most frequently used method of prepn. of \bar{C} is that from ethyl acetoacetate (1:1710) with PCl₅; this treatment leads to the formn. of a mixt. of the acid chlorides of \bar{C} and the stereoisomeric β -chlorocrotonic acid (3:2625) which upon hydrolysis with aq. gives a mixt. of the two acids; from this mixture \bar{C} is removed (together with any unreacted ethyl acetoacetate) by distillation with steam; the yield of mixed acids is variously reported, e.g., 43.7% (3), 36.5% (9); the yield of \bar{C} is relatively small, e.g., 26.8% (3), 13% (1). — The PCl₅ reactn. has often been carried out in dry C_6H_6 (8) (15) (9) (3), but its use is regarded (1) as disadvantageous. — For many important details of procedure see indic. refs.]

[For form. of \bar{C} from α,β,β -trichloro-n-butyric acid (3:0925) by removal of the α - and one β -chlorine atom with Zn see (16); from the stereoisomeric β -chlorocrotonic acid (3:2625) by htg. at 150-160° for 20 hrs. (17) or at 130° in s.t. (18) see indic. refs.]

Chemical behavior. [\bar{C} in alc. or in aq. NaOH with $H_2 + Pd/BasO_4(4)$, or \bar{C} (as NaA) with $2\frac{1}{2}\%$ Na/Hg in aq. (19), yields mainly isocrotonic acid (1:1045) together with some crotonic acid (1:0425) and tetrolic acid, $CH_3-C \equiv C-COOH$; note that \bar{C} is thus dehalogenated more rapidly (4) than the stereoisomeric β -chlorocrotonic acid (3:2625), and that with excess H_2 the products are further reduced to n-butyric acid (1:1035).]

 $\bar{\mathbb{C}}$ on oxidn. with aq. KMnO₄ yields (20) only AcOH (1:1010) and oxalic acid (1:0445). $\bar{\mathbb{C}}$ with Cl₂ in CS₂ soln. adds 1 mole halogen yielding (16) α,β,β -trichloro-n-butyric acid (3:0925), m.p. 52°; $\bar{\mathbb{C}}$ undoubtedly adds 1 Br₂ to yield β -chloro- α,β -dibromo-n-butyric acid but the latter has never been reported.

 \tilde{C} behaves as a monobasic acid; dissociation const. at $25^\circ = 9.47 \times 10^{-5}$ (21). — \tilde{C} on neutralization with cold dil. alk. gives Neut. Eq. 120.5. — Note, however, that with strong aq. KOH \tilde{C} is somewhat more resistant than its stereoisomer (3:2625); e.g., \tilde{C} with 3-4 N KOH at 115-120° (16) cf. (22) gives acetone (1:5400) + K_2CO_3 + KCl; with 7-8% KOH at 125-130° same + some tetrolic acid.

Salts. [NH₄HA.H₂O (11): NaA. $\frac{1}{2}$ H₂O, very sol. aq. or alc. (11): KA.H₂O, sol. in 13.2 pts. alc. at 14° (24): AgA, alm. insol. cold aq.; on htg. with aq. in s.t. at 170° dec. much more readily (24) than its stereoisomer (3:2625) into CO₂ + propadiene (allylene):

 $Mg\bar{A}_2.5H_2O$, $Ca\bar{A}_2.3H_2O$, $Ba\bar{A}_2.2H_2O$, $Zn\bar{A}_2.2J_2'H_2O$, $Mn\bar{A}_2.2H_2O$, $Co\bar{A}_2.6H_2O$, $Ni\bar{A}_2.6H_2O$, all sol. aq. (11): $Pb\bar{A}_2.4H_2O$, spar. sol. aq. (11).]

Č with PCl₅ (25) or with SOCl₂ (26) gives (yield 90% (26)) (29) β -chloroisocrotonyl chloride, b.p. 135–136° at 760 mm.; see also comments under β -chlorocrotonic acid (3:2625).

[\bar{C} (as $K\bar{A}$) with alc. NaOEt on htg. gives after acidification (17) β -ethoxycrotonic acid [Beil. III-371, III₁-(135)], m.p. 137-138° (17), 141° (27); note that during reactn. isomerization has occurred and that this prod. is the same as is similarly obtd. from β -chlorocrotonic acid (3:2625). — \bar{C} (as Na \bar{A}) with Na benzylate on htg. gives after acidification (28) β -benzyloxycrotonic acid, m.p. 121-122° (28), the same as does the stereoisomer. — \bar{C} (as Na \bar{A}) with Na salt of benzyl mercaptan in alc. on htg. gives after acidification (28) β -benzylmercaptoisocrotonic acid, m.p. 130°; note that here isomerization does not occur.]

[For behavior of \tilde{C} (as NH₄ \tilde{A}) with (NH₄)₂SO₃ yielding β -sulfocrotonic acid (3), or of \tilde{C} (as K \tilde{A}) with K₂AsO₃ yielding (10) β -arsonocrotonic acid, see indic. refs.; note that in both cases the products are identical with those obtd. by similar treatment of β -chlorocrotonic acid (3:2625).]

- Methyl β-chloroisocrotonate: b.p. 142°. See 3:8028. [For rate of esterification of C with MeOH see (30).]
- Ethyl β -chloroisocrotonate: b.p. 165°. See 3:8325.
- β-Chloroisocrotonamide: lfts. from aq., m.p. 109-110° (25). [From β-chloroisocrotonyl chloride (see above) with conc. aq. NH₄OH (25).] [For study of solubility in cis-1,2-dichloroethylene (3:5042) and in trans-1,2-dichloroethylene (3:5028) see (13).]
- β-Chloroisocrotonanilide: ndls. from alc., m.p. 106° (25). [From β-chloroisocrotonyl chloride (see above) with aniline + excess cold dil. aq. NaOH in 100% yield (25).]
- β-Chloroisocroton-α-naphthalide: ndls. from alc., m.p. 155° (25). [From β-chloroisocrotonyl chloride (see above) with α-naphthylamine + excess cold dil. aq. NaOH in 100% yield (25).]
- 3:1300 (1) Dadieu, Pongratz, Kohlrausch, Monatsh. 60, 211-212 (1932); Sitzber. Akad. Wiss. Wien, Math. naturw. Klasse, Abt. II-a, 140, 359-360 (1931). (2) Stelling, Z. physik. Chem. B-24, 423 (1934). (3) Backer, Beute, Rec. trav. chm 54, 552-553, 559-560 (1933). (4) Paal, Schiedewitz, Rauscher, Ber. 64, 1521-1530 (1931). (5) Bruylants, Castille, Bull. soc. chim. Belg. 34, 277 (1925). (6) von Auwers, Wissebach, Ber. 56, 724 (1923). (7) von Auwers, Ber. 45, 2807 (1912). (8) Michael, Schulthess, J. prakt. Chem. (2) 46, 236-237 (1892). (9) Skau, Saxton, J. Am. Chem. Soc. 50, 2693-2701 (1928). (10) Backer, van Oosten, Rec. trav. chim. 59, 50 (1940).
- (11) Geuther, Frölich, Zeit. Chem. 1869, 270-271. (12) Michael, Brown, Am. Chem. J. 9, 284 (1887). (13) Lebrun, Bull. soc. chim. 39, 429-430 (1930). (14) Skau, Saxton, J. phys. Chem. 37, 183-186 (1933). (15) Scheibler, Voss, Ber. 53, 381-382 (1920). (16) Szenic, Taggesell, Ber. 28, 2665-2667 (1895). (17) Friederich, Ann. 219, 327-346, 363 (1883). (18) Michael, Schulthess, J. prakt. Chem. (2) 46, 264-266 (1892). (19) Michael, Schulthess, J. prakt. Chem. (2) 46, 250-251 (1892). (20) Kondakow, J. Russ. Phys.-Chem. Soc. 24, 511 (1892).
- (21) Ostwald, Z. physik. Chem. 3, 245 (1889). (22) Michael, J. prakt. Chem. (2) 38, 9-10 (1888). (23) Michael, Schulthess, J. prakt. Chem. (2) 46, 254-255 (1892). (24) Michael, Clark, J. prakt. Chem. (2) 52, 326-329 (1895). (25) Autenrieth, Ber. 29, 1665-1670 (1896). (26) Scheibler, Topouzada, Schulze, J. prakt. Chem. (2) 124, 16 (1930). (27) Nef, Ann. 276, 234 (1893). (28) Autenrieth, Ber. 29, 1646-1648 (1896). (29) Scheibler, Voss, Ber. 53, 382 (1920). (30) Sudborough, Roberts, J. Chem. Soc. 87, 1846 (1905).

(31) Michael, Oechslin, Ber. 42, 322 (1909).

3:1310 1,3-DICHLORONAPHTHALENE

$$\begin{array}{c|c} Cl & C_{10}H_6Cl_2 & & Beil. \ V - 542 \\ \hline & V_{1^-}(262) \\ \hline & V_{2^-}(445) \\ \end{array}$$

Colorless ndls. from alc. — Volatile with steam (4).

[For prepn. of \bar{C} from 1-amino-2,4-dichloronaphthalene via diazotization and subsequent warming with alc. see (4) (5) (6) (1); similarly from 1-amino-5,7-dichloronaphthalene see (7); from 4-nitronaphthalene-sulfonyl chloride-2 by htg. with excess PCl_5 see (3) (8); from naphthalene-1,3-bis-(sulfonyl chloride) by distn. with PCl_5 see (2); from naphthalene-tetrachloride-1,2,3,4 (3:4750) with alc. KOH see (9) (10) (4) (11).]

[C in CHCl₃, satd. with Cl₂ at ord. temp. yields (4) 1,2,4-trichloronaphthalene (3:2490), m.p. 92° (4).]

[C on nitration yields (4) a mixt. of two dinitro cpds., m.p. 150° and 158° respectively.]

[C̄ in CS₂ treated with ClSO₃H (12) yields a mixt. of 1,3-dichloronaphthalenesulfonic acid-5 [Beil. XI-163] (corresp. sulfonyl chloride, m.p. 148.5°, corresp. sulfonamide, m.p. 272° (12)) and 1,3-dichloronaphthalenesulfonic acid-7 [Beil. XI-183] (corresp. sulfonyl chloride, m.p. 121°, corresp. sulfonamide, m.p. 228° (12)).]

 \bar{C} on oxidn. with CrO₃ in AcOH yields (4) phthalic acid (1:0820) + 2-chloronaphtho-quinone-1,4 (3:3580), m.p. 115° (4). — \bar{C} on oxidn. in s.t. with conc. HNO₃ yields (5) phthalic acid (1:0820).

3:1310 (1) Weissberger, Sängewald, Hampson, Trans. Faraday Soc. 30, 890 (1934). (2) Armstrong, Wynne, Chem. News 61, 93 (1890) (3) Cleve, Ber. 19, 2181 (1886). (4) Cleve, Ber. 23, 954-955 (1890). (5) Cleve, Ber. 20, 449 (1887). (6) Fridmann, Ann. 275, 260-261 (1893). (7) Erdmann, Ber. 21, 3445 (1888). (8) Cleve, Ber. 21, 3274 (1888). (9) Faust, Saame, Ann. 160, 69 (1871). (10) Widman, Ber. 15, 2161-2162 (1882).

(11) Armstrong, Wynne, Chem. News 58, 264-265 (1888). (12) Armstrong, Wynne, Chem. News 61, 274, 284 (1890).

Pr. from pet. eth. or MeOH.

[For prepn. of C from o-chloroiodobenzene [Beil. V-220, V₁-(119)] by htg. with Cu powder under various conditions (yield: 40% (1), 20% (11), 10% (2)) see indic. refs.; from 2,2'-dinitrobiphenyl [Beil. V-583, V₁-(273)] with SOCl₂ in s.t. at 200-210° for 10 hrs. see (7); from 2,2'-diaminobiphenyl [Beil. XIII-210, XIII₁-(57)] via tetrazotization and reaction with Cu₂Cl₂ (6) or by decomp. of HgCl₂ complex (80% yield (3)) see indic. refs.; for dis-

cussion of forms. from chlorobenzene (3:7903) during preps. of phenol by alk. fusion see (12).]

 \bar{C} on dinitration with mixt. of conc. HNO₃ and conc. H₂SO₄ as directed (13) (9) gives (41% yield (13)) 2,2'-dichloro-5,5'-dinitrobiphenyl, cryst. from acetone, m.p. 203-204° (13), 205° (9) (a small amt. of an isomer, m.p. 128-129°, is also formed (13)); \bar{C} on tetranitration by htg. with mixt. of 5 pts. fumg HNO₃ (D=16) + 20 pts. conc. H₂SO₄ at 100° for 2 hrs. (13) (4) gives (38% yield (13)) 2,2'-dichloro-3,5,3',5'-tetranitrobiphenyl, cryst. from dioxane, m.p. 307-308° (13) (this prod. after melting is converted to higher-melting form, m.p. 316°, recrystn. of which from alc. restores the lower-melting variety (9)).

3:1325 (1) Hampson, Weissberger, J. Am. Chem. Soc. 58, 2117 (1936). (2) Weissberger, Sängewald, Z. physik. Chem. B-20, 155 (1933). (3) Schwechten, Ber. 65, 1607 (1932). (4) van Alphen, Rec. trav. chim. 51, 454-455 (1932). (5) Williamson, Rodebush, J. Am. Chem. Soc. 63, 3019 (1941). (6) Dobbie, Fox, Gauge, J. Chem. Soc. 99, 1619 (1911). (7) Mascarelli, Gatti, Gazz. chim. ital. 59, 868 (1929). (8) Mascarelli, Gatti, Gazz. chim. ital. 63, 664 (1933). (9) Mascarelli, Gatti, Gazz. chim. ital. 65, 24 (1935).

(11) Bretscher, Helv. Phys. Acta 2, 266-267 (1929). (12) Hale, Britton, Ind. Eng. Chem. 20,

122 (1923). (13) Case, Schock, J. Am. Chem. Soc. 65, 2086-2087 (1943).

Cryst. from pet. ether. — Insol. cold aq.; spar. sol. hot aq.; eas. sol. alc., ether. — In small quantities can (with caution) be sublimed (2).

[For prepn. of \bar{C} from α,α,β -trichloro-n-butyraldehyde (butyrchloral) (3:5910) with fused Al(OEt)₃ in boilg. abs. alc. under H₂ or N₂ for 14 hrs. (92% yield (1)), or with fused Al(OEt)₃ + AlCl₃ in boilg abs. alc. under H₂ or N₂ for 14 hrs. (3), or with C₂H₅OMgBr in dry ether followed by aq. (5), or by treatment with diethylzine (60–70% yield (8)) (2), di-n-propylzine (6), or di-isobutylzine (6) followed by aq. see indic. refs.; for form. of \bar{C} from urobutyrchloralic acid (see below) by hydrolysis see (4).] [Note that dextrorotatory \bar{C} , m.p. 62°, is obtd. (7) from butyrchloral hydrate (3:1905) by action of fermenting yeast.]

[\bar{C} with Zn + very dil. HCl gives (2) 2-chlorobuten-2-ol-1 (3:8240), b.p. 158°. — \bar{C} reduces Fehling soln. on warming.]

 $\ddot{\mathbf{C}}$ on oxidn. with conc. HNO₃ gives α, α, β -trichloro-n-butyric acid (3:1280).

C with PCl₅ on htg. gives (30-40% yield (8)) (2) 1,2,2,3-tetrachlorobutane (3:9078) (volatile with steam) accompanied by much (non-volatile) *tris*-(2,2,3-trichloro-*n*-butyl)-phosphate, colorless ndls. from alc., m.p. 85.3-85.4° (8).

[\bar{C} is sol. in conc. H₂SO₄ on slight warming but readily decomposes if htg. is excessive (2). \bar{C} does not react with PCl₃, or with fumg. HBr even at 110° (2).]

C on administration to dogs is excreted in the urine as urobutyrochloralic acid [Beil. I-664] (4).

—— 2,2,3-Trichloro-n-butyl acetate: b.p. 217.5° at 730 mm., 131-132° at 70 mm. (2). [From C with AcCl in s.t. at 110° for several hrs. (2).]

3:1336-3:1355

3:1336 (1) Meerwein, Schmidt, Ann. 444, 233-234 (1925). (2) Garsarolli-Thurnlackh, Ann. 213, 369-379 (1882). (3) Meerwein (to F. Bayer and Co.), U.S. 1,572,742, Feb. 9, 1926; Cent. 1926, I 3627: Brit. 251,890, June 3, 1926, Cent. 1926, II 1097. (4) Mering, Z. physiol. Chem. 6, 491-496 (1882). (5) I.G., Brit. 384,156, Dec. 22, 1932; Cent. 1933, I 1351. (6) Garsarolli-Thurnlackh, Papper, Ann. 223, 166-169 (1884). (7) Rosenfeld, Biochem. Z. 156, 54-57 (1925); Cent. 1925, I 2301; C.A. 19, 2683 (1925). (8) Norton, Noyes, Am. Chem. J. 10, 432 (1888).

3:1340 2,3,5-TRICHLOROPHENOL

$$\begin{array}{c|c} \mathrm{OH} & \mathrm{C_6H_3OCl_3} & \quad \textbf{Beil. VI} -\\ & & \quad \text{VI}_1-\\ & \quad \text{VI}_2\text{-}(\textbf{180}) \end{array}$$

172

M.P. 62° (1) (2) (3)

Č when dislyd in hot solvents and cooled gives gels; e.g., a very dil hot aq. soln set on cooling to an almost solid translucent gel, partly fibrous and partly crystalline (1). When a soln of K_2CrO_4 is poured on such a gel contg. AgNO₃, distinct but not well-defined Liesegang rings are produced in the gel (1) cf. (4).

 \bar{C} is volatile with steam. — Ionization const. at 23° is 5.0×10^{-8} (3); \bar{C} can be titrated with N/10 alk. using phenolphthalein; Neut. Eq. 197.5 (2).

[For prepn. from 2,3,5-trichloroaniline via diazo reaction see (1) (70% yield) or (2) (57% yield).]

 \bar{C} (1.5 g.) dislyd. in 20% aq. NaOH (20 ml.) and shaken with $(CH_3)_2SO_4$ (5 g.) ppts. (1) methyl ether (1.5 g. = 94% yield), 2,3,5-trichloroanisole, ndls. from alc., m.p. 84° (1), cryst. from acetone, m.p. 82° (4).

D 2,3,5-Trichlorophenyl benzoate: from \ddot{C} + BzCl + aq. NaOH, ndls. from alc., m.p. 101° (4), from lgr., m.p. 103° (4).

3:1340 (1) Hodgson, Kershaw, J. Chem. Soc. **1929**, 2919–2921. (2) Tiessens, Rec. trav. chim. **50**, 114 (1931). (3) Tiessens, Rec. trav. chim. **48**, 1066–1068 (1929). (4) Holleman, Rec. trav. chim. **39**, 739–740 (1920).

3: 1355 2,4-DIMETHYLPHENACYL CHLORIDE $C_{10}H_{11}OCl$ Beil. VII - 324 $(\omega$ -Chloro-2,4-dimethyl-acetophenone) CH_3 $CO.CH_2Cl$ VII_1 -(172)

M.P. 62°

Long wh. lfts. (from alc.). [For prepn. from m-xylene, chloroacetyl chloride (3:5235) + AlCl₃ see {1) (3}.]

Č on oxida. with aqueous NaOBr soln. for 3 hrs. (2) yields 2,4-dimethylbenzoic ac. [Beil. IX-531], cryst. from dil. MeOH, m.p. 126°. With a large excess of NaOBr and longer time (20 hrs.) Č yields 5-bromo-2,4-dimethylbenzoic acid. [Beil. IX-533], m.p. 180-181° (2).

C on oxidn. with alk. KMnO₄ soln. gives (3) 2-methylterephthalic acid [Beil. IX-863], m.p. 325-330°, whose dimethyl ester has m.p. 73-74° (4).

Č treated with nicotinic acid hydrazide metho-p-toluenesulfonate in alc. gives corresp. hydrazone, cryst. from 1:1 EtOH/ether, m.p. 196° cor. (5).

3:1355 (1) Kunckell, Ber. 30, 579 (1897). (2) Fisher, Grant, J. Am. Chem. Soc. 57, 718-719 (1935). (3) Jörlander, Ber. 50, 1460 (1917). (4) Lacourt, Bull. soc. chim. Belg. 39, 136-138 (1930). (5) Allen, Gates, J. Org. Chem. 6, 596-601 (1941).

See 3:2240 under trans-β-chloroacrylic acid.

3: 1364 DIETHYL
$$meso-\alpha,\alpha'$$
- $COOC_2H_5$ $C_8H_{12}O_4Cl_2$ Beil. II - 619 $II_1 II_2-$ (558) $H-C-Cl$ $II_2 II_2 II$

M.P. 63° (1) B.P. 125.5° cor. at 12.5 mm. (1)
$$D_4^{99} = 1.1490$$
 (1) 61.75–62° (2) $n_D^{64.5} = 1.4266$ (1) 57° (3)

Ndls. from dil. alc.; very eas. sol. alc., ether. — Volatile with steam.

[For prepn. of \bar{C} from $meso-\alpha,\alpha'$ -dichlorosuccinic acid (3:4930) in EtOH with HCl gas see (2) (1); from diethyl fumarate with HOCl see (3)]

3:1364 (1) Kuhn, Wagner-Jauregg, Ber. 61, 485-486, 504 (1928). (2) Kirchhoff, Ann. 286, 214-215 (1894). (3) Henry, Bull. acad. roy. Belg. (3) 36, 31-54 (1898); Cent. 1898, II 663.

3:1370 CHLOROACETIC ACID H₂C—COOH C₂H₃O₂Cl Beil. II - 194 II₁-(87) II₂-(187)

M.P. α-form		M .P. β	-form	M.P. γ-	-form	B.P.		
63°	(1)(2)	56.68°	(99)	52.5°	(10)	189.35°	at 760 mm.	(27) (90) (92)
(3) (4)	(5) (6)	56.6°	(16)	51°	(25)	189°	at 771 mm.	(28)
62.80°	(7)		(17)	50.65°	(7)	189°		(12)
62.53°	(8)	56.3°	(7)	50.2°	(22)	188.8-189.4	•	(29)
62.5-63.	2° (9)	(21)	(99)	50.05°	(23)	188.6-189.4	•	(30)
62.5°	(36)	56.18°	(22)	50°	(20)	188.5-189.5	° cor.	(31)
62.3°	(10)	56.01°	(23)			187.8°	at 755.7 mm.	(32)
	(11)	56°	(2)	(25)		186°	at 760 mm.	(33)
62.0-62.	5° (9)	55°	(20)			149°	at 207 mm.	(34)
62°	(12)	(13)				145.2°	at 180 mm.	(34)
	(14)	(15)				140.5°	at 152 mm.	(34)
61.86°	(99)					139.0°	at 141 mm.	(34)
61.8°	(16)	(17)				135°	at 122 mm.	(34)
61.7°	(18)	(103)				130.1°	at 101 mm.	(34)
61.65°	(99)					122°	at 71 mm.	(34)
61.5°	(19)	(20)				108°	at 36 mm.	(34)
	(21)					102.5°	at 27 mm.	(34)
61.4°	(100)					104-105°	at 20 mm.	(1)
	(102)	(104)				101°	at 20 mm.	(36)
61.30°	(22)					93°	at 18 mm.	(34)
61.18°	(23)					94°	at 11 mm.	(35)
61-62°	(24)					85-86°	at 11 mm.	(2)
61°	(19)	(25)						
60-61°	(26)							

[See also dichloroacetic acid (3:6208) and trichloroacetic acid (3:1150).]

MISCELLANEOUS PHYSICAL PROPERTIES OF C

Polymorphism of \bar{C} . \bar{C} is known definitely in the above three α , β , and γ forms and perhaps also in a fourth δ form, m.p. 43.75° (23), although last could not be confirmed (22) cf. (7). — The stable (α) form results from rapid condensation of vapor (23), by crystallization of \bar{C} from aq. soln. (23), or from rapid cooling of fused \bar{C} (37), although last method could not be confirmed (25); it is also obtained from the β form by seeding with α (9) or from γ form by spontaneous transformation (20), or from either β or γ forms at -20° (22).

The β form results from cooling fused \bar{C} especially if melt is first htd. above 67° cf. (9) (23), or from γ form on stirring (23) (20) (37) (22) cf. (25) (7).

The γ form results from fused \bar{C} on cooling without stirring (23) (20) (37) (25) (7).

[For study of transformation points of α and β forms see (21); for studies of effect of pressure on m.p. of \bar{C} see (38) (39) (25) (8).]

Density and refractive index for fused \overline{C} . [Values for these constants are *not* in good accord, viz., $D_A^{65.4} = 1.3978$ (40), $D_A^{65} = 1.3703$ (41); $n_D^{65.4} = 1.4301$ (40), $n_D^{65} = 1.4297$ (41). — For D_A^t over range 80°-176° see (36).]

Vapor characteristics. [For study of vapor pressure of \bar{C} over range 85-180° see (42).—For study of volatility with steam see (43).]

Cryoscopic constant. [Molal f.p. constant for \bar{C} is 5.2° (for 1000 g. \bar{C}) (44) (37); for studies on use of \bar{C} as cryoscopic solvent see (44) (45) (46) (47).]

Association of \bar{C} . [For studies on extent of association of \bar{C} in C_6H_6 soln. at 30° (11), in *p*-chlorotoluene (3:8287) (48), in liquid HF (49), in ether (33), or in water (1-9.7% \bar{C}) (50) see indic. refs.]

Heat of combustion. [For studies on heat of combustion of \bar{C} see (51) (52) (53) (54) cf. (55).]

Exchange reactions. [For study of behavior of \bar{C} with D_2O see (56); with H_2O^{18} see (57).]

Adsorption of \overline{C} by various adsorbents. [For studies on adsorption of \overline{C} from aqueous solns, by various forms of carbon (58) (59) (60) (61) (62) (63) (64), by silica gel (60), by synthetic resins (65), by aniline black (66), by filter paper (67), by hide powder (68), by viscose (69), by $Zr(OH)_2$ (70), or by $Fe(OH)_3$ (71) see indic. refs]

[For studies on adsorption of \bar{C} from nonaqueous solvents by wood charcoal (72) or from aqueous alc. by charcoal (73) or by casein (74) see indic. refs.]

Distribution of \overline{C} between solvents. [For data on distribution of \overline{C} between aq. and ether at 18° (75) or at 25° (76) (77) cf. (81); between aq. and benzene at 25° (78) or at an unstated temp. (79); between aq. and toluene at 25° (78) (80); between aq. and isobutyl alcohol at 25° (80); between aq. and n-amyl alcohol at 25° (80); between aq. and isoamyl alcohol at 25° (80); between aq. and di-n-butyl ether at 25° (5); between aq. and olive oil at 25° and 37.5° (82) see indic. refs.]

[For data on distribution of \bar{C} between aq. and nitrobenzene at 25° (80); between aq. and mixts. of benzene + nitrobenzene (83); between aq. and o-nitrotoluene at 25° (80) (84) see indic. refs.]

[For data on distribution of \bar{C} between aq. and $CHCl_3$ (3:5050) at 25° (80) (85) (86); between aq. and CCl_4 (3:5100) at 25° (80) (87) (85); between aq. and EtBr at 25° (80) (77); between aq. and $CHBr_3$ at 25° (85); between aq. and MeI at 25° (80) (87) see indic. refs.]

[For data on distribution of \bar{C} between aq. and CS_2 at 25° (85); between aq. $MgSO_4$ or K_2SO_1 solns. and di-n-butyl ether at 25° (88) (5); between acetone and glycerol at 25° (89) see indic. refs.]

BINARY SYSTEMS CONTAINING C

Azeotropic systems. [\$\bar{C}\$ with mesitylene (1:7455) forms \$\mathbf{z}\$ const.-boilg. mixt., b.p. 162° at 760 mm., contg. 17 wt. % \$\bar{C}\$ (90); \$\bar{C}\$ with naphthalene (1:7200) forms a const.-boilg. mixt., b.p. 187.1° at 760 mm., contg. 78 wt. % \$\bar{C}\$ (91); \$\bar{C}\$ with o-cresol (1:1400) forms a const.-boilg. mixt., b.p. 187.5° at 760 mm., contg. 54 wt. % \$\bar{C}\$ (91).]

[C with 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) forms a const.-boilg. mixt., b.p. 146.25° at 760 mm., contg. 1.8 wt. % C (91); C with pentachloroethane (3:5880) forms a const.-boilg. mixt, b.p. 158.65° at 760 mm., contg. 9.9 wt. % C (91); C with hexachloroethane (3:4835) forms a const-boilg. mixt., b.p. 171.2° at 760 mm., contg. 25 wt. % C (27); C with 1,2,3-trichloropropane (3:5840) forms a const.-boilg. mixt., b.p. 154.5° at 760 mm., contg. 10 wt. % (92).]

[\bar{C} with p-dichlorobenzene (3:0980) forms a const.-boilg. mixt., b.p. 167.55° at 760 mm., contg. 24.5 wt. % \bar{C} (27); \bar{C} with benzal (dr)chloride (3:6327) forms a const.-boilg. mixt., b.p. 189.1° at 760 mm., contg. 97 wt. % \bar{C} (93).]

[\bar{C} with bromobenzene forms a const.-boilg. mixt., b.p. 154.3° at 760 mm., contg. 11 wt.% \bar{C} (90); \bar{C} with p-dibromobenzene forms a const.-boilg. mixt., b.p. 186.3° at 760 mm., contg. 75 wt. % \bar{C} (93)]

OTHER PHYSICAL DATA ON BINARY SYSTEMS CONTAINING Č

 $\ddot{\mathbf{C}}$ + aq. [$\ddot{\mathbf{C}}$ is very eas. sol. aq. (32); for study of hydration at low temps. see (94); for f.p./compn. data see (23). — Data on density of aq. $\ddot{\mathbf{C}}$ is fragmentary but for D_{20}^{20} (40), D_{25}^{25} (95), and D_{35}^{35} (95) for certain conens see indic. refs. (cf. (96) (97) (98)). — For refractive indices of aq. solns. of $\ddot{\mathbf{C}}$ see (20) (40). — For study of soly. of aq. in $\ddot{\mathbf{C}}$ + $\mathbf{C}_{6}\mathbf{H}_{5}$ see (105).]

 \bar{C} + H_2SO_4 . [For densities, viscosities, and elec. conductivity at 20°, 40°, and 60° over whole compn. range see (12); for f.p./compn. data over range 46–100% \bar{C} (no compound is formed) see (18).]

 $\ddot{\mathbf{C}}$ + acetic acid. (1.1010) [For f p /compn. data and diag., eutectic m.p. -4.0° , contg. 22 mole % $\ddot{\mathbf{C}}$, see (99) cf. (100) (103).]

 $\ddot{\mathbf{C}}$ + dichloroacetic acid (3:6208). [For f p./compn. data (100), eutectic m.p. -10.5° contg. 30.7 mole % $\ddot{\mathbf{C}}$ (101), see indic. refs.]

 $\ddot{\mathbf{C}}$ + trichloroacetic acid (3:1150). [For f.p./compn. data (100), eutectic m.p. 17.5° contg. 48.5 mole % $\ddot{\mathbf{C}}$ (101), see indic. refs.]

 $\ddot{\mathbf{C}}$ + miscellaneous organic compds. of Order 1. [For f.p./compn. data on following systems see indic. refs: $\ddot{C} + C_6H_6$ (1:7400) (103); \ddot{C} + naphthalene (1:7200) (99) (17) (20); \ddot{C} + phenol (1:1420) (17) (16) (102); \ddot{C} + o-cresol (1:1400) (16) (102); \ddot{C} + m-cresol (1:1300) (16); \ddot{C} + p-cresol (1:1410) (16); \ddot{C} + α -naphthol (1:1500) (16); \ddot{C} + β -naphthol (1:1540) (16); \ddot{C} + thymol (1:1430) (16); \ddot{C} + guaracol (1:1405) (16); \ddot{C} + cetyl alc. (1:5945) (99); \ddot{C} + meso-erythritol (1:5825) (14); \ddot{C} + benzoic acid (1:0715) (100); \ddot{C} + o-toluic acid (1:0690) (100); \ddot{C} + m-toluic acid (1:0705) (100); \ddot{C} + p-toluic acid (1:0795) (100); \ddot{C} + phenylacetic acid (1:0665) (100), \ddot{C} + cinnamic acid (1:0735) (100); \ddot{C} + crotonic acid (1:0425) (100); \ddot{C} + dimethyl oxalate (1:0415) (103); \ddot{C} + dimethyl succinate (1:3556) (103); \ddot{C} + methyl cinnamate (1:2090) (103); \ddot{C} + phenyl salicylate ("Salol") (1:1415) (99); \ddot{C} + piperonal (1:0010) (99) (104); \ddot{C} + vanillin (1:0050) (104); \ddot{C} + acetophenone (1:5515) (104); \ddot{C} + benzil (1:9015) (104); \ddot{C} + dibenzalacetone (1:9024) (104).

 $\ddot{\mathbf{C}}$ + miscellaneous compounds of Order 2. [For f.p./compn. data on following system see indic. refs.: $\ddot{\mathbf{C}}$ + urea (19); $\ddot{\mathbf{C}}$ + ethyl carbamate (urethane) (19).]

TERNARY SYSTEMS CONTAINING C

[For f.p./compn. data and diag. of following systems see indic. refs.: \tilde{C} (α -form) + phenol (1:1420) + naphthalene (1:7200) (17); \tilde{C} (β form) + phenol (1:1420) + naphthalene (1:7200) (17).]

USE OF C IN FOODS AND BEVERAGES

General. [For discussion of use of \bar{C} as fermentation and oxidn. inhibitor or stabilizer in fruit juices, carbonated beverages, etc. (sometimes as "Esterex" (106)), see (106) (107) (108) (109) (110); for study of persistence of \bar{C} in such use see (111); for patents on such use see (112); for studies of bactericidal action (113) or fungistatic props. (114) of \bar{C} see indic. refs.]

Toxicity of \overline{C} . [For studies on toxicity of \overline{C} see (115) (116).]

Detection and determination of \overline{C} in foods and beverages. [For studies on detection and detn. of \overline{C} in commercial preservatives (624), in non-alc. beverages (117) (118) or in wines (119) (120) cf. (117) see indic. refs.: for identification of \overline{C} as Ba \overline{A}_2 (optical and crystallographic props.) see (121) (623).]

PREPARATION OF C

From acetic acid. [For prepn. of \overline{C} from acetic acid (1:1010) by chlorination at 250-500° without cat. (625), with Cl_2 in sunlight (32), in light from Hg quartz lamp (122), in silent electric discharge (123), or more usually in presence of catalysts (123) (124) (125) especially sulfur (124) (126) (127) (128) (129), red P (123) (124) (130), iodine (124), mixtures of red P + PCl_5 + I_2 (123) (124) (125) (131) (132) (133) (134), or in acetic anhydride (138) (139) at 100° or in vapor phase over $NiCl_2$ at 350° (140) see indic. refs.]

[For prepn. of \bar{C} from acetic acid (1:1010) by chlorination with SO₂Cl₂ at 115–120° and 4–5 atm. press. (135) or in pres. of a little acetyl chloride (136) or in presence of dibenzoyl peroxide in CCl₄ (70% yield (137)) see indic. refs.; for formn. of \bar{C} from AcOH + HCl on electrolysis see (141).

From trichloroethylene. [For prepn. of \tilde{C} from trichloroethylene (3:5170) with conc. H_2SO_4 at 190–195° see (142) (143) (144) (145) (146); for patents on this process see (147) (148) (149) (150) (151) (152) (153) (154). — Note also that H_2SO_4 may be replaced by arom. sulfonic acids such as benzenesulfonic acid see (155). — Note also that a very similar process (156) starting from unsym.-tetrachloroethane (3:5555) doubtless first involves loss of HCl to trichloroethylene.]

From other chloro-compounds. \bar{C} is also formed by appropriate oxidation of many suitably constituted chloro-compounds [e.g., for formn. of \bar{C} from 1,2-dichloroethane (ethylene (di)chloride) (3:5130) with dry O_2 in u.v. light see (157)].

[For formn. of Č by oxidation of unsaturated chloro-compds. see the following examples: 1,2-dichlorobutene-2, low-boilg. isomer (3:5360), high-boilg. isomer (3:5615) with KMnO₄ in acetone (158); 1,4-dichlorobutene-2 (3:5725) with KMnO₄ or O₃ (159); 1,2,4-trichlorobutene-2 (3:9062) with aq. KMnO₄ (160); 1,4-dichloro-2-methylbutene-2 (3:9204) with O₃ followed by KMnO₄ (161); 4-chlorobutadiene-1,2 (3:7225) with aq. alk. KMnO₄ (162); 1,3-dichlorohexadiene-2,4 (3:9310) with aq. KMnO₄ (163); 3,3,6-trichlorohexadiene-1,4 (3:9308) with aq. KMnO₄ (164); 1,3,4,6-tetrachlorohexadiene-2,4 (3:9306) with aq. KMnO₄ (164); 3,6-dichlorohexatriene-1,3,4 (3:9304) with aq. KMnO₄ (164); 1-chloro-5-methoxypentadiene-2,3 with aq. KMnO₄ (165); ethyl 5-chloropenten-3-oate with aq. KMnO₄ (166); 1-chloro-5-methoxy-5-phenylpentene-2 with KMnO₄ in acetone (35); chloroacetylene (3:7000) with NaOCl (167).]

[For formn. of C from ethylene chlorohydrin (3:5552) by oxidn. with CrO₃ (168); from

1-chloropropanol-2 (propylene α -chlorohydrin) (3:7747) by oxidn. with HNO₃; from 1,3-dichloropropanol-2 (" α -dichlorohydrin") (3:5985) by oxidn. with conc. HNO₃ (169) cf. (170) see indic. refs.]

[For form. of \tilde{C} from chloroacetaldehyde (3:7212) by oxidn. with conc. HNO₃ (171) cf. (172), AgOH (172) or dil. H₂O₂ (173); from chloroacetone (3:5425) by oxidn. with KMnO₄ (161) (174), CrO₃ (174), HNO₃ (174), (175); from 1-chlorobutanone-2 (3:8012) by oxidn. with HNO₃ (176) (177) see indic. refs.]

From aminoacetic acid (glycine). [For formn. of \bar{C} from glycine with nitrous acid (40% yield (178)), with conc. HCl + conc. HNO₃ (179), or from glycine hydrochloride with satd. aq. MgCl₂, CaCl₂, or ZnCl₂ + NaNO₂ (180), see indic. refs.]

From miscellaneous sources. [For prepn. of \tilde{C} from ketene with Cl₂ in gas phase, CCl₄, or dry ether, followed by aq. (181); from ketene with aq. Ca(OCl)₂ (182); from formaldehyde + CO + HCl gas at 180° and 800-900 atm. (183); for formn. of \tilde{C} from atrioxymethylene with SO₂Cl₂ in pres. of ZnCl₂ or AlCl₃ in s.t. at 150° for 12 hrs. (2); from methyl formate (1:1000) with SO₂Cl₂ in s.t. at 165-170° (2); from ethylene with ClO₂ (184); from mtro-trichloromethane ("chlorpicrin") in AcOH on exposure to light (185) cf. (186) (187) (188).]

[For form. of \tilde{C} from α,β -dichlorovinyl ethyl ether (3:5540) on boilg, with excess aq. see (189) (note, however, that with calcd. amt. aq. ethyl chloroacetate (3:5700) results (190)); for formn of \tilde{C} from unsym.-tetrachloroacetone (3:6085) by hydrolytic cleavage with aq. KOH see (191).]

[For formation of \bar{C} from its own derivatives, e.g., chloroacetyl chloride (3:5235), chloroacetic acid anhydride (3:0730), methyl chloroacetate (3:5585), ethyl chloroacetate (3:5700), or other exters, etc., see these compds.]

CHEMICAL BEHAVIOR OF C

Pyrolysis of C

[\bar{C} on distn. through a red-hot tube decomposes giving (192) HCl + CO + CH₂O (1:0145) + sym.-dichlorodimethyl ether (3:5245). — \bar{C} at 250-340° over ThO₂, kaolin, or animal charcoal gives (193) HCl + CO + CO₂, but \bar{C} merely boiled with activated carbon undergoes no decomposition (194).]

[$\ddot{\mathbf{C}}$ on htg. in tertiary bases such as dimethylaniline (195) or pyridine (196) decomposes into CO_2 + MeCl (3:7005), undoubtedly by way of forms. and decomps. of intermediate quaternary ammonium compds. (betaines) (196).]

[\bar{C} in dry ether or C_6H_6 soln. on exposure to ultra-violet light decomposes giving (197) HCl + fumaric acid (1:0895) + a substance which on shaking with aq. yields glycolide (1:0667).]

REDUCTION OF C

[$\tilde{\mathbb{C}}$ on reduction in aq. or aq. alc. alk. with H_2 in pres. of Pd or Ni (198) (199) (200), or $\tilde{\mathbb{C}}$ with chromous sulfate (201), or $\tilde{\mathbb{C}}$ with finely divided Fe (202), or $\tilde{\mathbb{C}}$ in aq. EtOH in ultra-violet light (203), or $\tilde{\mathbb{C}}$ on electrolytic reduction (204) gives acetic acid (1:1010). — Note, however, that attempts to effect bimolecular hydrogenation of $\tilde{\mathbb{C}}$ to succinic acid have been unsuccessful (205).]

OXIDATION OF C

[\overline{C} on oxidn. with $K_2S_2O_8$ gives (206) methylene (di)chloride (3:5020); for study of oxidn. of \overline{C} to CO_2 with $K_2S_2O_8$ see (207). — \overline{C} (as Na \overline{A}) on electrolysis gives (208) cf. (209) methylene (di)chloride (3:5020), chloromethyl chloroacetate [Beil. II-198, II₂-

(193)], and other prods. — For study of photochemical oxidn. of \bar{C} with KMnO₄ in pres. of uranyl salts see (210).]

REACTIONS INVOLVING SUBSTITUTION OF H ATOMS OF ALKYL RADICAL OF C

Fluorination. The behavior of \bar{C} with F_2 appears not to have been studied: chloro-fluoroacetic acid is unknown; chloro-difluoroacetic acid [Beil. II-201] although known has been prepd. from difluoroacetic acid by chlorination.

Chlorination. [Č with Cl₂ (211) in pres. of I₂ (212) gives dichloroacetic acid (3:6208) very likely accompanied by some trichloroacetic acid (3:1150).]

Bromination. [\bar{C} with Br₂ at 160° is claimed (213) to give chloro-bromo-acetic acid [Beil. II-217, II₂-(204)], but this is best prepared by other means, e.g., from α,β -dichloro-vinyl ethyl ether (3:5540) by addn. of Br₂, conversion by distn. to chloro-bromo-acetyl chloride, and hydrolysis (214) (41) (215) (216). — Note that although dibromination of \bar{C} to chloro-dibromo-acetic acid [Beil. II-220] appears unreported, yet this product is obtd. by other means cf. (217)

Sulfonation. [\bar{C} with ClSO₃H on warming (218) or \bar{C} with SO₃ finally at 70° (219) cf. (220) gives sulfo-chloroacetic acid [Beil. III-598, III₁-(208), III₂-(387)], hygroscopic ndls. of monohydrate from aq., m.p. 83° (219) (corresp. bis-acid chloride, oil, b.p. 70° at 3 mm., D_{-}^{15} = 1.669, n_{D}^{23} = 1.4920 (121); corresp. N,N,N',N'-tetraphenyldiamide, m.p. 210° (121)), accompanied (218) (220) by some chloromethanedisulfonic acid (chloromethionic acid) [Beil. II-25]. — For resolution of d,l-sulfochloroacetic acid see (219).]

Miscellaneous substitution reactions. [\bar{C} (as $K\bar{A}$) on boilg, with aq. gives (222) the salt of chloromercuri-chloroacetic acid which with either acid or alk, gives glycolic acid (1:0430).]

REACTIONS INVOLVING THE —COOH GROUP OF C

Acidic Strength of \bar{C}

 $\bar{\mathbf{C}}$ behaves as a very strong monobasic acid; Neut. Eq. = 94.5. — [Ionization const. of $\bar{\mathbf{C}}$ in aq. at 25° is 1.55×10^{-3} (223) (224), 1.51×10^{-3} (224) (225), 1.396×10^{-3} (226), 1.378×10^{-3} (227). — For examples of other studies of ioniz. const. of $\bar{\mathbf{C}}$ in aq. see (228) (229); for study of temp. variation of ioniz. const. in aq. over range 0-40° see (227) (230); for H+ conc. of $\bar{\mathbf{C}}$ in aq. solns. (75), in aq. solns. of KCl or NaCl (231) (234), or in buffer mixts. of $\bar{\mathbf{C}}$ + Na $\bar{\mathbf{A}}$ (232) (233); for studies of elec. conductivity of $\bar{\mathbf{C}}$ in aq. soln. at 0° (235), at 60° (236), at 62.5° (45), or over range 0-78° (4) see indic. refs. — For discussion of resonance and acid strength of $\bar{\mathbf{C}}$ see (237) (238) (239). — For study of "sourness" of $\bar{\mathbf{C}}$ from taste aspect see (252).]

[Studies of acid strength of \bar{C} in other solvents include the following: in EtOH (240) (241), in n-BuOH (242), in 60% methyl "cellosolve" (ethylene glycol monomethyl ether) (243), in m-cresol (242), in ether (244), in formamide (245), in acetonitrile (246), in C_6H_6 (247), in chlorobenzene (248), or in CHCl₃ (244). — For studies on electrometric titration of \bar{C} in C_6H_6 (249), or use of indicators with \bar{C} in C_6H_6 soln. (250), see indic. refs. — For studies of elec. conductivity of \bar{C} in MeOH, EtOH, BuOH, acetone see (251).]

Catalytic Effect of Cupon Various Reactions

The catalytic influence of C upon diversified types of chem. reaction has been extensively examined; although this matter cannot be recorded exhaustively, the following examples are cited.

[For studies of catalytic effect of \bar{C} upon the inversion of *l*-menthone to *d*-isomenthone in C_6H_6 (253) or in chlorobenzene (254); upon racemization of methyl-phenyl-acetophenone

and of isobutyl-phenyl-acetophenone in various solvents (255); upon I_2 /acetone reaction (224) (234) (256) (257) (232); upon hydrogen disproportionation of limonene (622) see indic. refs.]

[For studies of catalytic effect of Č upon the hydrolysis of ethyl formate in neutral salt solns. at 25° (258); of EtOAc (259) (235) in pres. of NaĀ or NaCl (259) (225); of sucrose (260) (261) see indic. refs.]

[For studies of catalytic effect of \bar{C} upon forms. of ether from ethyl alcohol (262); upon depolymerization of paraldehyde (273) or of dimeric dihydroxyacetone (263); upon bromination of ethyl acetoacetate (264) see indic. refs.]

[For studies on catalytic effect of \bar{C} upon nitration of toluene (265) (266); upon decompn. of ethyl diazoacetate in C_6H_6 (253) (267); upon decompn. of nitramide (268); upon rearr. of N-chloroacetanilide in chlorobenzene soln. at 100° (269); upon rearr. of N-bromoacetanilide in chlorobenzene, C_6H_6 , or ethylene (di)chloride (270); upon rearr. of N-iodoformanilide in anisole (271); upon rearr. of N-bromobenzanilide in chlorobenzene at 25° (272) see indic. refs.]

Salts of C

This topic cannot be exhaustively treated here but following examples are cited.

Salts with inorganic bases. [NH₄ \bar{A} , from \bar{C} in abs. alc. with dry NH₃ gas (274). — Hydroxylamine salt, HONH₃ \bar{A} , cryst. from boilg. alc., m.p. 124-125° (275).]

[Na\(\tilde{A}\) on electrolysis gives (208) (209) methylene (di)chloride (3:5020), chloromethyl chloroacetate [Beil. II-198, II₂-(193)], and other prods.; on htg. gives (276) polyglycolid, for rate of decompn. by aq. see (277). — K\(\tilde{A}\), 3H₂O (32); K\(\tilde{A}\).1½H₂O (32) (277) (for study of rate of decompn. by aq. see (277)); K\(\tilde{A}\).\(\tilde{C}\), sparingly sol. aq. (32). — Ag\(\tilde{A}\), spar. sol. cold aq., more readily in hot aq. (32); for soly. in HNO₃ see (278); dry htg. gives (279) AgCl + polyglycolid; on htg. with a little aq. gives (279) AgCl + glycolic acid; for prepn. and study of activity coefficient in pres. of electrolytes see (280); for sensitivity to light see (281).]

[Be \bar{A}_2 , see (293); Mg \bar{A}_2 .2H₂O, very sol. aq. or alc. (277); Ca \bar{A}_2 .H₂O, very sol. aq. or alc. (277) (for use in eel worm control in soil see (282)); Sr \bar{A}_2 , spar. sol. aq. alc. (277); Ba \bar{A}_2 .H₂O (32) (277) (293) (for use in detn. of \bar{C} see (121) (623)); Cu \bar{A}_2 , 4H₂O (274), Cu \bar{A}_2 .3H₂O (283), Cu \bar{A}_2 (274) cf. (284); for study of electrolysis see (285); for dissoc. see (288); for various complexes with NH₃ and amines see (286) (287). — Zn \bar{A}_2 .2(4?)H₂O (274). — Cd \bar{A}_2 .6H₂O, for prepn. (289), crystallography (290), dissociation (288), and conductivity (291) see indic. refs. — Pb \bar{A}_2 , spar. sol. cold aq. (274). — Hg \bar{A}_2 , spar. sol. aq. (292). — Hg $_2\bar{A}_2$, spar. sol. aq. (292).]

[Al \bar{A}_3 , see (293). — Mn \bar{A}_2 . \bar{C} .H₂O (274); Mn \bar{A}_2 . \bar{C} .2H₂O (274); Mn \bar{A}_2 .1.5H₂O (289). — Co \bar{A}_2 .6H₂O, m.p. 68-69° (289), for study of complexes with pyridine see (294). — Ni \bar{A}_2 , 3H₂O (274), for complexes with various amines see (295). — For studies on complexes of \bar{C} with iron salts see (274) (296) (297).]

Salts with organic bases (amines). [Aniline chloroacetate, m.p. 88° (298) (best from \bar{C} in dry ether treated dropwise with aniline in dry ether with cooling (299); note that this salt with P_2O_5 on stdg. gives (299) ω -chloroacetanilide, m.p. 136° cor.). — o-Toluidine chloroacetate, m.p. 95° (300). — p-Toluidine chloroacetate, m.p. 97.5° (300) (note that this salt at 80-90° for 2 hrs. (301) or with P_2O_5 (302) gives chloroaceto-p-toluidide, m.p. 164° (302)).]

α-Phenylethylamine chloroacetate, from Č + base in EtOAc, m.p. 93.6-94.4° u.c., 94.7-95.5° cor. (303). — Benzylamine chloracetate, from Č + base in EtOAc, m.p. 118.4-119.4° u.c., 119.9-120.9° cor. (303) (note that this m.p. is practically identical with corresp. benzylamine salt of trichloroacetic acid (3:1150) q.v.). — Piperazine bis-(chloroacetate), m.p. 145-146° cor. (304). — Semicarbazide chloroacetate, m.p. 111-112° (305).

Phenylhydrazine chloroacetate, from \bar{C} with phenylhydrazine in C_6H_6 , m.p. 111° (306) (note that this product is definitely the salt since on titration with alk. it gives Neut. Eq. 204.7 as against calcd. value of 202.6 (306); however, during detn. of m.p. it is undoubtedly converted to chloroaceto-phenylhydrazide, m.p. 115° (307), directly obtd. from chloroacetyl chloride (3:5235) with phenylhydrazine in ether (307)).

Behavior of Acidic Hydrogen of C with Metals

[For study of rate of soln. of Mg in aq. solns. of \tilde{C} see (308); for behavior of \tilde{C} with Zn see (309); for study of 20% aq. solns. of \tilde{C} on silver see (310).]

Esterification of C

This book includes the following esters of \bar{C} under their own individual numbers q.v.: methyl chloroacetate (3:5585), ethyl chloroacetate (3:5700), n-propyl chloroacetate (3:0565), isopropyl chloroacetate (3:8160), n-butyl chloroacetate (3:8330), isobutyl chloroacetate (3:8375) sec-butyl chloroacetate (3:8350), ter-butyl chloroacetate (3:8220), ethylene glycol (mono)-chloroacetate (3:6780), ethylene glycol bis-(chloroacetate) (3:0720), β -methoxyethyl chloroacetate (3:9285), diethylene glycol (mono)chloroacetate (3:9390), triethylene glycol (mono)-chloroacetate (3:9588), and phenyl chloroacetate (3:0565).

[For studies of rate of esterification of \bar{C} under various conditions with MeOH (1:6120) (311) (312) (313) (314) (315), with EtOH (1:6130) (312) (313) (1) (316) (317) (318), with isobutyl alc. (1:6165) (319) (320), with amyl alc. (313), or with neopentyl alc. (1:5812) (321) see indic. refs. — For studies on esterification of \bar{C} with alcohols by BF₃ method (312) (322) or without cat. (328) see indic. refs.]

[For patents involving esterification of \bar{C} with alcs. (323) by use of Cl_2 (324) see indic. refs.]

[For study of use of \bar{C} in esterification of various carbohydrate derivs. (325) or of cellulose (326) cf. (327). — Note that the chemistry of poly (vinyl chloroacetate) cannot be considered here.]

Addition Reactions of C with Organic Compounds

Addition to unsaturated linkages. \bar{C} in presence of suitable cat. adds to unsaturated linkages giving the corresp. esters [e.g., \bar{C} with propylene + BF₃ at 60-70° gives (34.2% yield (329)) isopropyl chloroacetate (3:8160); \bar{C} with butene-2 + ZnCl₂ at 100° for 8 hrs. gives (330) sec-butyl chloroacetate (3:8350); similarly \bar{C} with pentene-2 (1:8215) gives (330) diethylcarbinyl chloroacetate, b.p. 177-178°. — Note, however, that no record can be found of reaction of \bar{C} with ethylene to give ethyl chloroacetate (3:5700)].

[Č with *n*-butylacetylene (hexyne-1) (1:8055) in pres. of HgO + MeOH + BF₃.Et₂O gives (68% yield (331)) 2-(chloroacetoxy)hexene-1, b.p. 100-101° at 20 mm., $D_{-}^{26} = 1.017$, $n_{-}^{25} = 1.4453$ (331). (For addition of Br₂ to this prod. giving 67% yield 1-bromohexanone-2 + 21% yield chloroacetyl bromide see (334)).]

Addition to epoxy compounds. [Č with ethylene oxide (1:6105) in dry ether at 0° for 4 days (332) or at 50° under press. for 6 days (333) gives ethylene glycol mono (chloroacetate) (3:6780).]

Conversion of C to Corresponding Acyl Halides

Conversion of \bar{C} to chloroacetyl fluoride. [\bar{C} on distn. with fluorosulfonic acid (335) or \bar{C} with KF + benzoyl chloride (3:6240) (336) gives (yields: 30% (336), 15% (335)) chloroacetyl fluoride, b.p. 74° (335), 74-76° (336).]

Conversion of C to chloroacetyl chloride. [C can by numerous methods be converted

to chloroacetyl chloride (3:5235) q.v. — Note also, however, that \bar{C} with large excess PCl_5 (4 moles) gives (337) tetrachloroethylene (3:5460) and other products.]

Conversion of \overline{C} to chloroacetyl bromide. [\overline{C} with Br₂ + red P (338) (339) or with PBr₃ (340) gives chloroacetyl bromide, b.p. 127° (338) (340), D_{-}^{0} = 1.840 (340).]

Conversion of C to Corresponding Anhydride

C can by numerous methods be converted to chloroacetic acid anhydride (3:0730) q.v.

REACTIONS INVOLVING THE CHLORINE ATOM OF C

Reduction of \bar{C}

See above as second heading under chemical behavior of \bar{C} .

Hydrolysis of \bar{C} (or its salts)

Hydrolysis of C to glycolic (hydroxyacetic) acid (1:0430) together with the formaunder certain conditions of diglycolic acid (1:0495) has been very extensively studied.

Hydrolysis of \overline{C} (or its salts) with aq. \overline{C} on protracted boilg, with aq. (341) (342) (343) or \overline{C} (as Na \overline{A} or K \overline{A}) on boiling with aq. (32) (344) (277) or C with aq. BaCO₃ (followed by pptn. of barium with H₂SO₄ (345)) gives (88.7% yield (345)) glycolic acid (1:0430).

[For studies on rate of hydrolysis of \bar{C} by aq. under various conditions (626) (342) (343) (346) (347) (348) (359) (351); for study of influence of ultra-violet light (352) (353) (354) (355); for influence of temperature (356); for study of ord. and in heavy aq. (357); for heat of hydrolysis with aq. (358); for study of abnormalities of hydrolysis of salts (359); for study of induction period of hydrolysis (360) (383); for acceleration of hydrolysis by colloidal Ag, Ag₂O, or CuO (349) see indic. refs.]

[For studies of quantum yields of hydrolysis of \bar{C} and use as standard see (361) (362) (363) (364) (365) (366) (367) (353).]

Hydrolysis of \overline{C} (or its salts) with alkalies. \overline{C} on hydrolysis with aq. alkalies also gives glycolic acid (1:0430) [for studies of this reaction see (368) (342) (346) (369) (370) (350) (371) (351) (372) (373); for studies of hydrol. of Na \overline{A} by salts of weak acids (374), for study of basic catalysts (375), for effect of high press. (376) see indic. refs.]

[For patents on conversion of \bar{C} to glycolic acid (1:0430) by alkaline hydrolysis see (377) (378); note, however, that the glycolic acid so formed may be converted (379) to glycolid (1:0667).]

Note also that under the influence of the alkaline medium some of the glycolic acid first formed may condense with unreacted \bar{C} to give diglycolic acid (1:0495): for studies of this aspect of the reaction see (380) (381) (382).

Behavior of C with NaSH or Its Relatives

[\bar{C} with aq. 15% KSH (384) or with freshly prepd. aq. 15% NaSH (385) at 95° for 1 hr., subsequently acidified with H₂SO₄ and extracted with ether, gives (99% yield (385)) mercaptoacetic acid (thioglycolic acid) [Beil. III-244, III₁-(95), III₂-(175)], b.p. 107-108° at 16 mm. (384) (385), m.p. = -16.5° (384), $D_{20}^{20} = 1.3253$ (384). — Note that this prod. is also preparable by many other methods some of which are cited below.]

[\bar{C} (2 moles) as Na \bar{A} with NaSH as directed (386) (387) (388), or as K \bar{A} with KSH (389) (390), or as Na \bar{A} with potassium sulfantimonite (391) or sodium sulfostannate (391), or as Ca \bar{A}_2 with excess Ca(SH)₂ + H₂S (381) gives (84% yield (387)) thiodiglycolic acid (thiodiacetic acid), S(CH₂COOH)₂ [Beil. III-253, III₁-(97), III₂-(178)], cryst. from AcOEt/C₆H₆ (1:9) (388) m.p. 130° (388), 129° (387) (386).]

[Č (2 moles) as NaĀ with aq. Na₂S₂ (392) (393) (394), with alk. or alk.-earth polysulfides (402), with sodium sulfantimonate Na₃SbS₄ (391) or sodium sulfarsenate Na₃AsS₄ (391) gives dithiodiglycolic acid, HOOC.CH₂—S—S—CH₂COOH [Beil. III-254, III₁-(97), III₂-(179)], lfts. from AcOEt/C₆H₆ (1:9) (388) 108-109° (391), 106° (388). — Note that this prod. on reduction gives mercaptoacetic acid (above): e.g., for reduction with Sn + HCl (395), with Zn + H₂SO₄ (393) (396) (401) (402), with Na/Hg (397), by electrolytic reduction in H₂SO₄ soln. using Pb electrodes (398), by shaking soln. of sodium salt with Fe powder at 38° under N₂ (399), or by shaking with alanine or phenylalanine in 1% soln. in pres. of active carbon at 38° under N₂ (400) see indic. refs.]

Behavior of C with Various Salts of Inorganic Acids

(For behavior with NaCN, etc., see further below.)

With halides. [\bar{C} with HBr.5H₂O in s.t. at 150° gives (403) bromoacetic acid [Beil. II-213, II₁-(95), II₂-(201)], m.p. 49-50°, b p. 208°; however, \bar{C} in aq. KBr at 50° shows only very slight tendency to form. of bromoacetic acid (for study of equilibrium see (404)).]

[\bar{C} with aq. KI at 50° (405) (406), or \bar{C} with NaI in acctone at room temp. (407) (or in ethyl methyl ketone, diethyl ketone, or AcOEt (407) but not in EtOH (408)) gives iodoacetic acid, cryst. from much pet. ether (405) (409), m.p. 83° (405), 82° (406); for study of equilibrium of \bar{C} with KI in aq. at 50° see (404); of \bar{C} with KI or NaI in acctone (ionic reaction) see (410).]

With salts of inorganic sulfur, nitrogen, or phosphorus acids. [\bar{C} with aq. Na₂SO₃ gives (41) (412) salts of sulfoacetic acid [Beil. IV-21, IV₁-(312), IV₂-(531)]; for study of rate of reaction of K \bar{A} with Na₂SO₃, K₂SO₃, or (NH₄)₂SO₃ under various conditions see (214) (413).]

[The salts of \bar{C} with aq. Na₂S₂O₃ give the corresp. salts of "glycolic acid thiosulfate" (carboxymethyl hydrogen sulfate) [Beil. III-235, III₁-(97), III₂-(171)]; for studies of this reaction see (414) (415) (416) (417) (418).]

The alkali salts of \bar{C} with aq. alkali nitrites give the corresp. alkali salts of nitroacetic acid; in fact from a conc. aq. soln. of the potassium nitroacetate, treatment with the calcd. amt. of conc. HCl and extraction with much ether gives (70% yield (419)) (420) free nitroacetic acid [Beil. II-225, II₁-(99), II₂-(207)], m.p. 87-89° dec. (420). — However, even aq. solns. of the alkali salts of nitroacetic acid on warming readily lose CO_2 yielding nitromethane [Beil. I-74, I₁-(19), I₂-(40)], b.p. 100.80-100.86° at 760 mm. (421), f.p. -29.2°, $D_4^{25} = 1.1322$ (421), $n_D^{22} = 1.38056$ (421), and although this product is now commercially available from other sources, the reaction is of considerable interest in connection with \bar{C} . — [For studies on the prepn. of nitromethane from $K\bar{A} + KNO_2$ (yield 47% (422)) (423) (424) or from $Na\bar{A} + NaNO_2$ (yields: 70% (428), 58% (426), 53% (429) (430) (431), 35-38% (425)) see indic. refs. — For studies on rate of decompn. of nitroacetic acid in aq. soln. at 20° (432), in HCl, or in acetate buffered solns. at 17.84° and 9.78° (433) cf. (434) (435) (436) see indic. refs.]

[The behavior of \bar{C} with NaN₃ appears to be unreported; note, however, that ethyl chloroacetate (3:5700) with NaN₃ gives (437) ethyl azidoacetate [Beil. II-229, II₁-(101), II₂-(208)], which upon hydrolysis with aq. KOH gives (437) azidoacetic acid.]

[For behavior of C with aq. Na₃PO₄ at 85° see (438).]

Behavior of C with Hydrocarbons

Č with certain aromatic hydrocarbons or their halogen derivs. at elevated temp. but without cat. condenses with elimination of HCl to give arylated acetic acids [e.g., Č with

naphthalene (1:7200) at $180-185^{\circ}$ for 48 hrs. gives (439) α -naphthylacetic acid (1:0728); \bar{C} with 1-chloronaphthalene (3:6878) in generally similar fashion gives (439) 1-chloronaphthalene-?-acetic acid, m.p. 124° : for generally analogous behavior of \bar{C} with acenaphthene, anthracene, fluorene, and even certain phenols and amines see (439).]

Behavior of Chlorine Atom of C with Organic OH and SH Reactants

With alkoxides. \bar{C} with excess alkali alkoxides condenses with elimination of alkali chloride to give the corresponding alkoxyacetic acids [e.g., \bar{C} with MeOH/NaOMe (440) (441) or probably also MeOH/Ba(OMe)₂ cf. (442) gives methoxyacetic acid (1:1065); \bar{C} with abs. EtOH/NaOEt (2 moles) gives (yields: 93% (441), 90% (443), 74% (444)) ethoxyacetic acid (1:1070); \bar{C} with NaO-n-Pr in n-PrOH gives (64% yield (445)) n-propoxyacetic acid [Beil. III-233, III₁-(90), III₂-(170)], b.p. 123° at 26 mm. (446), 108° at 10 mm. (445), $D_4^{20} = 1.0518$ (446), $n_D^{22} = 1.42249$ (446); \bar{C} with NaO-n-Bu gives (84% yield (445)) (447) n-butoxyacetic acid [Beil. III₁-(90), III₂-(170)], b.p. 115-116° at 10 mm. (445), 113-114° at 9-10 mm. (447), $D_4^{20} = 1.0243$ (447), $n_D^{20} = 1.42634$ (447); \bar{C} with Na isobutylate gives (441) isobutoxyacetic acid [Beil. III-233, III₁-(90)], b.p. 118° at 18 mm. (441), 114° at 9 mm. (447), $D_4^{20} = 1.0074$ (447), $n_D^{20} = 1.42004$ (445); for analogous behavior of \bar{C} with sodium derivs. of n-amyl alc. (1:6255) (445), n-hexyl alc. (1:6230) (445), n-heptyl alc. (1:6240) (445) (448), n-octyl alc. (1:6255) (445), n-hexyl alc. (1:6245) (448) cf. (449), geraniol (1:6270) (448), 1-menthol (1:5940) giving (yields: 78-84% (450), 78% (451), 75% (452)) 1-menthoxyacetic acid [Beil. VI₁-(25)], m.p. 53-54° (452); benzyl alc. (1:6480) giving (75% yield (453)) (448) benzyloxyacetic acid; etc., see indic. refs.]

With alkali salts of mercaptans. C with alkali salts of mercaptans should give the corresp, alkylthioacetic acids, but for the most part these have been prepd, by alkylation of mercaptoacetic (thioglycolic acid). - [C (as NaA) with NaSMe should give methylmercaptoacetic acid [Beil. III₂-(177)], b.p. 130-131° at 27 mm. (454), 122-123° at 20 mm. (455), $D_{20}^{20} = 1.223$ (454), $n_{\rm D}^{20} = 1.495$ (454), but this prepr. has not been reported, the product having generally been obtd. (454) (455) from sodium thioglycolate by methylation]. — C (as NaA) with NaSEt in conc. aq. soln. followed by acidification gives (456) ethylmercaptoacetic acid [Beil. III-248, III₁-(95)], b.p. 117-118° at 11 mm. (456), 118-119° at 10 mm. (455), m.p. -8.7° (456), $D_4^{20} = 1.1497$ (456). — Note that n-propylmercaptoacetic acid, b.p. $136.5-137^{\circ}$ at 18 mm. (455), 132° at 15 mm. (454), $D_{20}^{20} = 1.109$ (454), $n_{D}^{20} = 1.109$ 1.483 (454), and isopropylmercaptoacetic acid, b.p. 128° at 13 mm. (454), 124-125° at 9 mm. (455), have been reported only by alkylation of thioglycolic acid. — However, C (as NaA) with Na-S-n-C₄H₉ in aq. soln. gives (yields: 90% (457), 87% (458)) n-butylmercaptoacetic acid, b.p. 144-145° at 14 mm. (455) (corresp. p-bromophenacyl ester, m.p. 95° (458)); for constants on the isomeric isobutyl (455) (459), sec.-butyl (455), and terbutyl (460) mercaptoacetic acids prepd. by other means see indic. refs. — C (as NaA) with NaS-n-C7H15 gives (461) n-heptylmercaptoacetic acid.]

With phenols. \bar{C} (as Na \bar{A}) with salts of phenols, or often \bar{C} with phenols in aq. alk. soln., reacts to give the corresp. aryloxyacetic acids; this procedure comprises a valuable tool for derivatization in the identification (462) of phenols. Although the products of reaction of \bar{C} with all possible phenols cannot be recorded here, attention is directed to the 44 aryloxyacetic acids derived from phenols of Order 1 comprising the summary on page 641 of the "Tables of Order 1" (464), and to analogous aryl oxyacetic acids occurring in this present book as follows: o-chlorophenoxyacetic acid (3:4260); m-chlorophenoxyacetic acid (3:3325); p-chlorophenoxyacetic acid (3:4375); 2,4-dichlorophenoxyacetic acid (3:4095); 2,4,5-trichlorophenoxyacetic acid (3:4335). Many other individual cases which cannot be mentioned here may be found by the usual search methods.

Behavior of C with Salts of Organic Acids

With NaCN, KCN, etc. [\bar{C} on conversion to Na \bar{A} and reaction with aq. NaCN (465) (466) (475) (476) or KCN (467) (468) (469) gives (yields: 75% (469), 70% (468)) cyanoacetic acid (malonic acid mononitrile) [Beil. II-583, II₁-(253), II₂-(530)], m.p. 69-70° (468), 69° (470), 66.1-66.4° cor. (467), 65-66° (471), 65° (472) (473); for use of this reaction in prepn. of malonic acid (1:0480) see (476).]

Note, however, that the behavior of \bar{C} or its salts with KSCN, NH₄SeN, alkali xanthates, etc., is both complex and disputed and cannot be detailed here.

Behavior of C with NH3

 $\tilde{\mathbf{C}}$ with NH₃ under various conditions gives aminoacetic acid (glycine) [Beil. IV-333, IV₁-(462), IV₂-(771)].

[For behavior of \bar{C} with conc. aq. NH₄OH as method of prepn. of glycine (yields: 66-69% (477), 64-65% (478), 54% (479), 50% (480)) (481) (482) (486) (for numerous older refs. see Beilstein) see indic. refs.: for extensive studies on influence of conditions on this reaction see (483) (477); for study of rate of ammonolysis of \bar{C} see (484) (485). — For behavior of \bar{C} with liq. NH₃ see (487), note that \bar{C} in liq. NH₃ with Na splits out calcd. amt. NaCl and that no cyanide is formed (488). — For behavior of \bar{C} with (NH₄)₂CO₃ see (483) (477) (489).]

[Note that reaction of \bar{C} with NH₃ does not stop with formn. of aminoacetic acid (glycine) but that unchanged \bar{C} reacts with the latter to give (489) (490) (480) iminodiacetic acid ("diglycolamidic acid") HN(CH₂COOH)₂ [Beil. IV-365, IV₁-(481), IV₂-(800)], and/or trimethylamine- α,α',α'' -tricarboxylic acid ("triglycolamidic acid") [Beil. IV-369, IV₁-(482), IV₂-(801)], also obtd. from \bar{C} on fusion with ZnCl₂/NH₃ (492).]

Behavior of \bar{C} with Organic Amines

With primary aliphatic amines. [C with MeNH₂ as directed (497) gives (methylamino)-acetic acid (N-methylglycine = sarcosine) [Beil. IV-345, IV₁-(468), IV₂-(784)], but this prod. is usually prepd. in other ways. — Note, however, that C (2 moles) with MeNH₂ (1 mole) + excess aq. NaOH gives (63-71% yield (493)) (494) methyliminodiacetic acid, CH₃N(CH₂COOH)₂ [Beil. IV-367, IV₂-(800)], cryst. from aq. MeOH, m.p. 226-227° dec. (495), 226° dec. (496).]

[Č with excess aq. EtNH₂ as directed (498) gives ethylaminoacetic acid (N-ethylglycine) [Beil. IV-349, IV₂-(787)], m.p. 180-182° dec. (499), 181.5° dec. (500). — The homologous N-alkylglycines appear never to have been prepared from similar reaction of C with alkylamines, but for prepn. of N-(n-propyl)glycine [Beil. IV-352], m.p. 196-198° dec. (499), N-(isopropyl)glycine [Beil. IV₂-(787)], N-(n-butyl)glycine, m.p. 192° (501), N-(isobutyl)glycine, m.p. 188° (501), or N-(n-amyl)glycine, m.p. 201° (501), by other methods see indic. refs.]

With secondary aliphatic amines. [C with aq. Me₂NH (502) (29) for 4 hrs. at 55° under press. (503) or with aq. NaOH (504) as directed gives (yield Na salt 53% (504)) dimethylaminoacetic acid (N,N-dimethylglycine) [Beil. IV-346, IV₁-(469), IV₂-(785)], m.p. 177-182° (29), 176-178° (503) (for prepn. of this prod. from glycine with formic acid + formaldehyde see (505)). — C with Et₂NH similarly gives (506) N,N-diethylglycine [Beil. IV-350, IV₁-(472)].]

With tertiary aliphatic amines. [C with Me₃N (507) or C (as NaA) with Me₃N (508) gives betaine hydrochloride (CH₃)₃N (Cl).CH₂COOH [Beil. IV-347, IV₁-(470), IV₂-(786)].]

With primary aromatic amines. (See also below under D's.) [$\ddot{\textbf{C}}$ with aniline in a little ether boiled with a large volume of aq. (509), cf. (511), or $\ddot{\textbf{C}}$ with aniline (3 moles) boiled with aq. and subsequently made alkaline (510), or best $\ddot{\textbf{C}}$ with aq. aniline heated in presence

of an acid acceptor such as aq. NaOH (512), aq. NaOAc (573) cf. (514), or other alkali or alkaline-earth hydroxides or carbonates (515) (516) (517) (518) (519) gives (yields: 100% (514), 90% (510), 86% (512)) phenylaminoacetic acid (N-phenylglycine) [Beil. XII-468, XII₁-(263)], m.p. 127° (note that if htd. at 200°, however, bimolecular condensation occurs with elimination of 2H₂O and formn. (520) (521) of N,N'-diphenyl-2,5-diketopiperazine, m.p. 263° (520) (521) while distn. causes loss of CO₂ giving (522) N-methylaniline). — Note also that reaction of C with 2 moles aniline (523), or further reaction of C with N-phenylglycine (above) in aq. alk. (524) (525) (514) (526), gives (yields: 80–85% (526), 50–60% (525)) phenylimino-diacetic acid, C₆H₆N(CH₂COOH)₂ [Beil. XII-480, XII₁-(265)], m.p. 152–155° dec. (526). — Note also that reaction of C with aniline in pres. of NaOAc gives (525) much N-phenylglycine anilide, C₆H₆NHCH₂CONH.C₆H₆ [Beil. XII-556], m.p. 112°_]

[Note that C with many other primary aromatic amines reacts in analogous fashion, but details cannot be included here because of lack of space.]

With primary aromatic diamines. [\overline{C} with o-phenylenediamine in dry ether forms (327) a 1:1 cpd. presumably to be regarded as salt. — However, \overline{C} (1 mole) with o-phenylenediamine (1 mole) in 4 N HCl refluxed (528) for 45 min. and allowed to stand overnight (529) (530) gives (yields: 80-85% (529), 78-86% (530)) 2-(chloromethyl)benzimidazole, ndls. from EtOH/AcOEt (528), pr. from dioxane (529) or dry acctone (530), m.p. 165° (529), $160-161^{\circ}$ (528), $159-160^{\circ}$ cor. (530); note that value is sensitive to rate of htg. (529) (530). — For studies of behavior of this product with many amines (529) (530), with aq. (530), KI in acctone (530) (531) see indic. refs. — For general study of ortho condensations leading to benzimidazole formn. see (532).]

With hydrazines. [\ddot{C} (1 mole) with phenylhydrazine (2 moles) in boilg. aq. alc. K₂CO₃ (½ mole) gives (533) (534) a mixt. of both (α -phenylhydrazine)acetic acid, C₆H₆N(NH₂)-CH₂COOH [Beil. XV-316], tbls. from abs. EtOH, m.p. 168° (533), 167° deo. (535), and (β -phenylhydrazino)acetic acid, C₆H₆NH.NHCH₂COOH [Beil. XV-321], lfts. from alc., m.p. 153° (536), 152–153° (537); for separation of these isomers see (533).]

[For behavior of \bar{C} with N,N-diphenylhydrazine in aq. Na₂CO₃ or NaOAc see (538).]

With aromatic primary amines also containing other functional groups. With aminophenols. [Č with p-aminophenol on htg. in aq. soln. (539) (540) (541) (542) contg. also NaOAc (543) (544) gives (yields 45% (544), 35% (539) N-(p-hydroxyphenyl)glycine [Beil. XIII-488, XIII₁-(171)] (this product has considerable interest as a photographic developer); for its purification see (540) (545); for pat. on its decompn. at 160-170° in ketone solvents as method of prepn. of N-methyl-p-aminophenol [Beil. XIII-441, XIII₁-(149)] see (546). — Note also that in above reaction of Č with p-aminophenol some N-(p-hydroxyphenyl)iminodiacetic acid (542) is also formed.]

With amino acids. [\bar{C} with o-aminobenzoic (anthranilic) acid in aq. soln. (547) preferably also contg. Na₂CO₃ (548) (559) (550) gives (yields: 85–89% (550), 70–80% (549)) N-(o-carboxyphenyl)glycine (phenylglycine-o-carboxylic acid) [Beil. XIV-348, XIV₁-(544)], ndls. from MeOH, m.p. about 215° dec. (551); this product upon htg. loses CO₂ giving indoxyl and is therefore an important intermediate in mfg. of indigo; for use of this reaction for detection of \bar{C} in wine by conversion to indigo see (120) cf. (117). — Note also that in above reaction of \bar{C} with anthranilic acid some N-(o-carboxyphenyl)minodiacetic acid [Beil. XIV-354, XIV₁-(545)], m.p. 216° dec. (551), is also produced (551); although both phenylglycine-o-carboxylic acid (Neut. Eq. 97.5) and N-(o-carboxyphenyl)-iminodiacetic acid (Neut. Eq. 84.3) thus melt at same temp., their mixture melts at about 200° (551).]

With secondary aromatic amines. [C with N-methylaniline on htg. (552) or better in aq. NaOH on 4-hr. reflux (553) gives (74% yield (553)) N-methyl-N-phenylglycine [Beil. XII-473, XII₁-(264)], oil (B.HCl, m.p. 215-216° dec. (553)). — C with N-ethylaniline on

htg. gives (554) N-ethyl-N-phenylglycine [Beil. XII-475], oil. — \bar{C} with diphenylamine at 180-200° for 40-50 hrs. gives (5-10% yield (555)) N,N-diphenylglycine [Beil. XII₁-(264)].]

With tertiary aromatic amines. [C with dimethylaniline at 100° (556) for 12-18 hrs. (557) gives dimethyl-phenylbetaine hydrochloride [Beil. XII-474], m.p. 194-196° (556), from which silver oxide liberates (557) (558) free dimethyl-phenyl-betaine, m.p. 124-126° (557), 123-124° (558). — For corresp. betaine from N,N-diethylaniline see (559).]

With tertiary heterocyclic amines. [C with pyridine on htg. (560) (561) (194) cf. (556) at 60° for 5 hrs. (557) gives N-(carboxymethyl) pyridinium chloride (pyridinebetaine hydrochloride) [Beil. XX-226], m.p. 202-205° dec. (560) (thought by (194) to be typographical error for 102-105° dec.). — For behavior of C with quinoline see (556).]

Behavior of C with Amides, Thioamides, etc.

This topic cannot here be treated in full, but the following cases are reported as examples. With urea. [C] with carbamide (urea) might be expected under appropriate conditions to condense with elimination of HCl and formn. of ureidoacetic acid (hydantoic acid), NH₂CONH.CH₂COOH [Beil. IV-359, IV₁-(477), IV₂-(792)], m.p. 169-170° (562) (563), 160-161° (564), 160° (565), or its ring-closure product hydantoin [Beil. XXIV-242, XXIV₁-(287)], m.p. 220°; no report of the chemical behavior of C with urea can be found, however, the two above-mentioned expected products having been prepared by other means.—Note that f.p./compn. data on system C + urea have been recorded (19).]

With thiourea. [Č with thiourea (the latter reacting in its isothiourea mode) gives according to conditions either isothiohydantoic acid, H₂N—C(=NH)—S—CH₂COOH [Beil. III-251, III₁-(97)] (566) (567), or pseudothiohydantoin [Beil. XXVII-233, XXVII₁-(303)], (568) (569) (570) (571) (572) (573).]

With substituted thioureas. The behavior of \tilde{C} with substituted thioureas cannot be treated in full, but the following examples are cited (for reaction of \tilde{C} with various monosubstituted thioureas see (573) (574), with various disubstituted thioureas see (575) (576) (577)].

- --- Methyl chloroacetate: oil, b.p. 131° (see 3:5585).
- --- Ethyl chloroacetate: oil, b.p. 144° (see 3:5700).
- --- Phenyl chloroacetate: m.p. 44-45° (see 3.0565).
- —— o-Tolyl chloroacetate: oil, b.p. 127-127.6° at 10 mm. (578). [From C with o-cresol (1:1400) + POCl₃ in pyridine (574), or from chloroacetyl chloride (3:5235) with o-cresol (1:1400) at 130° for 4 hrs. (578); note that this prod. with AlCl₃ at 140° undergoes Fries rearr. giving (578) both 2-hydroxy-3-methylphenacyl chloride [Beil. VIII₁-(549)], m.p. 67°, and 4-hydroxy-3-methylphenacyl chloride [Beil. VIII₁-(550)], m.p. 144-145°.]
- m-Tolyl chloroacetate: oil, b.p. 153° at 30 mm. (580). [From chloroacetyl chloride (3:5235) with m-cresol (1:1730) (579) (580); note that this prod. with AlCl₃ at 150° gives (50% yield (580)) 2-hydroxy-4-methylphenacyl chloride [Beil. VIII-113, VIII₁-(550)], m.p. 101°.]
- p-Tolyl chloroacetate: m.p. 32° (580), $29-30^{\circ}$ (579); b.p. 162° at 45 mm. (580); $D_4^{35} = 1.1840$ (41), $n_2^{35} = 1.5150$ (41). [From \bar{C} with p-cresol (1:1410) + POCl₃ in pyridine (579), or from chloroacetyl chloride (3:5235) with p-cresol (1:1410) at 135° (580); note that this prod. with AlCl₃ at 140° gives (580) 2-hydroxy-5-methyl-phenacyl chloride [Beil. VIII-111], m.p. 65° (580).]
- Benzyl chloroacetate: oil, b.p. 147.5° at 9 mm., $D_4^4 = 1.2223$, $n_D^{18} = 1.5246$ (581). [From \bar{C} with benzyl alc. (1:6480) + HCl gas at 100° (581).]

- --- p-Nitrobenzyl chloroacetate: oil, unsuitable as (582).
- --- Phenacyl chloroacetate: unreported.
- --- p-Chlorophenacyl chloroacetate: unreported.
- D p-Bromophenacyl chloroacetate: m.p. 103.7° cor. (583).
- --- p-Iodophenacyl chloroacetate: unreported.
- (584). [From Č (as NaĀ) with p-phenylphenacyl bromide (584) (m.p. 124.5-125.5°) in aq. alc. on htg. (584).]
- © S-Benzylthiuronium chloroacetate: m.p. 159-160° (585). [Note that for corresp. salts from dichloroacetic acid (3:6208) and trichloroacetic acid (3:1150) m.p. values are respectively 178-179° and 148-149° (585).]
- S-(p-Chlorobenzyl)thiuronium chloroacetate: m.p. 158° cor. (586). [From C (as NaA) with S-(p-chlorobenzyl)thiuronium chloride (586) (m.p. 197°) in alc. (586); note that corresp. deriv. of trichloroacetic acid (3:1150) has m.p. 148° cor.]
- S-(p-Bromobenzyl)thiuronium chloroacetate: m.p. 154° cor. (587). [From C (as NaA) with S-(p-bromobenzyl)thiuronium bromide (587) (m.p. 213°) in alc. (587); note that corresp. deriv. of trichloroacetic acid (3:1150) has m.p. 146° cor. (587).]
- ω-Chloroacetamide: m.p. 120.5-121.5° (588), 120° (589), 119-120° (590), 119.5° (591), 118-120° (165), 118° (312), 116.4-116.9° (620). [From methyl chloroacetate (3:5585) (588) (593) or ethyl chloroacetate (3:5700) (590) (589) (592) (594) (595) (596) (597) with cold conc. NH₄OH (78-84% yield (590)), or from chloroacetyl chloride (3:5235) with dry NH₃ (597).]
- Φ-Chloroacetanilide: eryst. from hot aq. or 50% alc, m.p. 138° cor. (598), 136–137° (599), 136° cor. (600), 135° (601), 134–135° (602) (166), 134.5° (603) (604), 134° (605) (606), 133–134° (610). [From $\bar{\mathbb{C}}$ with aniline (606) in presence of P_2O_5 (600) (605), from $\bar{\mathbb{C}}$ with aniline salts + PCl₅ or SOCl₂ (607), from chloroacetyl chloride (3:5235) with aniline (2 moles) in ether (608) (603), C_6H_6 (602) (601), or AcOH/NaOAc (599) or with aniline (1 mole) + aq. NaOH in C_6H_6 or toluene (609), or from chloroacetic acid anhydride (3:0730) with aniline + P_2O_5 (610) | Note that this ω-chloroacetanilide with AlCl₃ (not more than 1.8 pts. (611)) at 225° (611) (612) loses HCl with ring closure giving (85% yield (611) (612)) oxindole [Beil. XXI-282, XXI₁-(289)]; also that ω-chloroacetanilide with alc. KOH undergoes bimolecular condensation giving (613) N,N'-diphenyl-2,5-diketopiperazine, m.p. 263°.]
- Φ ω-Chloroacet-o-toluidide: cryst. from dil. alc., m.p. 111-112° (614) (604), 111° (615). [From \bar{C} + o-toluidine + P_2O_5 (615), or from chloroacetyl chloride (3:5235) with o-toluidine (2 moles) in dry ether (616) or C_6H_6 (614).] [Note that this prod. with AlCl₃ at 225° loses HCl with ring closure giving (612) 7-methyloxindole, m.p. 200°; also that with alc. KOH it undergoes bimolecular condensation giving (614) N,N'-di-o-tolyl-2,5-diketopiperazine.]
- ω-Chloroacet-p-toluidide: m.p. 164° (615), 162° (608) (617), 161.5° (603). [From \bar{C} (2 moles) with p-toluidine (1 mole) at 80-90° (617) in presence of P_2O_5 (615), or from chloroacetyl chloride (3:5235) with p-toluidine (2 moles) (608) in ether (603).] [Note that this prod. with AlCl₃ at 230° for 2 hrs. loses HCl with ring closure giving (612) 5-methyloxindole [Beil. XXI-291], m.p. 168° (612).]
- ω-Chloroacet-N-benzylamide: cryst. from C₆H₆ or lgr., m.p. 93.5-94.5° cor. (618), 93.0-93.6° cor. (619), 92.2-92.8° u.c. (619). [From ethyl chloroacetate (3:5700) with aq. benzylamine on shaking in cold (619) cf. (621), or from chloroacetyl chloride (3:5235) with benzylamine + aq. KOH (618); note, however, that the corresp. derivs. from dichloroacetic acid (3:6208) and from trichloroacetic acid (3:150) have almost the same m.p.'s, viz., 93.8-95.6° cor. and 93.6-94.4° cor. respectively (619); note also that the simple salt of C with benzylamine has m.p. 119.9-120.9° cor. (304).]

3:1370 (1) Sudborough, Lloyd, J. Chem. Soc. 75, 476 (1899).
(2) Fuchs, Katscher, Ber. 57, 1257 (1924).
(3) Benrath, Hertel, Z. wiss. Phot. 23, 34 (1925).
(4) Rabinowitsch, Z. physik. Chem. 119, 65 (1926); J. Russ. Phys.-Chem. Soc. 58, 231 (1926).
(5) Randall, Failey, Chem. Ress. 4, 301-318 (1927).
(6) Dezelic, Ann. 520, 290-300 (1935).
(7) Michel, Bull. soc. chim. Belg. 48, 127-129 (1939).
(8) Bridgman, Phys. Rev. (2) 3, 189 (1914).
(9) Tollens, Ber. 17, 665 (1884).
(10) Grinakovskii, J. Russ. Phys.-Chem. Soc. 45, 1236 (1913), Cent. 1913, II 2076; [C.A. 8, 287 (1914)].

(11) Pohl, Hobbs, Gross, J. Chem. Phys. 9, 408-414 (1941). (12) Tartakovskaya, Bondarenko, Emel'yahova, Acta Physicochim. (U.S.S.R.), 6, 609-624 (1937); Cent. 1938, I 293; [C.A., 32, 4401 (1938)]; J. Phys. Chem. (U.S.S.R.) 9, 407-416 (1937); [Cent. 1938, I 3889]; C.A. 31, 6955 (1937). (13) Westheimer, J. Am. Chem. Soc. 56, 1962-1963 (1934). (14) Puschin, Dezelic, Monatsh. 60, 432, 435-436 (1932). (15) Piutti, Badolato, Atti accad. Lincei (5) 33, I 476 (1924); Cent. 1924, II 1893. (16) Mameli, Cocconi, Gazz. chim. ital. 53, 149-158 (1923). (17) Mameli, Mannessier-Mameli, Gazz. chim. ital. 63, 12-16 (1933). (18) Kendall, Carpenter, J. Am. Chem. Soc. 36, 2505 (1914). (19) Puschin, Rikovsky, Monatsh. 60, 438-448 (1932). (20) Miers, Isaac, Cent. 1909, II 116; Proc. Roy. Soc. (London), 82, 184-187 (1909).

(21) Schenck, Z. physik. Chem. 33, 451-452 (1900). (22) Müeller, Z. physik. Chem. 86, 196-201 (1914). (23) Pickering, J. Chem. Soc. 67, 664-684 (1895). (24) Wooten, Hamnett, J. Am. Chem. Soc. 57, 2289-2296 (1935). (25) Steiner, Johnston, J. Phys. Chem. 32, 935 (1932). (26) Coffmann, J. Am. Chem. Soc. 58, 1983 (1935). (27) Lecat, Ann soc. sci Bruxelles 45, I 290 (1926). (22) Walden, Z. physik. Chem. 70, 577 (1910). (29) Kahovec, Kohlrausch, Monatsh. 68, 371-372 (1936). (30) Kohlrausch, Koppl, Pongratz, Z. physik. Chem. B-21, 254 (1933).

(31) Perkin, J. Chem. Soc. 65, 421 (1894). (32) Hoffmann, Ann. 102, 1-20 (1857). (33) Landee, Johns, J. Am. Chem. Soc. 63, 2892-2894 (1941). (34) Patterson, Ber. 38, 212 (1905). (35) Straus, Thiel, Ann. 525, 166 (1936). (36) Jaeger, Z. anorg. allgem. Chem. 101, 64 (1917). (37) Mameli, Mannessier, Gazz. chim. ital. 42, II, 571-576 (1912). (38) Hulett, Z. physik. Chem. 28, 668-669 (1899). (39) Korber, Z. physik. Chem. 82, 52-55 (1913). (40) Hantzsch, Dürigen, Z. physik. Chem. 136, 15 (1928).

(41) Vanderstichele, J. Chem. Soc. 123, 1226-1228 (1923).
(42) Kireev, Popov, J. Gen. Chem. (U.S.S.R.) 5, 1399-1401 (1935); Cent. 1937, I 3127, C.A. 30, 2441 (1936).
(43) Virtanen, Pulkki, J. Am. Chem. Soc. 50, 3144 (1928).
(44) Mameli, Gazz. chim. ital. 38, II 579-586 (1909).
(45) Walden, Z. angew. Chem. 38, 812-813 (1925).
(46) Walden, Z. physik. Chem., Bodenstein Festband, 28 (1931).
(47) Walden, Z. physik. Chem. A-162, 1-8 (1932).
(48) Bell, Baughan, Vaughan-Jackson, J. Chem. Soc. 1934, 1969-1972.
(49) Klatt, Z. anorg allgem Chem. 222, 293-294 (1935).
(50) Frankel, Biochem. Z. 227, 304-318 (1930); Cent. 1931, I 1060; C.A. 25, 451 (1931).

(51) Berthelot, Ann. chim. (6) 28, 136-137 (1893). (52) Berthelot, Matignon, Ann. chim. (6) 28, 565-567 (1893). (53) Schjanberg, Svensk Kem. Tid. 44, 227-231 (1932); Cent. 1932, II 3685; C.A. 27, 3133 (1933). (54) Schjanberg, Z. physik. Chem. A-172, 228 (1935). (55) Kharasch, J. Research Natl. Bur. Standards, 2, 418 (1929). (56) Munzberg, Z. physik. Chem B-31, 18-22 (1936). (57) Cohn, Urey, J. Am. Chem. Soc. 60, 679-687 (1938). (58) Ockrent, J. Chem. Soc. 1932, 613-630. (59) Ockrent, J. Chem. Soc. 1932, 1864-1875. (60) Swearingen, Dickinson, J. Phys. Chem. 36, 534-545 (1932).

(61) Sabalitschka, Pharm. Zty. 74, 382-384 (1929); Cent. 1929, I 2288; C.A. 23, 2627 (1929). (62) Namasivayan, J. Indian Chem. Soc. 4, 449-458 (1927). (63) Schilow, Nekrassow, Z. physik. Chem. 130, 68 (1927). (67) Traube, Somogyi, Biochem. Z. 120, 95 (1921). (65) S. S. Bhatnagar, A. N. Kapur, M. S. Bhatnagar, J. Indian Chem. Soc. 17, 367 (1940). (66) Stadnikow, Kolloid-Z. 35, 233 (1924). (67) Mokruschin, Kryloff, Kolloid-Z. 43, 389 (1927). (68) Kubelka, Taussig, Kolloid-Beihefte 22, 150-190 (1926). (69) Brass, Frei, Kolloid-Z. 45, 248-249 (1928). (70) Chakravarty, Sen, Z. anorg. allgem. Chem. 186, 360 (1930).

(71) Sen, J. Phys. Chem. 31, 526 (1927).
(72) Ermolenko, Ginzburg, Colloid J. (U.S.S.R.)
5, 263-270 (1939); Cent. 1939, II 3556; C.A. 33, 8469 (1939).
(73) Griffin, Richardson, Robertson, J. Chem. Soc. 1928, 2705-2709.
(74) von Euler, Bucht, Z. anorg. allgem. Chem. 126, 269-277 (1923).
(75) Schreiner, Z. anorg. allgem. Chem. 122, 203-204 (1922).
(76) Dermer, Markham, Trimble, J. Am. Chem. Soc. 63, 3524-3525 (1941).
(77) Smith, J. Phys. Chem. 25, 620 (1921).
(78) Herz, Fischer, Ber. 38, 1141 (1905).
(79) von Georgievics, Monatsh. 36, 400-401 (1915); Z. physik. Chem. 90, 54 (1915).
(80) Kolosovskii, Kulikov, Z. physik. Chem. A-169, 459-471 (1934).

(81) Hantzsch, Vagt, Z. physik. Chem. 38, 741 (1901).
(82) Bodansky, Meigs, J. Phys. Chem. 36, 816 (1932).
(83) Andreasov, Davydova, Trans. Inst. Chem. Kharkov Univ. 4, No. 13, 131-136 (1940).
(84) Kolosovskii, Kulikov, J. Gen. Chem. (U.S.S.R.) 4, 1370-1377 (1934); Cent. 1936, II 1511; C.A. 29, 3898 (1935).
(85) Herz, Levy, Z. Elektrochem.

- 11, 819 (1905). (86) Smith, J. Phys. Chem. 25, 618 (1921). (87) Kolosovskii, Kulikov, J. Gen. Chem. (U.S.S.R.) 5, 63-68 (1935); Cent. 1936, II 2880; C.A. 29, 4652 (1935). (88) Randall, Failey, J. Am. Chem. Soc. 49, 2678-2681 (1927). (89) Smith, J. Phys. Chem. 25, 730 (1921). (90) Lecat, Rec. trav. chim. 46, 243 (1927).
- (91) Lecat, Ann. soc. sci. Bruxelles 47, I 25, 151 (1927). (92) Lecat, Rec. trav. chim. 47, 17 (1928). (93) Lecat, Ann. soc. sci. Bruxelles 48, I 15, 120 (1928). (94) Colles, J. Chem. Soc. 89, 1253 (1906). (95) Drucker, Z. physik. Chem. 52, 648 (1905). (96) LeBlanc, Z. physik. Chem. 4, 557 (1889). (97) LeBlanc, Rohland, Z. physik. Chem. 19, 265 (1896). (98) Polowzow, Z. physik. Chem. 75, 518 (1911). (99) Mameli, Mannessier, Gazz. chim. ital. 43, II 586-609 (1913). (100) Kendall, J. Am. Chem. Soc. 36, 1722-1734 (1914).
- Kendall, J. Am. Chem. Soc. 36, 1722-1734 (1914).

 (101) "Int. Crit. Tables," IV, 101, 105 (1928). (102) Kendall, J. Am. Chem. Soc. 38, 1313, 1321-1322 (1916). (103) Kendall, Booge, J. Am. Chem. Soc. 38, 1727, 1733-1734 (1916). (104) Kendall, Gibbons, J. Am. Chem. Soc. 37, 155-159 (1915). (105) Bell, Z. physik. Chem. A-159, 20-30 (1935). (106) Walker, Canner 92, No. 15, 20-21 (1941); C.A. 36, 3858 (1942). (107) Fabian, Bloom, Fruit Products J. 21, 292-296 (1942); C.A. 37, 2834 (1943). (108) Joslyn, Cruess, Food Industries 14, No. 9, 110-111 (1942); C.A. 36, 6256 (1942). (109) Morrison, Leake, Univ. Cal. Pub. Pharmacol. 1, 397-421 (1941); C.A. 35, 8125 (1941). (110) Leake, Food Industries 14, No. 6, 102-104 (1942); C.A. 36, 4917 (1942).
- (111) Wilson, J. Assoc. Official Agr. Chem. 27, 195-200 (1944). (112) Schapiro, U.S. 2,157,632, 2,157,633, May 9, 1939, Cent. 1939, II 1990; C.A. 33, 6469 (1939). (113) Tetsumoto, J. Agr.-Chem. Soc. Japan 12, 22-26, 184-190 (1936); Cent. 1936, II 817; C.A. 30, 4530 (1936); Japan. J. Expll. Med. 15, 1-8 (1937); C.A. 31, 5010 (1937). (114) Hoffmann, Schweitzer, Daley, J. Am. Chem. Soc. 62, 988-989 (1940). (115) Woodard, Lange, Nelson, Calvery, J. Ind. Hyg. Toxicol. 23, 78-82 (1941). (116) Genevois, Briscoe, Compt. rend. soc. biol. 112, 1389-1390 (1933); C.A. 27, 3750 (1933). (117) Wilson, J. Assoc. Official Agr. Chem. 27, 339-340 (1944); 25, 145-153 (1942). (118) Jahn, Mitt. Lebensm. Hyg. 33, 272-275 (1942); Cent. 1943, I 1832; C.A. 38, 3740 (1944). (119) Wilson, J. Assoc. Official Agr. Chem. 26, 477-478 (1943). (120) Mallory, Love, Ind. Eng. Chem., Anal. Ed. 15, 207-209 (1943).
- (121) Wilson, Kennan, J. Assoc Official Agr. Chem. 27, 445-447 (1944). (122) Benrath, Hertel, Z. viss. Phot. 23, 33-35 (1925). (123) Isomura, Bull. Chem. Soc. Japan 14, 258-270 (1939); J. Electrochem. Assoc. Japan 7, 251-260 (1939), Cent. 1939, II 3399. (124) Brückner, Z. angev. Chem. 41, 226 229 (1928); 40, 973-974 (1927). (125) Magidson, Zilberg, Preobrazhenskii, J. Chem. Ind. (Moscow) 5, 528-529 (1928); Cent. 1928, II 2234; C.A. 22, 4105 (1928), (126) Auger, Béhal, Bull. soc. chim. (3) 2, 145 (1889). (127) Germuth, Maryland Acad. Sci. Bull. 8, 3 (1929); C.A. 24, 61 (1930). (128) Horsley and United Alkali Co., British 6031 (1910); C.A. 5, 2918 (1911). (129) Strosacker (to Dow Chem. Co.) U.S. 1,757,100, May 6, 1930; Cent. 1930, II 981; C.A. 24, 3250 (1930). (130) Russanow, J. Russ. Phys.-Chem. Soc. 23, 222-223 (1891); Ber. 25, Referate 334 (1892).
- (131) Lyubarskii, Zhur. Priklad. Khim. 2, 621-627 (1929); C.A. 24, 827 (1930). (132) Lyubarskii, Ber. ukrain. wiss. Forsch.-Inst. physik. Chem. 3, 85-91 (1934); C.A. 29, 2509 (1935). (133) Shilov, J. Chem. Ind. (Moscow) 6, 538-540 (1929); Cent. 1929, II 2658; C.A. 24, 827-828 (1930). (134) Bruckner, Ger. 506,280, Sept. 1, 1930; Cent. 1930, II 2830; C.A. 25, 304 (1931). (135) Wohl, Ger. 146,796, Nov. 12, 1903; Cent. 1903, II 1299. (136) Blank, Ger. 157,816, Jan. 18, 1905; Cent. 1905, I 414. (137) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940). (138) Gruber, Kauffer, Moldenhauer (to Wacker Soc. Elektrochem. Ind.), Ger. 638,117, Nov. 10, 1936; Cent. 1937, I 1015, C.A. 31, 1044 (1937). (139) Hentschel, Ber. 17, 1286 (1884). (140) Akashi, Bull. Inst. Phys. Chem. Research (Tokyo) 12, 329-340 (1933); Sci. Papers Inst. Phys. Chem. Research (Tokyo) 20, 411-413 (1933); Cent. 1933, I 3066; C.A. 27, 3447 (1933).
- (141) Youtz, J. Am. Chem. Soc. 46, 549 (1924). (142) Klebanskii, Gosudarst. Inst. Priklad. Khim., Sbornik Staten, 1919-1939, 359-383 (1939); C.A. 36, 2521 (1942). (143) Shagalov, Trans. & Mendeleev Congr. Theoret. Applied Chem. 1932, 2, Pt. 1, 730-737 (1935); Cent. 1936, II 2226; [C.A. 30, 1893 (1936)]. (144) Suknevich, Shagalov, Dobromil'skaya, Trans. State Inst. Applied Chem. (U.S.S.R.), 24, 89-96 (1935), not in Cent., [C.A. 29, 7272 (1935)]. (145) Torres, Socias, Anales soc. españ. fis. quim. 28, 490-494 (1930); C.A. 24, 3755 (1930). (146) Simon, Chavanne, Compt. rend. 176, 309-311 (1923), Bull. soc. chim. Belg. 32, 285-287 (1923); Cent 1923, III 1212; C.A. 18, 1112 (1924). (147) Simon, Chavanne, U.S. 1,304,108, May 20, 1919; C.A. 13, 2039 (1919); Brit. 129,301, May 21, 1917; C.A. 13, 2878 (1919); French 22,304, June 30, 1921; Cent. 1922, II 1172; not in C.A. (148) Guyot, U.S. 1,322,898, Nov. 25, 1919; C.A. 14, 287 (1920). (149) Comp. Prod. Chim. d'Alais, etc., Ger. 359,910, Sept. 28, 1922; Cent. 1923, II 404; not in C.A. (150) Comp. Prod. Chim. d'Alais, etc., Ger. 377,524, June 21, 1923; Cent. 1923, IV 536; not in C.A.
 - (151) Comp. Prod. Chim. d'Alais, etc., Ger. 383,029, Oct. 9, 1923; [Cent. 1924, I 1712]; not in

C.A.: Austrian 88,199, Aug. 10, 1932; Cent. 1923, IV 591; not in C.A. (152) Comp. Prod. Chim. d'Alais, etc., French 602,395, March 17, 1926; Cent. 1928, I 1710; not in C.A. (153) A. Wacker Soc. Elektrochem. Ind., French 705,905, June 16, 1931; Ger. 531,580, March 1, 1930; Cent. 1931, II 1489; C.A. 26,154 (1932). (154) Ikawa, Isikawa, Japan 95,415, April 11, 1932; C.A. 27, 2695 (1933). (155) Comp. Prod. Chim. d'Alais, etc., Ger. 377,411, June 19, 1923; [Cent. 1923, IV 591]; not in C.A.: French 519,813, June 16, 1921; Cent. 1921, IV 653; not in C.A. (156) Comp. Prod. Chim. d'Alais, French 774,172, Dec. 3, 1934; Cent. 1935, I 2895; C.A. 29, 2179 (1935): Ger. 610,318, March 7, 1935; [C.A. 29, 3691 (1935)]; not in Cent. (157) Muller, Ehrmann, Ber. 69, 2208-2209 (1936). (158) Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 658-662 (1937); Cent. 1937, II 371; C.A. 31, 5754 (1937). (159) Muskat, Northrup, J. Am. Chem. Soc. 53, 4043-4055 (1930). (160) Carothers, Berchet, J. Am. Chem. Soc. 55, 1628-1631 (1933).

(161) Jones, Williams, J. Chem. Soc. 1934, 829-834. (162) Carothers, Berchet, Collins, J. Am. Chem. Soc. 54, 4066-4070 (1932). (163) Coffman, Nieuwland, Carothers, J. Am. Chem. Soc. 55, 2048-2051 (1933). (164) Coffman, Carothers, J. Am. Chem. Soc. 55, 2040-2047 (1933). (165) Dykstra, J. Am. Chem. Soc. 58, 1749 (1936). (166) Coffman, J. Am. Chem. Soc. 57, 1983 (1935). (167) Ingold, J. Chem. Soc. 125, 1536-1537 (1924). (168) Kriwaxin, Zeit. Chemre

1871, 265. (169) Aschan, Ber. 23, 1831 (1890). (170) Claus, Ber. 5, 355 (1872).

(171) Natterer, Monatsh. 3, 457-458 (1882). (172) Reisse, Ann. 257, 334-336 (1890). (173) Filachione, J. Am. Chem. Soc. 61, 1706 (1939). (174) N.V. de Bataafsche Petroleum Maatschappij, French 797,943, May 6, 1936; Cent. 1936, II 865; C.A. 30, 7124 (1936). (175) deSimo, Allen (to Shell Development Co.), U.S. 2,051,470, Aug. 18, 1936; Cent. 1936, II 3469; [C.A. 30, 6764 (1936)]. (176) van Reymenant, Bull. acad. roy. Belg. 1900, 724-742; Cent. 1901, I 95-96. (177) Henry, Bull. acad. roy. Belg. 1900, 57-63; Cent. 1900, I 1123. (178) Jochem, Z. physiol. Chem. 31, 123 (1900). (179) Chem. Fabrik Flora, Ger. 348,671, Feb. 14, 1922; [Cent. 1922, II 873]; not in C.A.: Dutch, 6121, Sept. 15, 1921; Cent. 1921, IV 1140; Ich. ont in C.A. (180) Kuhn, Eichenberger, French 663,236, Aug. 19, 1929; Cent. 1929, II 3069; [C.A. 24, 627 (1930)].

(181) Matsukov, Trudy Leningrad. Inst. Sovet Torglovi 1939, No. 2, 30-4, C.A. 37, 3054 (1943). (182) Dashkevich, Russ. 56,513, Feb. 29, 1940; C.A. 36, 2869 (1942). (183) Loder (to du Pont Co.), U.S. 2,298,138, Oct. 6, 1942; C.A. 37, 1449 (1943). (184) Fürst, Ann. 206, 78-82 (1880). (185) Piutti, Badolato, Atti accad. Lincei (5) 33, I 475-479 (1924); Cent. 1924, II 1893. (186) Piutti, Atti congr. naz. chim. pura applicata 1923, 437-438; Cent. 1924, I 514, C.A. 18, 3007 (1924). (187) Piutti, Gazz. chim. ital. 51, I 145-146 (1921). (188) Piutti, Mazza, Gazz. chim. ital. 57, 610-614 (1927). (189) Imbert and Consortium für Elektrochem. Ind., Ger. 216,716, Nov. 30, 1909; Cent. 1910, I 214; C.A. 4, 152 (1910). (190) Imbert, Consortium für Elektrochem. Ind., Ger. 209,268, April 27, 1909; Cent. 1909, I 1785; C.A. 3, 2203 (1909).

(191) Brochet, Bull. soc. chim. (3) 13, 119 (1895); Ann. chim. (7) 10, 138-139 (1897). (192) Grassi-Cristaldi, Gazz. chim. ital. 27, II 502-505 (1897). (193) Senderens, Compt. rend. 172, 155-157 (1921). (194) Senderens, Compt. rend. 204, 211 (1937). (195) Silberstein, Ber. 17, 2660-2661 (1884). (196) Bezzi, Atti ist. Veneto Sci., Pt. II, 94, 167-182 (1935); Cent. 1937, II 3605; C.A. 33, 6311 (1939). (197) von Euler, Ber. 49, 1366-1371 (1916). (198) Kelber, Ber. 49, 1366-1371 (1916). (198) Kelber, Ber. 49, 1368-1371 (1916).

1071 (1916).

(201) Traube, Lange, Ber. 58, 2776 (1925). (202) Calcott (to du Pont Co.), U.S. 1,547,201, July 28, 1925; Cent. 1925, II 2295; [C.A. 19, 283 (1925)]. (203) Cassel, Z. physik. Chem. 92, 119-120 (1917). (204) Hood, Imes, J. Phys. Chem. 36, 927-929 (1932). (205) Busch, Weber, J. prdkt. Chem. (2) 146, 54 (1936). (206) Panizzon, Helv. Chim. Acta 15, 1191-1192 (1932). (207) Osburn, Weikman, Ind. Eng. Chem., Anal. Ed. 4, 421-423 (1932). (208) Kaufler, Herzog, Ber. 42, 3864-3868 (1909). (209) Troeger, Ewers, J. prakt. Chem. (2) 58, 127-128 (1898). (210) Ghosh, Ray, J. Indian Chem. Soc. 13, 1-10 (1936).

(211) Maumene, Ann. 133, 154-156 (1865); Bull. soc. chim. (2) 1, 417-420 (1864). (212) Müller, Ann. 133, 156-161 (1865). (213) Cech, Steiner, Ber. 8, 1174 (1875). (214) Racker, van Mels, Rec. trav. chim. 49, 177-194 (1930). (215) Crompton, Triffitt, J. Chem. Soc. 119, 1874-1875 (1921). (216) Crompton, Vanderstichele, J. Chem. Soc. 117, 691-693 (1920). (217) Sutherland, Aston, J. Am. Chem. Soc. 61, 243 (1939). (218) Andreasch, Monatsh. 7, 159-167 171-175 (1886). (219) Backer, Burgers, J. Chem. Soc. 127, 233-237 (1925). (220) Backer, Rec. trav. chim. 49, 729-734 (1930).

(221) Vieillefosse, Bull. soc. chim. (5) 5, 808 (1938). (222) Hofmann, Ber. 32, 880 (1899). (223) Ostwald, Z. physik. Chem. 3, 176-177 (1889). (224) Dawson, Hall, Key, J. Chem. Soc. 1928, 2844-2853. (225) Dawson, Lowson, J. Chem. Soc. 1929, 1219, 1223. (226) Saxton, Lange, J. Am. Chem. Soc. 55, 3638-3645 (1933). (227) Wright, J. Am. Chem. Soc. 56, 314-317 (1934). (228) Bhagwat, J. Indian Chem. Soc. 16, 235-236 (1939). (229) Grove, J. Am. Chem. Soc. 52, 1404-1407 (1930). (230) Harned, Embree, J. Am. Chem. Soc. 56, 1050-1053 (1934).

(231) Larsson, Adell, Z. physik. Chem. A-157, 347-348, 354-355 (1931). (232) Dawson, Carter, J. Chem. Soc. 1926, 2282-2296. (233) Cray, Westrip, Trans. Faraday Soc. 21, 331 (1925/6). (234) Dawson, Key, J. Chem. Soc. 1928, 1239-1248. (235) Kendall, King, J. Chem. Soc. 127, 1784, 1789 (1925). (236) Kendall, Gross, J. Am. Chem. Soc. 43, 1428, 1434-1435 (1921). (237) Jenkins, Nature 145, 625 (1940). (238) Bell, Nature 146, 166-167 (1940). (239) Baughan, Nature 146, 461 (1940). (240) Deyrup, J. Am. Chem. Soc. 56, 60-64 (1934).

(241) Welcher, Briscoe, Proc. Indiana Acad. Sci. 43, 142-153 (1934); C.A. 28, 7116 (1934). (242) Mason, Kilpatrick, J. Am. Chem. Soc. 59, 572-578 (1937). (243) Westheimer, J. Am. Chem. Soc. 56, 1962-1965 (1934). (244) Hantzsch, Voigt, Ber. 62, 975-984 (1929). (245) Verhoek, J. Am. Chem. Soc. 58, 2577-2584 (1936). (246) Martin Kilpatrick, Mary Kilpatrick, Chem. Revs. 13, 131-137 (1933). (247) Bronsted, Ber. 61, 2062 (1928). (248) Griffiths, J. Chem. Soc. 1938, 818-823. (249) Rabinovich, Trav. inst. chim. Kharkov. 1, 99-107 (1935); C.A. 32, 4085 (1938). (250) La Mer, Downes, J. Am. Chem. Soc. 55, 1840-1864 (1933).

(251) Hunt, Briscoe, J. Phys. Chem. 33, 190-199, 1495-1513 (1929). (252) Beatty, Cragg, J. Am. Chem. Soc. 57, 2347-2351 (1935). (253) Weissberger, J. Am. Chem. Soc. 65, 245-246 (1943). (254) Bell, Caldin, J. Chem. Soc. 1938, 382-389. (255) Bell, Lidwell, Wright, J. Chem. Soc. 1938, 1861-1865. (256) Dawson, J. Chem. Soc. 1927, 221. (257) Dawson, Carter, J. Chem. Soc. 1926, 2872-2878. (258) Harned, Hawkins, J. Am. Chem. Soc. 50, 85-93 (1928). (259) Dawson, Lowson, J. Chem. Soc. 1929, 393-401. (260) Ostwald, J. prakt. Chem. (2) 29. 396 (1884).

(261) Hantzsch, Weissberger, Z. physik. Chem. 125, 255 (1927). (262) van Alphen, Rec. trav. chim. 49, 754-761 (1930). (263) Bell, Baughan, J. Chem. Soc. 1937, 1947-1953. (264) Pedersen, J. Phys. Chem. 38, 610-611 (1934). (265) Usanovich, Sushkevich, J. Gen. Chem. (U.S.S.R.) 10, 230-232 (1940); C.A. 34, 7285 (1940). (266) Usanovich, J. Gen. Chem. (U.S.S.R.) 10, 219-222 (1940), C.A. 34, 7285 (1940). (267) Bronsted, Bell, J. Am. Chem. Soc. 53, 2478-2498 (1931). (268) Baughan, Bell, Proc. Roy. Soc. (London) A-158, 464-478 (1937). (269) Bell, Danckwerts, J. Chem. Soc. 1939, 1774-1776. (270) Bell, Proc. Roy. Soc. (London) A-143, 377-399 (1934).

(271) Bell, Brown, J. Chem. Soc. 1936, 1520-1524. (272) Bell, Lidwell, J. Chem. Soc. 1939. 1096-1099. (273) Bell, Lidwell, Vaughan-Jackson, J. Chem. Soc. 1936, 1792-1799. (274) Bateman, Hoel, J. Am. Chem. Soc. 36, 2517-2521 (1914). (275) Jones, Werner, J. Am. Chem. Soc. 39, 417-418 (1917). (276) Bischoff, Walden, Ann. 279, 46 (1894). (277) Kastle, Kaiser, Am. Chem. J. 15, 471-493 (1893). (278) Hill, Simmons, J. Am. Chem. Soc. 31, 825-826 (1909); Z. physik. Chem. 67, 599, 606 (1909). (279) Beckurts, Otto, Ber. 14, 577-578 (1881). (280) MacDougall, Rehner, J. Am. Chem. Soc. 56, 368-372 (1934).

(281) Schaum, Scheld, Z. wiss. Phot. 36, 135, 138 (1937). (282) Lean, Armstrong (to Imperial Chem. Ind.), U.S. 2,282,732, May 12, 1942; C.A. 36, 5947 (1942). (283) Grossmann, Jager. Z. anorg. allgem. Chem. 73, 50 (1911). (284) Sidgwick, Tizard, J. Chem. Soc. 93, 191 (1908). (285) Kraytzoff, Compt. rend. 187, 137-140 (1933); Cent. 1933, II 3542; C A. 27, 4817 (1933). (286) Ablov, Ann. sci. Univ. Jassy 18, 297-317 (1933); Cent. 1934, I 2708; not in C.A. (287) Costachescu, Ablov, Ann. sci. Univ. Jassy 17, 149-172 (1933); Cent. 1933, I 3038; not in C.A. (288) Ferrell, Ridgion, Riley, J. Chem. Soc. 1934, 1440-1443. (289) Fogel, Rubinsztein, Tauman, Roczniki Chem. 9, 348-353 (1929), Cent. 1930, II 227; C.A. 23, 3900 (1929). (290) Luszkiewicz, Arch. minéral soc. sci. Varsonie 6, 119-136 (1930); C.A. 26, 4518 (1932).

(291) Kertesz, J. chim. phys. 35, 395-406 (1938). (292) Bateman, Conrad, J. Am. Chem. Soc. 37, 2557-2559 (1915). (293) Sirucek, Collection Czechoslov. Chem. Commun. 10, 117-128 (1938): Cent. 1938, I 1971; C.A. 32, 5782 (1938). (294) Costacheschu, Ablov, Ann. sci. Univ. Jassy 25, 385-394 (1939); Cent. 1939, I 2546; C.A. 33, 9180 (1939). (295) Ablov, Bull. soc. chim. (5) 1, 1489-1494 (1934). (296) Treadwell, Wettstein, Helv. Chim. Acta 18, 200-210 (1935). (297) Treadwell, Fisch, Helv. Chim. Acta 13, 1219-1227 (1930). (298) Beamer, Clarke, Ber. 12, 1067 (1879). (299) Derick, Bornmann, J. Am. Chem. Soc. 35, 1285 (1913). (300) Bischoff, Suchin, Bcr. 21, 1259-1260 (1888).

(301) Eckenroth, Donner, Ber 23, 3287-3288 (1890). (302) Grothe, Arch. Pharm. 238 588-589 (1900). (303) Buehler, Carson, Edds, J. Am. Chem. Soc. 57, 2181-2182 (1935). (304) Pollard, Adelson, Bain, J. Am. Chem. Soc. 56, 1759-1760 (1934). (305) Michael, J. Am. Chem. Soc. 41, 415 (1919). (306) Stempel, Schaffel, J. Am. Chem. Soc. 64, 470-471 (1942). (307) Gattermann, Johnson, Holzle, Ber. 25, 1080-1081 (1892). (308) Kilpatrick, Rushton, J. Phys. Chem. 34, 2180-2186 (1930); 38, 269-306 (1934). (309) Doughty, Lacoss, J. Am. Chem. Soc. 51, 852-855 (1929). (310) Butts, Giacobbe, Chem. Met. Eng. 48, No. 12, 76-79 (1941); C.A. 36, 997 (1942).

(311) Palomaa, Ber. 75, 336-339 (1942). (312) Toole, Sowa, J. Am. Chem. Soc., 59, 1971-1973 (1937). (313) Akoyan, J. Gen. Chem. (U.S.S.R.) 7, 1687-1689 (1937); Cent. 1937, II 3594; [C.A. 31, 8504 (1937)]. (314) Sudborough, Turner, J. Chem. Soc. 101, 238 (1912). (315) Gyr,

Ber. 41, 4316 (1908). (316) Prager, J. Am. Chem. Soc. 30, 1910-1911 (1908); Z. physik. Chem. 66, 296 (1909). (317) Goldschmidt, Udby, Z. physik. Chem. 60, 747 (1907). (318) Lichty, Am. Chem. J. 18, 590-600 (1896). (319) Goldschmidt, Z. physik. Chem. 124, 30 (1926). (320) Goldschmidt, Z. Elektrochem. 15, 7 (1909).

(321) Quayle, Norton, J. Am. Chem. Soc. 62, 1170-1171 (1940). (322) Meerwein, Ber. 66, 412-413 (1933). (323) Bannister (to Comml. Solvents Corp.), U.S. 1,695,449, Dec. 18, 1928; Cent. 1929, I 1505; [C.A. 23, 846 (1929)]. (324) Chem. Fabrik Stockhausen et Cie, Ger. 564,591, Nov. 21, 1932; Cent. 1933, I 673; [C.A. 27, 997 (1933)]. (325) Brass, Kurz, Ber. 66, 442-446 (1933). (326) Rudy, Cellulosechem. 13, 49-58 (1932); Cent. 1932, II 199, C.A. 26, 5203 (1932). (327) Soc. des Usines Chim. Rhone-Poulenc, French 672,220, Dec. 24, 1929; Cent. 1930, I 1876; [C.A. 24, 2290 (1930)]. (328) Liston, Dehn, J. Am. Chem. Soc. 60, 1264-1265 (1938). (329) Dorris, Sowa, Nieuwland, J. Am. Chem. Soc. 56, 2689-2690 (1934). (330) Aldoschin, J. Gen. Chem. (U.S.S.R.) 8, 1385-1389 (1938); Cent. 1939, II 2223; C.A. 33, 4194 (1939).

(331) Hennion, Nieuwland, J. Am. Chem. Soc. 56, 1802-1803 (1934). (332) Allen, Hibbert, J. Am. Chem. Soc. 56, 1399 (1934). (333) Meerwein, Sönke, J. prakt. Chem. (2) 137, 316-317 (1933). (334) Slanina, Hennion, Nieuwland, J. Am. Chem. Soc. 58, 891 (1936). (335) Traube, Krahmer, Ber. 52, 1297-1298 (1919). (336) Nesmeyanov, Kahn, Ber. 67, 372 (1934); J. Gen. Chem. (U.S.S.R.) 4, 1247-1249 (1936); Cent. 1936, I 4288; not in C.A. (337) Michael, Am. Chem. J 9, 215-216 (1887); J. prakt. Chem. (2) 35, 95-96 (1887). (338) de Wilde, Ann. 132, 180 (1864). (340) Aschan, Ber. 46, 2199-2170 (1913).

(341) Heintz, Ann. Physik 115, 462-464 (1862). (342) Buchanan, Ber. 4, 340-342, 863 (1871). (343) Fittig, Thomson, Ann. 200, 75-79 (1879). (344) Kekulé, Ann. 105, 288-292 (1858). (345) Witzemann, J. Am. Chem. Soc. 39, 109-112 (1917). (346) Lossen, Eichloff, Ann. 342, 115-122 (1905). (347) Senter, J. Chem. Soc. 91, 460-474 (1907); Z. physik. Chem. 70, 511-518 (1910). (348) Drushel, Simpson, J. Am. Chem. Soc. 39, 2453-2460 (1917). (349) von Euler, Fahlander, Z. physik. Chem. 100, 171-181 (1922). (350) Petrenko-Kritschenko, Opotzky, Ber. 59, 2137-2138 (1926).

(351) Matuura, Bull. Chem. Soc. Japan 8, 113-120 (1933). (352) Kailan, Kunze, Monatsh. 71, 373-423 (1938). (353) Rudberg, Z. Physik 24, 247-263 (1924). (354) Euler, Cassel, Z. Physik. Chem. 84, 371-379 (1913). (355) Benrath, Ann. 382, 223, 234 (1911). (356) Kunze, Merkader, Z. physik. Chem. A-187, 285-288 (1940). (357) Reitz, Z. physik. Chem. A-177, 85-94 (1936). (358) Moelwyn-Hughes, J. Chem. Soc. 1932, 101-102. (359) Tian, Bull. soc. chim. (5) 1, 115-119 (1934). (360) Dawson, Lowson, Proc. Leeds Phil. Lit. Soc., Sci. Sect. 2, 435-439 (1933); Cent. 1934, I 176; C.A. 27, 5622 (1933).

(361) Thomas, J. Am. Chem. Soc. 62, 1879-1880 (1940). (362) R. N. Smith, P. A. Leighton, W. G. Leighton, J. Am. Chem. Soc. 61, 2299-2301 (1939). (363) Kuchler, Pick, Z. physik. Chem. B-45, 116-120 (1939). (364) W. G. Leighton, R. N. Smith, P. A. Leighton, J. Am. Chem. Soc. 60, 2566 (1938). (365) Harris, Kaminksy, J. Am. Chem. Soc. 57, 1158 (1935). (366) Dain, Pusenkin, Ber. ukrain. wiss. Forsch.-Inst. physik. Chem. 4, 75-81 (1934); Cent. 1934, II 2660; C.A. 29, 2451-2452 (1935); J. Phys. Chem. (U.S.S.R.) 4, 478-482 (1933); Cent. 1934, II 2660; not in C.A. (367) Farkas, Z. physik. Chem. B-23, 90-93 (1933). (368) Hentz, Ann. Physik. 199, 475 (1860); 112, 87, (1861). (369) Johansson, Z. physik. Chem. 79, 632-637 (1912). (370) Redelius, Z. physik. Chem. 96, 348-349, 359-361 (1920).

(371) Abderhalden, Zeisset, Fermentforschung 11, 170-182 (1930); Cent. 1931, I 2862; C.A. 24, 1622 (1930). (372) Dawson, Pycock, J. Chem. Soc. 1934, 778-783. (373) Dawson, Pycock, J. Chem. Soc. 1936, 153-158. (374) Dawson, Pycock, Smith, J. Chem. Soc. 1943, 517-520. (375) Smith, J. Chem. Soc. 1943, 521-523. (376) Williams, Perrin, Gibson, Proc. Roy. Soc. (London) A-154, 686-687 (1936). (377) Grether, DuVall (to Dow Chem. Co.), U.S. 2,028,064, Jan. 14, 1936; Cent. 1936, I 3013; C.A. 30, 1394 (1936). (378) Wacker Soc. Elektrochem. Ind., Ger. 463,139, July 23, 1928; Cent. 1929, I 1046; C.A. 22, 4131 (1928). (379) Deutsche Goldund Silber-Scheide-Anstalt vorm. Rössler, Ger. 379,752, Aug. 28, 1923; Cent. 1924, I 1101; not in C.A. (380) Heintz, Ann. 144, 91-94 (1867).

(381) Schreiber, J. prakt. Chem. (2) 13, 436-475 (1876). (382) Darapsky, Stauber, J. prakt. Chem. (2) 146, 211-212 (1936). (383) Bevan, Proc. Cambridge Philos. Soc. 13, 269-281; Cent. 1996, II 106. (384) Klason, Carlson, Ber. 39, 732-738 (1906). (385) Schutz, Angew. Chem. 46, 780-781 (1933). (386) Dey, Dutt, J. Indian Chem. Soc. 5, 640 (1928). (387) Loven, Ber. 27, 3059-3060 (1894); Ber. 17, 2818 (1884). (388) Adell, Z. physic. Chem. A-185, 166 (1939). (389) Claesson, Ann. 187, 114-115 (1877). (390) Andreasch, Ber. 12, 1390-1391 (1879).

(389) Claesson, Ann. 187, 114-115 (1877).
(390) Andreasch, Ber. 12, 1390-1391 (1879).
(391) Holmberg, Z. anorg. Chem. 56, 385-390 (1907).
(392) Blanksma, Rec. trav. chim. 20, 136 (1901).
(393) Friedländer, Chwala, Monatsh. 28, 250-251 (1907).
(394) Friedländer, Ber. 39, 1066 (1906).
(395) Ginsburg, Bondzynski, Ber. 19, 117 (1886).
(396) Klason, Ber. 14, 409-411 (1881).
(397) Larsson, Z. anorg. allgem. Chem. 172, 379 (1928).
(398) Larsson, Ber.

61, 1439-1443 (1928); Svensk Kem. Tid. 40, 149-150 (1928); Cent. 1928, II 234; C.A. 22, 4469-4470 (1928). (399) Wieland, Franke, Ann. 469, 305 (1929). (400) Wieland, Bergel, Ann. 439, 205 (1924).

(401) Holmberg, Mattisson, Ann. 353, 124 (1907). (402) Kalle and Co., Ger. 180,875, Feb. 19, 1907; Cent. 1907; I 856; C.A. 1, 1656 (1907). (403) Demole, Ber. 9, 561 (1876). (404) Hannerz, Svensk Kem. Tud. 46, 233-250 (1934); Cent. 1935, II 675-676; C.A. 29, 2913-2914 (1935). (405) Abderhalden, Guggenheim, Ber. 41, 2853 (1908). (406) Kailan, Jungermann, Monatsh. 64, 213 (1934). (407) Knoll und Co., Ger. 230,172, Jan. 16, 1911; Cent. 1911, I 359; C.A. 5, 2699 (1911). (408) McMath, Read, J. Chem. Soc. 1927, 539. (409) Abderhalden, Wybert Rev. 49, 2456 (1916). (410) Duttoit Demierra Lehim splus A 565-575 (1906)

Wybert, Ber. 49, 2456 (1916). (410) Dutoit, Demierre, J. chim. phys. 4, 565-575 (1906). (411) Collmann, Ann. 148, 109-110 (1868). (412) Stillich, J. prakt. Chem. (2) 73, 538-544 (1906). (413) Bacher, van Mels, Rec. trav. chim. 49, 363-380 (1930). (414) Purgotti, Gazz. chim. ital. 22, I 422-423 (1892). (415) Slator, J. Chem. Soc. 87, 487 (1905). (416) Krapiwin, J. chim. phys. 10, 289-305 (1912). (417) Kappana, J. Indian Chem. Soc. 5, 293-298 (1928). (418) Bekier, Zelazna, Roczniki Chem. 14, 994-1003 (1934); Cent. 1936, I 952; C.A. 29, 6130 (1935). (419) Steinkopf, Supan, Ber. 43, 3249 (1910). (420) Steinkopf, Ber. 42, 3928-3929 (1909).

(421) Williams, J. Am. Chem. Soc. 47, 2644-2652 (1925). (422) Steinkopf, Ber. 41, 4457-4458 (1908). (423) Preibische, J. prakt. Chem. (2) 8, 310-311 (1873). (424) Kolbe, J. prakt. Chem. (2) 5, 427-432 (1872). (425) F. C. Whitmore, M. G. Whitmore, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 401-403 (1941), (1st ed.), 393-395 (1932); 3, 83-85 (1923). (426) Wang, Tseng, Sci. Repts. Natl. Central Univ. A-1, 27-38 (1930); C.A. 25, 681 (1931). (427) Hirano, J. Pharm. Soc. Japan 56, 869-871 (1930); C.A. 25, 69 (1931). (428) Pritzl, Adkins, J. Am. Chem. Soc. 53, 234-237 (1931). (429) Wahl, Bull. soc. chim. (4) 5, 180-182 (1909). (430) Steinkopf, Kirchhoff, Ber. 42, 3438-3440 (1909).

(431) Auger, Bull. soc. chim. (3) 23, 333 (1900). (432) Pedersen, J. Am. Chem. Soc. 49, 2688 (1927). (433) Pedersen, J. Phys. Chem. 38, 559-571 (1934). (434) Heuberger, Svensk Kem. Trd. 38, 340-344 (1926); Cent. 1927, I 834; [C.A. 21, 2591 (1927)]. (435) Heuberger, Svensk Kem. Trd. 38, 378-384 (1926); Cent. 1927, I 1259; C.A. 21, 1580 (1927). (436) Pedersen, Trans. Faraday Soc. 23, 316-328 (1927); Cent. 1927, II 1230; C.A. 22, 1068 (1928). (437) Forster, Fierz, J. Chem. Soc. 93, 76-80 (1908). (438) Bailly, Ann. chim. (9) 6, 153-154 (1916). (439) Wolfram, Schörnig, Hausdorfer (to I.G.), Brit. 330,916, July 17, 1930; Cent. 1930, II 2054; C.A. 24, 6031 (1930): French 688,964, Sept. 1, 1930, Cent. 1931, I 2677; [C.A. 25, 971 (1931)]: Ger. 562,391, Nov. 1, 1932; Cent. 1933, I 849; C.A. 27, 734-735 (1933). (440) Heintz, Ann. Physik. 109, 305 (1860).

(441) Rothstein, Bull. soc. chim. (4) 51, 838-845 (1932). (442) Malm, Nadeau (to E.K.C.), U.S. 1,987,121, Jan. 8, 1935; Cent. 1935, I 2732; C.A. 29, 1437 (1935). (443) Sommelet, Bull. soc. chim. (4) 1, 366-367 (1907); Ann. chim. (8) 9, 489-490 (1906). (444) Fuson, Wojcik, Org. Syntheses, Coll. Vol. 2 (1st ed.), 260-262 (1943); 13, 42-44 (1933). (445) Rule, Hay, Paul, J. Chem. Soc. 1928, 1355-1357. (446) Karvonen, Ann. Acad. Sci. Fennicae A-10, No. 7, 1-7 (1916); [Cent. 1919, III 987]; [C.A. 14, 3594 (1920)]. (447) Palomaa, Ann. Acad. Sci. Fennicae A-3, No. 2, 1-34 (1911); Cent. 1912, II 595-597; not in C.A. (448) Rothstein, Bull. soc. chim. (4) 51, 691-696 (1932). (449) Bruson (to Resinous Products and Chem. Co.), U.S. 1,920,137, July 25, 1933; Cent. 1933, II 2595; C.A. 27, 4817 (1933). (450) Leffler, Calkins, Org. Syntheses 23, 52-54 (1943).

(451) Rule, Todd, J. Chem. Soc. 1931, 1932. (452) Frankland, O'Sullivan, J. Chem. Soc. 29, 2329-2331 (1911). (453) Fischer, Gohlke, Helv. Chim. Acta 16, 1132 (1933). (454) Larrson, Ber. 63, 1349-1351 (1930). (455) Hellström, Z. physik. Chem. A-177, 339-340 (1936). (456) Ramberg, Ber. 40, 2588-2589 (1907). (457) Pomerantz, Connor, J. Am. Chem. Soc. 61, 3144 (1939). (458) Uyeda, Reid, J. Am. Chem. Soc. 42, 2385-2389 (1920). (459) Kharasch, Read, Mayo, Chemistry & Industry 57, 752 (1938). (460) Hellström, Lauritzson, Ber. 69, 2004-2005 (1936).

(461) Urquhart, Connor, J. Am. Chem. Soc. 63, 1483 (1941). (462) Koelsch, J. Am. Chem. Soc. 53, 304-305 (1931). (463) Steinkopf, Höpner, J. prakt. Chem. (2) 113, 140-141, 153-154 (1926). (464) Huntress, Mulliken, "Tables of Data on Selected Compounds of Order 1" (1941), John Wiley & Sons, New York. (465) Inglis, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 254-256 (1941); Coll. Vol. 1 (1st ed.), 249-251 (1932); 8, 74-76 (1928). (466) Kohler, Allen, Org. Syntheses 3, 53-56 (1923). (467) Phelps, Tillotson, Am. J. Sci. (4) 26, 275-280 (1908). (468) Fiquet, Ann. chim. (6) 29, 439-442 (1893). (469) Grimaux, Tcherniak, Bull. soc. chim. (3) 31, 338 (1904). (470) Meisenheimer, Schwarz, Ber. 39, 2551 (1906).

(471) Henry, Compt. rend. 194, 1621 (1887). (472) Wightman, Jones, Am. Chem. J. 46, 472 (1911). (473) Guinchant, Ann. chim. (9) 9, 85 (1918). (474) Claesson, Ber. 18, 1347 (1877).

(475) Lapworth, Baker, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 181 (1941); Coll. Vol. 1 (1st ed.), 175 (1932); 7, 20 (1927). (476) Weiner, Org. Syntheses, Coll. Vol. 2 (1st ed.), 376-378 (1943); 18, 50-53 (1938). (477) Cheronis, Spitzmueller, J. Org. Chem. 6, 349-375 (1941). (478) Orten, Hill, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 300-301 (1941); Coll. Vol. 1 (1st ed.), 293-295 (1932); J. Am. Chem. Soc. 53, 2797-2799 (1931). (479) Boutwell, Kuisk, J. Am. Chem. Soc. 52, 4166-4167 (1930). (480) Robertson, J. Am. Chem. Soc. 49, 2889-2894 (1927).

(481) Contardi, Ravazzoni, Rend. 1st. lombardo sci. 66, 786-790 (1933); Cent. 1934, I 1186; C.A. 29, 3309 (1935). (482) Krause, Chem. Ztq. 55, 666 (1931); Cent. 1931, II 2596, not in C.A. (483) Dunn, Butler, Frieden, J. Phys. Chem. 45, 1123-1137 (1941). (484) Chadwick, Pacsu, J. Am. Chem. Soc. 63, 2427-2431 (1941). (485) Shaposhnikov, J. Russ. Phys.-Chem. Soc. 59, 125-136 (1927); Cent. 1927, II 1115; not in C.A. (486) Tishchenko, J. Russ. Phys.-Chem. Soc. 53, I 300-305 (1921); Cent. 1923, III 1001; C.A. 18, 2328 (1924). (487) Sisler, Cheronis, J. Org. Chem. 6, 467-478 (1941). (488) Dains, Brewster, J. Am. Chem. Soc. 42, 1575, 1578 (1920). (489) Nencki, Ber. 16, 2827-2828 (1883). (490) Heintz, Ann. 122, 257-276 (1862); Ann. 124, 297-310 (1862); Ann. 136, 213-223 (1865).

(491) Heintz, Ann. 145, 49-53 (1868).
(492) Curtius, J. prakt. Chem. (2) 96, 213-214 (1918).
(493) Berchet, Org. Syntheses, Coll. Vol. 2 (1st ed.), 397-399 (1943); 18, 56-58 (1938).
(494) Schubert, J. Biol. Chem. 116, 442 (1936).
(495) Eschweiler, Ann. 279, 41 (1894).
(496) Fichter, Schmid, Helv. Chim. Acta 3, 710, Note 1 (1920).
(497) Abderhalden, Schwab, Valdecasas, Fermentforschung 13, 396-407 (1932); Cent. 1933, I 2420; C.A. 27, 106 (1933).
(498) Heintz, Ann. 129, 33-39 (1864); 132, 2-6 (1864).
(499) Cocker, J. Chem. Soc. 1937, 1695-1696.

(501) Cocker, Harris, J. Chem. Soc. 1940, 1292-1293. (502) Friedman, Beitr. Chem. Physiol. Path. 11, 194-195 (1908); Cent. 1908, I 971, C.A. 2, 2097 (1908). (503) Anslow, Kıng, Buchem. J. 22, 1257-1258 (1928). (504) Michaelis, Schubert, J. Biol. Chem. 116, 221-222 (1936). (505) Clark, Gillespie, Weisshaus, J. Am. Chem. Soc. 55, 4579 (1933). (506) Heintz, Ann. 140, 217-225 (1866). (507) Liebrich, Ber. 2, 13 (1869). (508) A.G.F.A., Ger. 269,701, Jan. 28, 1914; Cent. 1914, I 592; not in C.A. (509) Rebuffat, Gazz. chim. ital. 17, 233-234 (1887); 20, 122-123 (1890). (510) Strosacker (to Dow Chem. Co.), U.S. 1,442,743, Jan. 16, 1923; Cent. 1925, II 1805; [C.A. 17, 1029 (1923)].

(511) Schwebel, Ber. 10, 2046-2047 (1877). (512) Houben, Ber. 46, 3988 (1913). (513) Mai, Ber. 35, 579-580 (1902). (514) Hausdörfer, Ber. 22, 1799 (1889). (515) Wohl, Blank, Ger. 167,698, Feb. 8, 1906; Cent. 1906, I 1069. (516) M.L.B. Ger. 177,491, Oct. 30, 1906; Cent. 1906, II 1746. (517) Chem. Fabr. Griesheim-Elektron, Ger. 244,603, March 11, 1912; Cent. 1912, I 1065; [C.A. 6, 2294 (1912)]. (518) Chem. Fabrik Weiler ter Meer, Ger. 244,825, March 16, 1912; Cent. 1912, I 1163; [C.A. 6, 2294 (1912)]. (519) Cone (to Dow Chem. Co.), U.S. 1,419,-720, June 13, 1922; Cent. 1923, IV 1004; C.A. 16, 2695 (1922). (520) Read, Hendry, Ber. 71, 2552 (1938).

(521) Meyer, Ber. 10, 1967 (1877). (522) Bischoff, Hausdörfer, Ber. 25, 2271 (1892). (523)
Meyer, Ber. 14, 1325-1326 (1881). (524) Vorlander, Mumme, Ber. 34, 1647 (1901). (525)
Bischoff, Hausdorfer, Ber. 23, 1990 (1890). (526) Johnson, Bengis, J. Am. Chem. Soc. 33, 749-750 (1911). (527) Feigl, Popp-Halpern, Monatsh. 59, 137, 139 (1932). (528) Hughes, Lions, J. Proc. Roy. Soc. N.S. Wales 71, 209 222 (1938); Cent. 1938, II 1597; C.A. 32, 5830 (1938).
(529) Bloom, Day, J. Org. Chem. 4, 16-19 (1939). (530) Skolnik, Miller, Day, J. Am. Chem. Soc. 65, 1856-1858 (1943).

(531) Skolnik, Day, Miller, J. Am. Chem. Soc. 65, 1858-1862 (1943). (532) McCoy, Day, J. Am. Chem. Soc. 65, 2159-2162 (1943). (533) Busch, Schneider, Walter, Ber. 36, 3879-3883 (1903). (534) Busch, Meussdörffer, J. prakt. Chem. (2) 75, 124-125 (1907). (535) Harries, Ber. 28, 1225-1226 (1895). (536) Steyrer, Seng, Monatsh. 17, 631 (1896). (537) Ghosh, Guha, J. Indian Inst. Sci. A-16, 103-112 (1933); Cent. 1934, I 3050; C.A. 28, 2692 (1934). (538) Vorländer, Bittins, Ber. 68, 2274-2275 (1935). (539) Vater, J. prakt. Chem. (2) 29, 289-292 (1884). (540) Teronteev, Chernin, Khim. Farm. Prom. 1933, 18-19; Cent. 1934, I 2824-2825; C.A. 27, 3459 (1933).

(541) Gillice (to Eastman Kodak Co.), U.S. 1,933,799, Nov. 7, 1933; Cent. 1934, I 614; C.A. 28, 494 (1934). (542) Galatis, Helv. Chim. Acta 4, 574-579 (1921). (543) Meldola, Foster, Brightman, J. Chem. Soc. 111, 552 (1917). (544) Kulikov, Zepalova-Michailova, J. Gen. Chem. (U.S.S.R.) 2, 730-735 (1932); Cent. 1933, II 1960; C.A. 27, 2641 (1933). (545) Bulgatsch, Russ. 43,004, May 31, 1935; Cent. 1936, I 1506; not in C.A. (546) Norman (to Industrial Dyestuff Co.), U.S. 2,101,749 and 2,101,750, Dec. 7, 1937; Cent. 1938, 2060; C.A. 32, 958 (1938). (547) B.A.S.F., Ger. 56,273, Feb. 18, 1891, Friedlander 3, 281 (1896). (548) Heumann, Ber. 23, 3431-3433 (1890). (549) Mauthner, Suida, Monatsh. 9, 728-732 (1888). (550) Haller, J. Ind. Eng. Chem. 14, 1040-1044 (1922).

- (551) Jackson, Kenner, J. Chem. Soc. 1928, 579-580. (552) St. Warunis, Sacks, Ber. 37, 2637 (1904). (553) Houben, Ber. 46, 3993 (1913). (554) Heumann, Ber. 24, 978 (1891). (555) Stollé, J. prakt. Chem. (2) 90, 273-275 (1914). (556) Reitzenstein, Ann. 326, 322-327 (1903). (557) Edsall, Wyman, J. Am. Chem. Soc. 57, 1964-1965 (1935). (558) Willstätter, Kahn, Ber. 37, 415-416 (1904). (559) Guaisnet, Rilaud, Compt. rend. 198, 1520-1522 (1934). (560) von Gerichten, Ber. 15, 1251-1253 (1882).
- (561) Krüger, J. prakt. Chem. (2) 43, 287-293 (1891). (562) Zief, Edsall, J. Am. Chem. Soc. 59, 2245 (1937). (563) McMeekin, Cohn, Weare, J. Am. Chem. Soc. 57, 627 (1935). (564) Davis, Blanchard, J. Am. Chem. Soc. 51, 1797-1798 (1929). (565) Sah, Liu, Science Repts. Natl. Tsing Hua Univ. A-4, 31-33 (1937), Cent. 1937, II 2349; C.A. 31, 6203 (1937). (566) Maly, Ann. 189, 380-384 (1877). (567) Ray, Fernandes, J. Chem. Soc. 105, 2159-2160 (1914). (568) Maly, Ann. 168, 133-137 (1873). (569) Volhard, Ann. 166, 383-384 (1873); J. prakt. Chem. (2) 9, 6-10 (1874). (570) Andreasch, Monatsh. 8, 424 (1887).
- (571) Mulder, Ber. 8, 1264 (1875). (572) Schmidt, Arch. Pharm. 258, 229-230 (1920). (573) Desai, Hunter, Koppar, Rec. trav. chim. 54, 118-121 (1935). (574) Eberly, Dains, J. Am. Chem. Soc. 58, 2545 (1936). (575) Chowdhury, Desai, Hunter, Solang, Rec. trav. chim. 52, 857-861 (1933). (576) Markely, Reid, J. Am. Chem. Soc. 52, 2137-2141 (1930). (577) Dains, Irvin, Harrel, J. Am. Chem. Soc. 43, 613-618 (1921). (578) von Auwers, Ber. 49, 812-813 (1916). (579) Einhorn, Hutz, Arch. Pharm. 240, 634-635 (1902). (580) Fries, Finck, Ber. 41, 4276-4278 (1908).
- (581) Seubert, Ber. 21, 281-283 (1888). (582) Lyons, Reid, J. Am. Chem. Soc. 39, 1742 (1917). (583) Lund, Langvad, J. Am. Chem. Soc. 54, 4107 (1932). (584) Drake, Bronitsky, J. Am. Chem. Soc. 52, 3719 (1930). (585) Veibel, Ottung, Bull. soc. chim. (5) 6, 1435 (1939). (586) Dewey, Sperry, J. Am. Chem. Soc. 61, 3251-3252 (1939). (587) Dewey, Shasky, J. Am. Chem. Soc. 63, 3526-3527 (1941). (588) Steinkopf, Malinowski, Ber. 44, 2901 (1911). (589). Curtius, J. prakt. Chem. (2) 38, 429 (1888). (590) Jacobs, Heidelberger, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 153-154 (1941); (1st ed.), 147-148 (1932); 7, 16-17 (1927).
- (591) Menschutkin, Jermolajew, Z. fur Chemie, 1871, 5. (592) Hellström, Z. physik. Chem. A-187, 246 (1931). (593) Henry, Rec. trav. chim. 24, 165, Note 3 (1905). (594) Tröger, Hille, J. prakt. Chem. (2) 71, 204, Note (1905). (595) Scholl, Ber. 29, 2417, Note (1896). (596) Bauer, Ann. 229, 165 (1885). (597) Willim, Ann. 102, 109-111 (1857). (598) Abderhalden, Brockman, Fermentforschung 10, 159-172 (1928); Cent. 1929, I 2314, C.A. 23, 1112 (1929). (599) Jacobs, Heidelberger, J. Am. Chem. Soc. 39, 1441 (1917). (600) Derick, Bornmann, J. Am. Chem. Soc. 35, 1285 (1913).
- (601) Votocek, Burda, Ber. 48, 1003-1004 (1915). (602) Holmberg, Psilanderhielm, J. prakt. Chem. (2) 82, 442 (1910). (603) Meyer, Ber. 8, 1152-1158 (1875). (604) Motylewski, Bull. intern. acad. polon. Sci. 1926-A, 93-101; Cent. 1926, II 392; [C.A. 21, 1801 (1927)]. (605) Cech, Ber. 10, 1376-1378 (1877). (606) Zincke, Kegel, Ber. 23, 244 (1890). (607) von Janson, Ger. 175,586, Nov. 16, 1906; Cent. 1906, II 1694. (608) Tommasi, Bull. soc. chim. (2) 19, 400-401 (1873). (609) Jacobs, Heidelberger, J. Biol. Chem. 21, 104 (1915). (610) Dubsky, Gränächer, Ber. 50, 1693 (1917).
- (611) Sugasawa, Satoda, Yanagisawa, J. Pharm. Soc. Japan 58, 29-31 (1938); Cent. 1938, II 1410; [C.A. 32, 4161 (1938)]. (612) Stollé, et al., J. prakt. Chem. (2) 128, 1-2 (1930). (613) Abenius, J. prakt. Chem. (2) 40, 426 (1889). (614) Abenius, Widman, J. prakt. Chem. (2) 38, 299 (1888). (615) Grothe, Arch. Pharm. 238, 588-589 (1900). (616) von Euler, Erdtman, Ann. 520, 6 (1935). (617) Eckenroth, Donner, Ber. 23, 3287-3288 (1890). (618) Jacobs, Heidelberger, J. Biol. Chem. 20, 686 (1915). (619) Buehler, Mackenzie, J. Am. Chem. Soc. 59, 421-422 (1937). (620) Vandewijer, Bull. soc. chim. Belg. 45, 254-255 (1936).
- (621) Dermer, King, J. Org. Chem. 8, 168-173 (1943). (622) Ipatieff, Pines, Alberg, J. Am. Chem. Soc. 67, 694-695 (1945). (623) Eisenberg, J. Assoc Official Agr. Chem. 28, 427-428 (1945); C.A. 39, 4028 (1945). (624) Wilson, J. Assoc. Official Agr. Chem. 28, 302-304 (1945); C.A. 39, 3854 (1945). (625) Spence, Haas (to Rohm and Haas Co.), U.S. 2,379,759, July 3, 1945; C.A. 39, 4621 (1945). (626) Cristol, Benezech, Merzer, Bull. soc. chim. (5) 11, 58-63 (1944); C.A. 39, 696 (1945).

3:1375
$$\alpha,\beta$$
-DICHLORO- n -BUTYRIC $C_4H_6O_2Cl_2$ Beil. II - 279 ACID (low-melting isomer) H H H II_1-(124) (Crotonic acid dichloride) CH_3 -C-COOH II_2 -

196

[See also α,β -dichloro-n-butyric acid (high-melting isomer) (isocrotonic acid dichloride) (3:1903).]

Colorless cryst. from pet. ether, lgr. or dry ether. — \bar{C} is eas. sol. alc., C_6H_6 , CHCl₃, or CS₂; spar. sol. cold lgr.; at 10.5° 3.28 pts. \bar{C} are sol. in 1 part dry ether. — \bar{C} deliquesces with a little aq. (5); \bar{C} with 1 mole H_2O forms (4) an oil, probably a monohydrate (ortho acid), which in much aq. gives an emulsion gradually separating into two clear layers; note, however, that \bar{C} has later (11) been claimed to be nonhygroscopic.

[For prepn. of \overline{C} from crotonic acid (1:0425) with Cl_2 in CS_2 (1) (2) (3) (4) (11) or in $CCl_4 + CS_2$ (6) in cold see indic. refs.; for form. of \overline{C} from isocrotonic acid (1:1045) with Cl_2 in $CHCl_3$, CCl_4 , or CS_2 see (6) (4); for prepn. of \overline{C} from its corresp. acid chloride (see below) by hydrolysis with aq. NaHCO₃ see (5) (9).]

Č boils at 212-216° under ord. press. with some loss of HCl (4).

[C with 6 pts. conc. aq. HCl (satd. at 0°) in s.t. at 100° for 50 hrs. (1) is partially isomerized to the high-melting stereoisomer (isocrotonic acid dichloride) (3:1903).]

 $\tilde{\mathbf{C}}$ behaves as a fairly strong monobasic acid of ionization const. $K = 8.2 \times 10^{-3}$ (1); $\tilde{\mathbf{C}}$ with dil. aq. AgNO₃ ppts. the spar. sol. AgĀ₂ (5); no other salts, however, appear to have been reported.

 $\tilde{\mathbf{C}}$ with aq. NaOH in cold is neutralized without serious decomposition (4); Neut. Eq. = 157 (11); however, if to the resulting soln. further conc. aq. NaOH is added (4) (7), or if $\tilde{\mathbf{C}}$ in alc. is treated with alc. KOH (6) (2), 1 HCl is split away and the corresp. salt of α -chloroisocrotonic acid (3:1615) (accompanied by the salt of its isomeric α -chlorocrotonic acid (3:2760)) is formed.

Č with aq. Na₂CO₃ at ord. temp. is neutralized without decompn. (4); however, Č with excess aq. Na₂CO₃ above 80° also is further attacked giving (4) (25–30% yield (4)) 1-chloropropene-1 (3:7030), accompanied by some propional dehyde (1:0110), α-chlorocrotonic acid (3:2760), α-chloroisocrotonic acid (3:1615), and other products.

 \ddot{C} in pyridine at 100° for 3 hrs. loses HCl giving (yield not reported (8)) α -chlorocrotonic acid (3:2760), m.p. 99.5° (8).

[$\bar{\mathbf{C}}$ with PCl₅ or SOCl₂, although not actually reported, would be expected to yield the corresp. acid chloride; this α,β -dichloro-n-butyryl chloride, b.p. 163.3-164.3° cor. at 747 mm. (5), 67.5-71° at 30 mm. (5), has, however, been prepd. indirectly from crotonic acid (1:0425) with PCl₅ (2 moles) at 160° for 2 hrs. (9) or from crotonaldehyde (1:0150) with Cl₂ at 0° in dark (5).]

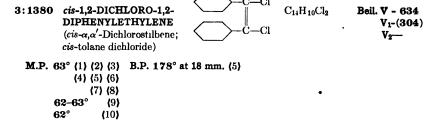
Methyl α,β -dichloro-n-butyrate: b.p. 174–180° sl. dec. at ord. press. (5), 82.7–85.7° cor. at 28 mm. (5); $D_4^{18.3} = 1.2614$ (5). [From the above α,β -dichloro-n-butyryl chloride with MeOH (5).]

- Ethyl α,β-dichloro-n-butyrate: b.p. 180-200° at 760 mm. (10), 97° at 35 mm. (10), 96° at 35 mm. (2). [From Č in abs. EtOH with dry HCl (2), or indirectly from butyr-chloral hydrate (3:1905) (1 mole) in EtOH with dry KCN (1 mole) below 15° (10); note, however, that this ester loses HCl with great ease even at ord. temp. giving ethyl α-chlorocrotonate (3:8523) and this dehydrohalogenation is greatly accelerated by KCN (10).]
- —— α,β-Dichloro-n-butyramide: unreported. [Note that the amide from the higher-melting stereoisomer of C

 (3:1903) has m.p. 121°.]

3:1375 (1) Michael, Bunge, Ber. 41, 2910-2912 (1908). (2) Michael, Browne, Am. Chem. J. 9, 281-287 (1887). (3) Michael, Browne, J. prakt Chem. (2) 36, 174-176 (1887). (4) Wislicenus, Ann. 248, 281-301 (1888) (5) Zeisel, Monatsh. 7, 360-370 (1886). (6) Michael, Schulthess, J. prakt. Chem. (2) 46, 238-240, 255-259 (1892). (7) Wislicenus, Ber. 20, 1008-1010 (1887). (8) Pfeiffer, Ber. 43, 3041-3042 (1910). (9) Clarke, J. Chem. Soc. 97, 898 (1910). (10) Chattaway, Irvine, J. Chem. Soc. 1929, 1043-1044.

(11) Stelling, Z. physik. Chem. B-24, 427 (1934).



61° (11) 60° (12) 59.5-60° (13) 58° (14)

[See also trans-1,2-dichloro-1,2-diphenulethulene (3:4210).]

Colorless ndls. — \bar{C} is much less sol. in alc. than its higher-melting stereoisomer (3:4210); 100 pts. abs. alc. at 24.4° dis. 10.51 pts. \bar{C} (14). — \bar{C} like its isomer is very sol. in ether.

Note that \bar{C} (the lower-melting tolane dichloride) has now been shown (12) to have the css configuration, many earlier reports to the contrary notwithstanding.

Note also that \bar{C} (2 moles) with (1 mole) diphenylacetylene (tolane) [Beil. V-656, V₁-(319), V₂-(568)], m.p. 60°, gives (12) a 2:1 molecular cpd., m.p. 67-69° (12).

 \tilde{C} on distn. is partially transformed (32% (14)) into its higher-melting trans stereoisomer (3:4210) q.v.

Since the methods of prepn. and the chemical behavior of $\ddot{\mathbf{C}}$ are the same as those given in detail under its stereoisomer (3:4210) q.v. they are not repeated here.

3:1380 (1) Fuson, Ross, J. Am. Chem. Soc. 55, 723 (1933). (2) Davidson, J. Am. Chem. Soc. 40, 397-399 (1918). (3) Sudborough, J. Chem. Soc. 71, 221-222 (1897). (4) Lachowics, Ber. 17, 1165 (1884). (5) Blank, Ann. 248, 17-25, 33-34 (1888). (6) Liebermann, Homeyer, Ber. 12, 1973-1974 (1879). (7) Limpricht, Schwanert, Ber. 4, 379 (1871). (8) Zinin, Ber. 4, 289 (1871). (9) Staudinger, Ber. 49, 1971-1972 (1916). (10) Onufrowicz, Ber. 17, 835 (1884).

(11) Busch, Weber, J. prakt. Chem. (2) 146, 50-52 (1936). (12) Bergmann, J. Chem. Soc. 1936, 403, 405. (13) Stelling, Z. physik. Chem. B-24, 425 (1934). (14) Eiloart, Am. Chem. J. 12, 221, 232 (1936).

12, 231–253 (1890).

3:1385 1,7-DICHLORONAPHTHALENE Cl
$$C_{10}H_6Cl_2$$
 Beil. V - 543 (2,8-Dichloronaphthalene) Cl V_{1} -(263) V_{2} -(446)

M.P.
$$64^{\circ}$$
 (19) B.P. 286° u.c. (5) $D_{4}^{99.5} = 1.2611$ (19) $63.5-64.5^{\circ}$ (1) $285-286^{\circ}$ (2) $n_{D}^{99.5} = 1.60921$ (19) 62.5° (3) (18) 61.5° u.c. (4) (5) (9) (12) (13) 61° (8) (12)

Lfts. from hot dil. alc.; cryst. from alc , other, C_6H_6 , or AcOH. — Sublimes readily. — Volatile with steam.

[For prepn. of C̄ from 7-chloronaphthalenesulfonyl chloride-1 [Beil. XI-161] (4), from 7-bromonaphthalenesulfonyl chloride-1 [Beil. XI-166] (6), from 1-chloronaphthalenesulfonyl chloride-7 [Beil. XI-181] (2), from 7-chloro-1-nitronaphthalene [Beil V-556] (poor yield (2)) (7), from 1-nitronaphthalenesulfonyl chloride-7 [Beil. XI-187] (8) (9) (10) (11), from 7-chloronaphthol-1 [Beil. VI-612, VI₁-(308)] (12), from K or Na naphthol-2-sulfonate-8 [Beil. XI-286, XI₁-(67)] (5) (13), or from naphthalene-1,7-bis-(sulfonyl chloride) [Beil. XI-215] (14) on htg. with PCl₅ as directed see indic. refs: from α-chloronaphthalene (3:6878) with SO₂Cl₂ at 100–180° see (15); from K 4,5-dichloronaphthalenesulfonate-2 [Beil. XI-182] or from K 4,6-dichloronaphthalenesulfonate-2 [Beil. XI-182] on hydrolysis in H₂SO₄ or H₃PO₄ with superhtd. steam see (16); from 4,6-dichloronaphthalene-2-sulfonyl chloride [Beil. XI-182] on htg with cone. HCl in s.t. at 290° see (16); from 7-chloronaphthylamine-1 [Beil. XII-1256] via diazotization and htg. with Cu₂Cl₂ see (12); from 8-sulfonaphthylamine-2 [Beil. XIV-750, XIV₁-(733)] via diazotization and htg. the diazonium salt with PCl₅ in PCl₃ see (2); from 1,7-diaminonaphthalene [Beil. XIII-204] via tetrazotization and treatment with Cu pdr. see (17)]

- Č (1 g.) in AcOH (5 ml.) with highest conen. HNO₃ (2 ml.) yields (3) 1,7-dichloro-x-nitronaphthalene [Beil. V-556], ndls. from McOH, m.p. 138-139° (3).
- [C with ClSO₃H yields (1) (18) 1,7-dichloronaphthalenesulfonic acid-4 [Beil. XI-162] (corresp. sulfonyl chloride, m.p. 118° (1) (18), corresp. sulfonamide, m.p. 226° (18))
- 3:1385 (1) Hampson, Weissberger, J. Chem. Soc. 1936, 394. (2) Armstrong, Wynne, Chem. News 59, 189 (1889). (3) Erdmann, Ann. 275, 257 (1893). (4) Arnell, Bull. soc. chim. (2) 45, 184 (1886). (5) Claus, Volz, Ber. 18, 3157 (1885). (6) Sindall, Chem. News 60, 58 (1889). (7) Armstrong, Wynne, Chem. News 59, 225 (1889). (8) Palmaer, Ber. 21, 3261 (1888). (9) Cleve, Bull. soc. chim. (2) 29, 415 (1878). (10) Armstrong, Wynne, Chem. News 59, 94 (1889).
- (11) Erdmann, Suvern, Ann. 275, 252 (1893). (12) Erdmann, Kirchhoff, Ann. 247, 379 (1888). (13) Forsling, Ber. 20, 2102 (1887). (14) Armstrong, Wynne, Chem. News 62, 162 (1890). (15) Armstrong, Rossiter, Chem. News 68, 189 (1892). (16) Armstrong, Wynne, Chem. News 76, 69-70 (1897). (17) Friedlander, Szymanski, Ber. 25, 2083 (1892). (18) Armstrong, Wynne, Chem. News 61, 274-275 (1890). (19) Krollpfeiffer, Ann. 430, 198, 204 (1923).

Colorless cryst.; cas. sol. ether, C_6H_6 , lgr., CS_2 ; spar. sol. cold alc. or 50% AcOH; volatile with steam. [For thermal anal. of mixts. of \bar{C} with 1,2,4-trichlorobenzene (3:6420) or for m.p./compn. data on ternary system of \bar{C} with 1,2,3-trichlorobenzene (3:0990) and 1,2,4-trichlorobenzene (3:6420) see (9)]

[For use of \bar{C} in mfg. of electric insulating material see (12) (13).]

[For prepn. of \bar{C} from 2,4,6-trichloroaniline [Beil. XII-627, XII₁-(312)] via diazotization and reaction with alc. (yield: 92% (14), 90% (15), 72.6% (8), 67% (33)) (4) (1) (16) (17), or from 2,4,6-tribromoaniline [Beil. XII-663, XII₁-(329)] via diazotization and subsequent treatment with HCl gas in alc. (18), see indic. refs.; from 3,5-dichloroaniline [Beil. XII-626, XII₁-(312)] via diazotization and reaction with Cu₂Cl₂ or Cu (yield 58% (5), 40-50% (9)) (4) see indic. refs.; from chlorobenzene-3,5-disulfonyl chloride with 4 moles PCl₅ in s.t. at 200-210° for 4 hrs. (60% yield (6)) or similarly from bromobenzene-3,5-disulfonyl chloride (7) see indic. refs [

[For formn. of $\bar{\mathbb{C}}$ from 2,4,6-trichloroiodobenzene with alc. NaOEt see (19); from 1,3,5-trinitrobenzene with conc. HCl in s.t. at 260° see (20); from 2,4,6-trichloroacetophenone on fusion with KOH (10) or from 2,4,6-trichlorobenzaldehyde on warming with 50% NaOH or KOH (3) see indic. refs.; from chloroacetylene (3:7000) by polymerization in light see (21); for formn. of $\bar{\mathbb{C}}$ from $\mathbb{C}_6\mathbb{H}_6$ or chlorobenzene (3:7903) with \mathbb{C}_2 at 400–700° (22), or from mixt. of m- and p-dichlorobenzenes with \mathbb{C}_2 + $\mathbb{A}\mathbb{C}_3$ (23) cf. (24), or from hexachlorobenzene (3:4939) by cat. hydrogenation (25) see indic. refs.; from α -benzene-hexachloride (3:4410) with alc. KOH, pyridine, or quinoline (9) from β - or γ -benzene-hexachlorides with alc. KOH see (9) cf. (26).]

[\tilde{C} with Cl₂ in pres. of Al/Hg yields (27) 1,2,3,5-tetrachlorobenzene (3:0915); for behavior of \tilde{C} with liq. Cl₂ yielding addn. products see (28)]

[C with MeOH/NaOMe in s.t. at 180° yields mainly (29) 3,5-dichloroanisole, m.p. 39° (29), accompanied by some 3,5-dichlorophenol (3:1670).]

 $[\bar{C}$ on hydrolysis with steam at 550-800° over cat. yields (30) phloroglucinol (1:1620); for behavior of \bar{C} with F_2 see (31); for behavior of \bar{C} with NH₃ at 700-800° see (32).]

 \bar{C} on mononitration, e.g., by warming \bar{C} (1 g.) with 5 ml. fumg. HNO₃ (D=1.49) at 100° for 15 min., then pouring onto ice (38), gives (2) (8) (100% yield (38)) 1,3,5-trichloro-2-nitrobenzene [Beil. V-247], ndls. from alc., m.p. 69° (8), 67-68° (38). — \bar{C} on dinitration, e.g., by refluxing for 1 hr. a soln. of \bar{C} (1 g.) in 5 ml. fumg. HNO₃ (D=1.49) + 5 ml. conc. H₂SO₄ (38), gives (yield: 100% (38) (34), 82% (35), 80% (15)) (14) (33) 1,3,5-trichloro-2,4-dinitrobenzene [Beil. V-265], m.p. 131-131.5° (35) (36), 129-130° (34), 129.5° (14) (15) (3), 128.5° (38) (this prod. on htg. with 5 pts. aniline yields (38) 1,3,5-trianilino-2,4-dinitrobenzene, m.p. 179-180° (38)). — \bar{C} on trinitration, e.g., by boilg. 2 days with mixt. of

fumg. HNO₃ and fumg. H₂SO₄ as directed (37) (39), yields (37) (33) (17) 1,3,5-trichloro-2,4,6-trinitrobenzene [Beil. V-275], m.p. 187° (33), 193° (15), 192-193° (39).

Č with conc. H₂SO₄ is unchanged even after htg. 56 hrs. at 100° and is only partially sulfonated on htg. 6 hrs. at 100° with fumg. H₂SO₄ (12% SO₃) (16); however, Č with 3 pts. fumg. H₂SO₄ (SO₃ = 72%) htd. at 100° for 15 hrs. completely sulfonates yielding (16) 1,3,5-trichlorobenzene-2,4-disulfonic acid (corresp. disulfonyl chloride, m.p. 161.5° (16), corresp. disulfonamide, m.p. 248° (16)).

Č with chlorosulfonic acid in CHCl₃ (38) gives 1,3,5-trichlorobenzenesulfonyl chloride, m.p. 35-40° u.c. (38); this prod. with (NH₄)₂CO₃ readily yields (38) 1,3,5-trichlorobenzenesulfonamide, m.p. 210-212° u.c. dec. (38).

3:1400 (1) Dadieu, Pongratz, Kohlrausch, Monatsh. 61, 432-433 (1932). (2) Beilstein, Kurbatow, Ann. 192, 232-233 (1878). (3) Lock, Ber. 66, 1532 (1933). (4) Körner, Gazz. chim. ital. 4, 411-412 (1874). (5) Holleman, Rec. trav. chim. 37, 197-198 (1918). (6) Olivier, Rec. trav. chim. 37, 313 (1918). (7) Olivier, de Kleermaeker, Rec. trav. chim. 39, 643 (1920). (8) Holleman, van Haeften, Rec. trav. chim. 40, 74 (1921). (9) van der Linden, Ber. 45, 231-247 (1912). (10) Lock, Böck, Ber. 70, 925 (1937).

(11) Lecat, Ann. soc. sci. Bruxelles B-49, 109-118 (1929); Cent. 1929, II 2162. (12) Ford (to Westinghouse Electric and Mfg. Co.), U.S. 2,139,945-2,139,948, Dec. 13, 1938; Cent. 1939, 2047; C.A. 33, 2253-2254 (1939). (13) Zünderwerke E. Brünn, A.G., Ger. 570,460, Feb. 16, 1933; Cent. 1933, I 2770. (14) Jackson, Lamar, Am. Chem. J. 18, 667-668 (1896). (15) Backer, van der Baan, Rec. trav. chim. 56, 1177-11478 (1937). (16) Davies, Poole, J. Chem. Soc. 1927, 1122-1123. (17) Turek, Chimie & industrie 26, 781-794 (1931). (18) Hantzsch, Ber. 39, 2351 (1897). (19) Jackson, Gazzolo, Am. Chem. J. 22, 53-54 (1899). (20) Lobry de Bruyn, van Leent, Rec. trav. chim. 15, 86 (1896).

(21) Ingold, J. Chem. Soc. 125, 1536 (1924). (22) Wibaut, van der Lande, Wallagh (to Dow Chem. Co.), U.S. 2,123,857, July 12, 1938; Cent. 1939, I 250; C.A. 32, 7058 (1938). (23) Mouneyrat, Pouret, Compt. rend. 127, 1028 (1898). (24) Olivier, Rec. trav. chim. 39, 411-413 (1920). (25) Mailhe, Cent. 1921, III 467. (26) Jungfleisch, Ann. chim. (4) 15, 301 (1868). (27) Cohen, Hartley, J. Chem. Soc. 87, 1366 (1905). (28) van der Linden, Rec. trav. chim. 55, 315-324 (1936), (29) Ref. 5, pp. 201-204. (30) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994; C.A. 26, 2747 (1932).

(31) Bancroft, Whearty, Proc. Natl. Acad. Sci. 17, 183-186 (1931). (32) Heslinga, Rec. trav. chim. 43, 178-180 (1924). (33) Jackson, Wing, Ann. Chem. J. 9, 348-355 (1887). (34) Huffer, Rec. trav. chim. 40, 451 (1921). (35) Schlubach, Mergenthaler, Ber. 58, 2735 (1925). (36) Borsche, Trautner, Ann. 447, 6 (1926). (37) Jackson, Smith, Am. Chem. J. 32, 171-172 (1904). (38) Huntress, Carten, J. Am. Chem. Soc. 62, 512-513 (1940). (39) Schmitt, Z. ges. Schiessus. Sprengstoffw. Nitrocellulose 38, 198-199 (1943); C.A. 38, 3962 (1944).

M.P. 64° (1) (2) (3) 63-64° (5)

Colorless lfts. from alc. — 100 pts. 90–92% alc. dis. at room temp. 5.40 pts. \bar{C} ; in hot 37.28 pts. \bar{C} (4).

[For prepn. of \bar{C} from chloral (3:5210) with C_6H_6 (2 moles) + conc. H_2SO_4 (almost quant. yield) see (3); from chloral hydrate (3:1270) with C_6H_6 + a little AlCl₃ at 0° see (5) cf. (2); note that both types of this same condensation take place through intermediate formn. of trichloromethyl-phenyl-carbinol [Beil. VI-476, VI₁-(237)], m.p. 37°, b.p. 145° at 15 mm. (1) (corresp. acetate, m.p. 87.5° (1)) as formerly suspected (6) and subsequently confirmed (1).]

C on reduction gives various products according to conditions [e.g., C with Na/Hg in

alc. is claimed (7) to give 1,1-diphenylethane [Beil. V-605, V_1 -(285), V_2 -(509)], but this prod. was not obtd. in pure form and was accompanied by 1,1-dichloro-2,2-diphenylethylene (3:1938) (from \ddot{C} by loss of HCl under alk. conditions)].

[$\tilde{\mathbf{C}}$ in boilg. 95% alc. contg. trace of CuCl₂ with finely powdered Al/Cu/Zn (Devarda) alloy or Cu/Mg (Arnd) alloy for 6-10 hrs. gives (13-19% yield (8)) 2,2,3,3-tetrachloro-1,1,4,4 tetraphenylbutane [Beil. V₂-(676)], ndls. from AcOH, m.p. 188-190° (8), accompanied by some 2,3-dichloro-1,1,4,4-tetraphenylbutene-2 (see next paragraph). $\tilde{\mathbf{C}}$ with Zn dust + conc. aq. NH₄OH in alc. soln. gives (18) (4) stilbene (1:7250) + 1,1-diphenylethane (above).]

[\bar{C} on reduction with H₂ in pres. of Pd/BaCO₃ in alc./pyridine soln. gives (54-60% yield (9)) 2,2,3,3-tetrachloro-1,1,4,4-tetraphenylbutane (see preceding paragraph) accompanied by both high-melting (137-138°) and low-melting (108-110°) stereoisomers of 2,3-dichloro-1,1,4,4-tetraphenylbutene-2 [Beil. V₂-(685)]; using Ni as cat. the same prods. result (9) in lower yield sometimes accompanied also by 1,1-dichloro2,2-diphenylethylene (3:1938) (from \bar{C} by loss of HCl).]

[$\overline{\mathbf{C}}$ on reduction by electrolytic means in various types of solution, with various metallic electrodes, and at various temperatures gives (10) (11) numerous products including 1,1-dichloro-2,2-diphenylethane (3:1938), 1-chloro-2,2-diphenylethane [Beil. V-606, V₁-(285)], 1,1,4,4-tetraphenylbutine-2 [Beil. V₁-(379), V₂-(694)], etc.; for details see (10) (11).]

[$\bar{\mathbf{C}}$ with Cl₂ under suitable conditions should give 1,1,1,2-tetrachloro-2,2-diphenylethane [Beil. V-606], m.p. 85°, but this reaction has not actually been reported. — However, $\bar{\mathbf{C}}$ with a very large excess (15 pts.) pure liquid Br₂ gives (12) 2-bromo-1,1,1-trichloro-2,2-diphenylethane, m.p. 87.5° (12)]

[No mono- or di-nitration products derived from C have been reported.]

Č on distillation (13), or on boilg, with alc. KOH (2) (14) (for study of rate see (15)), or during course of other reactions involving alkaline conditions (see above) loses HCl giving 1,1-dichloro-2,2-diphenylethylene (3:1938). m.p. 80° (2).

[Č with NaOEt in s.t. at 180° ultimately gives (2) cf. (16) (and presumably through intermediate 1,1-dichloro-2,2-diphenylethylene (3:1938)) diphenylacetic acid (1:0765).]

 \bar{C} with Na in C_6H_6 refluxed 10-12 hrs. and then treated with alc. gives (17) cf. (2) trans-1,2-diphenylethylene (stilbene) (1:7250), m.p. 124°, cis-1,2-diphenylethylene (isostilbene) [Beil. V-633, V₁-(303), V₂-(539)], and diphenylacetylene (tolane) [Beil. V-656, V₁-(319), V₂-(568)]. — \bar{C} with Zn dust on dry distn. gives (13) stilbene (1:7250).

[\bar{C} in C_6H_6 with AlCl₃ gives (10% yield (20)) 1,1,2,2-tetraphenylethane [Beil. V-739, V_1 -(371), V_2 -(673)], m.p. 211°.]

[For use of \bar{C} as addn. agent to improve lubricating power of mineral oils under high pressures see (19).]

3:1420 (1) Chattaway, Muir, J. Chem. Soc. 1934, 701-703. (2) Harris, Frankforter, J. Am. Chem. Soc. 48, 3144-3150 (1926). (3) Baeyer, Ber. 5, 1098-1099 (1872). (4) Elbs, J. prakt. Chem. (2) 47, 45-46, 77 (1893). (5) Frankforter, Kritchevsky, J. Am. Chem. Soc. 36, 1515-1518 (1914). (6) Dinesmann, Compt. rend. 141, 201 (1905). (7) Goldschmiedt, Ber. 6, 1502-1503 (1873). (8) Brand, Ber. 54, 1995-1996 (1921). (9) Brand, Horn, J. prakt. Chem. (2) 115, 359-362 (1926). (10) Brand, Z. Elektrochem. 16, 669 (1910); Ber. 54, 2017 (1921).

(11) Brand, Ber. 46, 2935-2942 (1913). (12) Schlenk, Ann. 493, 213 (1912). (13) Goldschmiedt, Ber. 6, 987, 990 (1873). (14) Baeyer, Ber. 6, 223 (1873). (15) Brand, Busse-Sundermann, Ber. 75, 1822 (1942). (16) Scheibley, Prutton, J. Am. Chem. Soc. 62, 840-841 (1940). (17) Harris, J. Am. Chem. Soc. 52, 3635 (1930). (18) Elbs, Forster, J. prakt. chem. (2) 39, 299 (1889). (19) Klipstein (to Calco Chem. Co.), U.S. 2,161,678, June 6, 1939; Cent. 1939, II 4634 [C.A. 33, 7556 (1939)]. (20) Fleck, Preston, Haller, J. Am. Chem. Soc. 67, 1420 (1945).

3:1430 1-CHLORO-2,2-bis-(p-CHLOROPHENYL)ETHYLENE

$$C_{14}H_9Cl_3$$
 Beil. S.N. 480
 C_1
 C_2
 C_1
 C_1
 C_1

M.P. 64-65° (1)

Cryst. from lgr. — Note that \tilde{C} may occur as a minor impurity in technical grade " DDT " (3:3298).

[For prepn. of $\bar{\mathbf{C}}$ from "p,p'-DDD" (3:3320) by elimination of 1 HCl with alc. KOH (77% yield) see (1).]

C on oxidn. with CrO3 gives (84% yield (1)) 4,4'-dichlorobenzophenone (3:4270).

3:1430 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., J. Am. Chem. Soc. 67, 1600 (1945).

3:1445
$$\alpha$$
-CHLOROACRYLIC ACID Cl C₃H₃O₂Cl Beil. I - 401 CH₂—C—COOH I_1 — I_2 —

Cryst. from pet. ether (2), ndls. from ether (1). — Eas. volatile, subliming even at room temp. (1) (4); volatile with steam.

[For prepn. of \bar{C} from α,α -dichloropropionic acid (3:6162) with alc. KOH see (4); from methyl α,β -dichloropropionate (3:9103) with aq. Ba(OH)₂ (62% yield (2)) (1) or alc. KOH (5) see indic. refs.; from α -chloro- β -hydroxypropionic acid (α -chlorohydracrylic acid) [Beil. III-298] by distn. with H₂SO₄ see (6) (7); from trichloroethylene (3:5170) with formaldehyde or paraformaldehyde + H₂SO₄ as directed see (3).]

 \overline{C} on treatment with Ag₂O dec. yielding (1) Ag + AgCl.

 \tilde{C} with fumg. HCl in s.t. at 100° yields (5) (4) α,β -dichloropropionic acid (3:0855), m.p. 50°.

[The esters of \bar{C} (usually prepd. from the corresp. alkyl α,β -dichloropropionates by elimination of HCl) have assumed special importance because of their ability to polymerize to useful resins; for methyl α -chloroacrylate see 3:9096; for ethyl α -chloroacrylate see 3:9242; for sec-butyl α -chloroacrylate, and its mechanism of polymerization, see (8) (9); for studies on the electrical properties of β -chloroethyl α -chloroacrylate see (10).]

C readily polymerizes in ultra-violet light or in pres. of peroxides (2).

3:1445 (1) Werigo, Werner, Ann. 170, 168-171 (1874). (2) Marvel, Dec, Cooke, Cowan, J. Am. Chem. Soc. 62, 3495-3498 (1940). (3) Imperial Chem. Ind., Ltd., French 845,230, Aug. 16, 1939; C.A. 35, 1070 (1941); Brit. 528,761, Nov. 6, 1940; C.A. 35, 7975 (1941). (4) Otto, Beckurts, Ber. 18, 241-246 (1885). (5) Werigo, Melikov, Ber. 10, 1499-1500 (1877). (6) Melikov, J. prakt. Chem. (2) 61, 554-555 (1900). (7) Koelsch, J. Am. Chem. Soc. 52, 3365 (1930). (8) Marvel, Dec, Cooke, J. Am. Chem. Soc. 62, 3499-3504 (1940). (9) Price, Kell, J. Am. Chem. Soc. 63, 2798-2801 (1941). (10) Mead, Fuoss, J. Am. Chem. Soc. 64, 2389-2393 (1942).

M.P. 65° (1) (3) B.P. 253.5° at 767 mm. (2) 68° (2)

Ndls. (from C_6H_6 by addn. of pet. ether (2)). — Volatile with steam (1). [For study of ionization const. see (4).]

[For prepn. from 3,4-dichloroaniline [Beil. XII-626] via diazo reaction see (2) (3) (5) (1).] [For use of $\bar{\mathbf{C}}$ in prepn. of 2-chloro-1,4-dihydroxyanthraquinone (2-chloroquinizarin) [Beil. VIII-452] by htg. with phthalic anhydride + H₂SO₄ + H₃BO₃ at 195-200° see (7) (8); for use of $\bar{\mathbf{C}}$ in prepn. of tetrachlorofluoran [Beil. XIX-148], m.p. 255°, by htg. with phthalic anhydride see (3).]

 \bar{C} dis. eas. in conc. H_2SO_4 ; on stdg. small pl. of 3,4-dichlorophenol-6-sulfonic acid separate; these are sol. in aq., alc., AcOH, EtOAc; insol in C_6H_6 , pct eth.; spar. sol. CHCl₈; cryst. from latter, m.p. 75–76° (6).

 \bar{C} on htg. with mixt. of fumg H₂SO₄ (25% SO₃) + conc. H₂SO₄, and resultant solid treated with conc. HNO₃ (D=1.5) as directed (1) gives (69% yield (1)) of 3,4-dichloro-2-nitrophenol, yel. ndls., from lt. pet. ether, m p. 76° (1).

C dislyd. in 3 pts. AcOH contg. anhyd. NaOAc, treated with Cl₂ and the prod. pptd. by addn. of aq., yields (5) 2,3,4-trichlorophenol (3:2185).

 \tilde{C} dislyd. in aq. NaOH and shaken with $(CH_3)_2SO_4$ yields (2) the methyl ether, 3,4-dichloroanisole, m.p. -8° (2).

3:1460 (1) Hodgson, Kershaw, J. Chem. Soc. 1929, 2922. (2) Holleman, Rec. trav. chim. 37, 102-104 (1918). (3) Badische Anilin- und Soda-Fabrik, Ger. 156,333, Nov. 14, 1904; Cent. 1904, II 1673. (4) Murray, Gordon, J. Am. Chem. Soc. 57, 110-111 (1935). (5) Groves, Turner, Sharp, J. Chem. Soc. 1929, 523. (6) Kraay, Rec. trav. chim. 48, 1084-1085 (1930). (7) Gubelmann, Lee (to Newport Co.), U.S. 1,655,462, Jan. 10, 1928; Cent. 1929, I 3149. (8) Gubelmann, U.S. 1,655,863, Jan. 10, 1928, C.A. 22, 966 (1928).

3:1475 3,5-DICHLOROBENZALDEHYDE

C₇H₄OCl₂ Beil. S.N. 635

M.P. 65° (1) B.P. 235-240° at 748 mm. (1)

Colorless ndls. or lfts. from pet. ether or dil. MeOH (1). — Spar. sol. hot aq. but eas. volatile with steam. — Eas. sol. most organic solvents.

[For prepn. of \bar{C} from 3,5-dichlorotoluene (3:6310) via chlorination to 3,5-dichlorobenzal (di)chloride (3:0370) and subsequent hydrolysis with conc. H₂SO₄ (70-80% overall yield) see (1) (4).]

 \tilde{C} with satd. aq. NaHSO₃ yields a cpd. \tilde{C} .NaHSO₃; this is exceptionally sol. in aq., and on htg. the soln. yields \tilde{C} (1).

 \bar{C} on oxidn. with excess KMnO₄ at 100° gives (74% yield (1)) 3,5-dichlorobenzoic acid (3:4840), m.p. 188° (1). — \bar{C} with 50% aq. KOH for 4 hrs. at 100° gives (90% yield (1)) 3,5-dichlorobenzyl alc., cryst. from C₆H₆, m.p. 82° (1), and 8,5-dichlorobenzoic ac. (90% yield (1)) (3:4840).

 $\ddot{\mathbf{C}}$ with PCl₅ gives (80% yield (1)) 3,5-dichlorobenzal (di)chloride (3:0370) cryst. from MeOH or dil. AcOH, m.p. 36.5° (1).

Č on nitration with fumg. HNO₃ (D=1.48) at 0° as directed (2) gives (99% yield (2)) 3,5-dichloro-2-nitrobenzaldehyde, cryst. from AcOH or lgr., m.p. 91.5° (2), 91° (4). [This deriv. yields an oxime, m.p. 97°, a phenylhydrazone, m.p. 175°, and on oxidn. with KMnO₄ gives 3,5-dichloro-2-nitrobenzoic ac., m.p. 194° cor. (2).]

C htd. with NaOAc + Ac₂O for 18 hrs. at 180-210° gives (76% yield (1)) 3,5-dichlorocinnamic acid, ndls. from C₆H₆ + pet. eth. or from dil. AcOH, m.p. 176° cor. (1).

[For conversion of \tilde{C} to 3,5-dichlorostyrene (5) (6) in a reaction with MeMgI giving (yields: 69% (5), 55% (3)) 3,5-dichlorophenyl-methyl-carbinol, m.p. 46° (3), b.p. 126° at 4 mm. (5), $n_D^{20} = 1.5573$ (5), and dehydration of latter with KHSO₄ (43% yield (5)) see indic. refs.]

- ② 3,5-Dichlorobenzaldoxime: cryst. from lgr., C₆H₆ + pet. eth., or dil. AcOH, m.p. 112° (1).
 - 3,5-Dichlorobenzaldehyde phenylhydrazone: yel. ndls. from pet. eth., m.p. 106.5° (1).
 - ---- 3,5-Dichlorobenzaldehyde p-nitrophenylhydrazone: unrecorded.
 - --- 3,5-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.
 - 3,5-Dichlorobenzaldehyde semicarbazone: unrecorded.

3:1475 (1) Asinger, Lock, Monatsh. 62, 344-348 (1933). (2) Asinger, Monatsh. 63, 386-387 (1934). (3) Lock, Bock, Bcr. 70, 922-923 (1937). (4) Ruggli, Zaeslin, Lang, Helv. Chim. Acta 21, 1247 (1938). (5) Marvel, Overberger, Allen, Johnston, Saunders, Young, J. Am. Chem. Soc. 68, 884 (1946). (6) Michalek, Clark, Chem. & Eng. News 22, 1559-1563 (1944)

3:1480 2,3-DICHLOROBENZALDEHYDE

C₇H₄OCl₂

Beil. S.N. 635



M.P. 65-67° (1)

Cryst. from 1:1 aq EtOH.

[For prepn. of C from 2,3-dichlorotoluene (3:6345) by bromination at 180-200° (presumably to 2,3-dichlorobenzal (di)bromide) followed by hydrolysis with conc. H₂SO₄ at 100-140° (71% yield) see (1).]

C with MeMgI gives (76% yield (1)) 2,3-dichlorophenyl-methyl-carbinol, m.p. 55-57°, b.p. 112-113° at 2 mm. (corresp. 3,5-dinitrobenzoate, m.p. 145-146° (1)); note that dehydration of the carbinol with KHSO₄ gives (44% yield (1)) 2,3-dichlorostyrene.

- ---- 2,3-Dichlorobenzaldoxime: unreported.
- ---- 2,3-Dichlorobenzaldehyde phenylhydrazone: unreported.
- ---- 2,3-Dichlorobenzaldehyde p-nitrophenylhydrazone: unreported.
- ---- 2,3-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.
- ---- 2,3-Dichlorobenzaldehyde semicarbazone: unreported.
- 3:1480 (1) Marvel, Overberger, Allen, Johnston, Saunders, Young, J. Am. Chem. Soc. 68, 862 (1946).

3:1490 2-CHLORONAPHTHOL-1

$$\begin{array}{cccc} OH & C_{10}H_7OCl & \text{Beil. VI - 611} \\ & & \text{VI}_{1}\text{-}(308) \\ & & \text{VI}_{2}\text{-}(581) \\ \end{array}$$

Ndls. from lgr.; exceptionally easily sol. in alc., ether, C_6H_6 . — More volatile with steam than the isomeric 4-chloronaphthol-1 (3:3720) (use in sepn. (2)).

[For prepn. of \bar{C} from α-naphthol (1:1500) with aq. alk. NaOCl (3) (4) (5) or with SO₂Cl₂ in CHCl₃ soln. (18% yield, together with 42% yield of 4-chloronaphthol-1 (3:3720) (2)), see indic. refs.; from sodium 1-hydroxynaphthalenesulfonate-2 [Beil. XI-269, XI₁-(63)] with PCl₅ see (6); from 2-chloro-1-hydroxynaphthalenesulfonic acid-4 (1) by hydrolysis in boilg. dil. H₂SO₄ see (1).]

C on stdg. in aq. Na₂CO₂ soln. gives blue flocks (7).

Č with 1 mole Br₂ in 20% AcOH yields alm. quant. (7) 4-bromo-2-chloro-naphthol-1, ndls., m.p. 112° (7).

[$\bar{\mathbf{C}}$ with conc. HI (D=1 5) in boilg. AcOH for 12 hrs. reduces (4) to α -naphthol (1:1500), but $\bar{\mathbf{C}}$ is unaffected by SnCl₂ + HCl in alc. even after 28 hrs.' boilg. (4).]

[\bar{C} on oxidn. with p-diamines gives (3) indophenols; \bar{C} on coupling with diazonium salts gives (3) azo dyestuffs, cf. (1); \bar{C} with isatın chloride [Beil. XXI-302, XXI₁-(296)] yields (5) a chloronaphthalene indolindigo.]

[C dislvd. in a little alc., made ammoniacal with conc. NH₄OH, and treated at 5° with nitrosobenzene in alc. gives (84% yield (8)) 2-chloronaphthoquinone-1,4-monoanil-4 (see under 3:3580), very red ncls. from alc., m p. 112° (8).

3:1490 (1) Hodgson, Rosenberg, J. Soc. Chem. Ind. 48-T, 287-289 (1929). (2) Lesser, Gad, Ber. 56, 972-973 (1923). (3) Kalle and Co., Ger. 167,458, Jan 22, 1906; Cent. 1906, I 1067. (4) Franzen, Steuble, J. prakt. Chem. (2) 103, 383-384 (1921/2). (5) Bedzik, Friedländer, Monatsh. 29, 380-381 (1908). (6) Claus, Oehler, Ber. 15, 314 (1882). (7) Willstätter, Schuler, Ber. 61, 365 Note, 367 (1928). (8) Friedlander, Sander, Ber. 57, 646-647 (1924).

CHAPTER V

DIVISION A. SOLIDS

(3:1500-3:1999)

3:1505 3.5-DICHLOROBENZOPHENONE

C₁₃H₈OCl₂

Beil. S.N. 652

(3,5-Dichlorophenyl phenyl ketone)

CI C=0

M.P. 65° (1) (2)

Ndls. (from MeOH (1)).

[For prepn. from 3,5-dichloro-4-aminobenzophenone (1) by removal of amino group via diazo reaction see (1); for prepn. from 3,5-dichlorobenzohydrol by oxidn. with CrO₃ (75% yield) see (2).]

 \overline{C} fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (2) BzOH (1:0715) and a trace of m-dichlorobenzene (3:5960).

- ₱ 3,5-Dichlorobenzophenone oxime: from C in alc. on refluxing 8 hrs with NH₂OH HCl + excess NaOH: after distilling off the alcohol, the mixt of two stereoisomeric oximes is pptd. by pouring into aq.; sepn. of the two isomers can be effected by fractnl. crystn. from dil. MeOH or dil. EtOH (1).
- α-form (less-soluble isomer), pl. or fine ndls., m.p. 137°. [With PCl₅ in dry ether, followed by water, this form yields quant. 3,5-dichlorobenzanilide, ndls. from dil. alc., m.p. 148° (1).]
- β-form (more-soluble isomer), constituting 70% of reaction mixt., pr. m.p. 118°. [With PCl₅ in dry ether, followed by water, this form yields a gummy product from which some benz-3,5-dichloroanilide, ndls. m.p. 148.5°, can be sepd. (1).]
- 3:1505 (1) Waters, J. Chem. Soc. 1929, 2108-2109. (2) Lock, Rödiger, Ber. 72, 869-870 (1939).

3:1535 4-CHLORO-3-METHYLPHENOL OH C₇H₇OCl Beil. VI - 381 VI₁-(187) VI₂-(355)

M.P. 66° (1) (11) B.P. 235° (1) 57° (2) 234–236° (11) 55.5° (3)

Note that C is often designated in the literature as "p-chloro-m-cresol" or even as "6-chloro-m-cresol"; care must be taken to avoid confusion with the isomeric 6-chloro-3methylphenol (3:0700).

Odorless cryst. (from lgr.). — Volatile with steam (3).

Both the low-melting and high-melting forms appear to be authentic; whether they are different cryst. forms has never been detd.

[For prepn. of C from 2-chloro-5-aminotoluene (4-chloro-3-methylaniline) [Beil. XII-871] via diazo reaction see (3); for comml. prepn. from m-cresol (1:1730) by chlorination with SO₂Cl₂ see (1) (4) (84% yield (11)).]

[C on monobromination with Br2 in AcOH gives (8) 4-chloro-6-bromo-3-methylphenol, m.p. 70.0-70.5° (8); C on dibromination yields (9) 4-chloro-2,6-dibromo-3-methylphenol, m.p. $68.5-69.5^{\circ}$ (9) (for use of latter in bromometric detn. of \bar{C} see (10)).

 \bar{C} treated with $(CH_3)_2SO_4 + aq$. NaOH gives its methyl ether, 4-chloro-3-methylanisole, b.p. 213.5° (2). [This methyl ether on oxidn. with dil. KMnO₄ (6.7 hrs. for 5 g.) gave (2) 2-chloro-5-methoxybenzoic ac. [Beil. X-143], ndls. from dil. AcOH (5), m.p. 173.5° (2), 170-171° (5), Neut. Eq. 186.5.

- \oplus 4-Chloro-3-methylphenyl benzoate: from $\bar{C} + BzCl + pyridine$, pl. from alc., m.p. 86° (2) (3). [This benzoate htd. with 0.7 of its wt of AlCl3 for 10 min. at 140° gives by Fries rearrangement 100% yield (6) of 2-hydroxy-5-chloro-4-methylbenzophenone. vel. ndls. from dil. alc., m.p. 142° (6)]
- \odot 4-Chloro-3-methylphenyl benzenesulfonate: from \ddot{C} + benzenesulfonyl chloride + pyridine, pl. from alc., m.p. 66° (3). [Note that this value is numerically the same as orig. C and that the deriv. must therefore be distinguished from it, e.g., by mixed m.p. or behavior with alk.l
- \oplus 4-Chloro-3-methylphenyl p-toluenesulfonate: from \bullet + p-toluenesulfonyl chloride + pyridine, pl. from alc. (2) (3), ndls. from lt. pet (2), m.p. 98° (2) (3). [Note that this deriv. does not distinguish C from 6-chloro-3-methylphenol (3:0700) or 2-chloro-3methylphenol (3:1055).]
- ① 4-Chloro-3-methylphenyl $N-\alpha$ -naphthylcarbamate: from $\ddot{C} + \alpha$ -naphthyl isocyanate in presence of trace of trimethyl- or triethyl-amine in ether; cryst. from lgr., m.p. 153-154° (7).
- 3:1535 (1) Kalle and Co., Jan. 11, 1897, Ger. 90,847, Friedländer 4, 94 (1894 /7). (2) Gibson, J. Chem. Soc. 1926, 1425-1428. (3) Huston, Chen, J. Am. Chem. Soc. 55, 4214-4218 (1933). (4) Laschinger, U.S. 1,847,566, March 1, 1932, Cent. 1932, II 1512, C.A. 26, 2471 (1932). (5) Hodgson, Beard, J. Chem. Soc. 1926, 154. (6) Rosenmund, Schnurr, Ann. 460, 86 (1928). (7) French, Wirtel, J. Am. Chem. Soc. 48, 1736-1739 (1926). (8) von Walther, Zipper, J. prakt. Chem. (2) 91, 378-379 (1915). (9) Huston, Neeley, J. Am. Chem. Soc. 57, 2178 (1935). (10) Deshusses, Mitt. Lebensm. Hyg. 32, 250-254 (1941), C.A. 37, 3023 (1943).

(11) Sah, Anderson, J. Am. Chem. Soc 63, 3165 (1941).

M.P. 66-67° (1) (2) (3)

Colorless lfts. or ndls., sol. in alc., ether, CHCl3, or C6H6. [For prepn. of C from 2,5-dimethylhexanediol-2,5 [Beil. I-492, I₁-(256), I₂-(557)] with fumg. HCl (1) or AcCl (1) or in AcOH with HCl gas (100% yield (3)) see (1) (3); from the ring-closed internal ether of the above diol, viz., 2,2,5,5-tetramethyltetrahydrofuran [Beil. XVII-17], with fumg. HCl see (2); for prepn. of \bar{C} from 2,5-dimethylhexadiene-2,4 (di-isocrotyl) [Beil. I-259, I_1 -(122), I_2 -(237)] with HCl in s.t. see (2).]

C on htg. boils at 180° with evolution of HCl (1).

[\bar{C} on slow distn. at 12-20 mm. over CO₂ saturated soda-lime at 255-270° gives (3) by loss of 2 HCl 2,5-dimethylhexadiene-2,4 (see above), m.p. + 6° (2).]

[For study of behavior of \vec{C} with aq. alc. N/10 NaOH see (4).]

3:1550 (1) Henry, Compt. rend. 143, 496-497 (1906). (2) Pogorzelski, J. Russ. Phys.-Chem. Soc. 30, 977-992 (1898); Cent. 1899, I 773. (3) Staudinger, Muntwyler, Ruzicka, Seibt, Helv. Chim. Acta 7, 395-396 (1924). (4) Tishchenko, J. Gen. Chem. (U.S.S.R.) 9, 1380-1388 (1939), C.A. 34, 1611 (1940).

3:1565 2,4'-DICHLOROBENZOPHENONE

(o-Chlorophenyl p-chlorophenyl ketone)

Co

C13H8OCl2

Beil. VII - 420 VII₁---

M.P. 66.5-67.0° (1) (2) B.P. 214-215° at 22 mm. (2) 66° (3) (4) 64.2-65.2° cor. (5)

Pr. (from alc.). — [For crystallographic consts. see (3) (4).] — Sol. in most org. solv.; cryst. best from lgr. or cold dil. (60-75%) alc. (2).

[For prepn. from o-chlorobenzoyl chloride (3:6640) + chlorobenzene (3:7903) + AlCl₃ in CS₂ see (2); as by-product (besides 4,4'-dichlorobenzophenone (3:4270)) from p-chlorobenzoyl chloride (3:6550) + chlorobenzene (3:7903) + AlCl₃ + CS₂ see (3), or from p-chlorobenzoic acid (3:4940) + chlorobenzene (3:7903) + AlCl₃ (yield 9-12%) see (1).]

[For form. of \bar{C} from 1,1-dichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)ethylene (3:1925) by oxidn. with $CrO_3/AcOH$ see (5).]

[Č with aq. NaOH + trace CuO in Fe bomb (or in pres. of Fe powder) at 240° for 6 hrs. both ring-closes and hydrolyzes giving (87% yield (6)) crude 3-hydroxyfluorenone, m.p. 184-192° (6).]

2.4'-Dichlorobenzophenone 2.4-dinitrophenylhydrazone: m.p. 230-231° (5).

3:1565 (1) Newton, Groggins, Ind. Eng. Chem. 27, 1399 (1935). (2) Norris, Twieg, Am. Chem. J. 36, 397 (1903). (3) Montagne, Rec. trav. chim. 25, 385-387 (1906). (4) Jaeger, Z. Krist. 56, 52 (1921). (5) Haller, Bartlett, Drake, Newman, Cristol, Magerlein, Mueller, Schneider, J. Am. Chem. Soc. 67, 1599, 1602 (1945). (6) Britton, Moyle, Bryner (to Dow Chem. Co.), U.S. 2,377,751, June 5, 1945; C.A. 39, 4097 (1945).

3:1595 2,8-DICHLOROPHENOL OH C₆H₄OCl₂ Beil. VI - 190 VI₁-(103) VI₂-(179)

M.P. 67° (1) (2) B.P. 219–220° at 740 mm. (2) cf. (3) 66–68° (8) 80–85° at 4 mm. (2)

Cryst. from pet. eth. with penetrating odor suggesting o-chlorophenol or (if dilute) iodoform. — Misc. with alc., ether, volatile with steam.

[For prepn. from p-hydroxybenzoic ac. (1:0840) by chlorination in AcOH followed by elimin. of CO_2 by htg. in quinoline see (4) (5) (8); for prepn. from phenol (1:1420) by prelim. sulfonation, subsequent chlorination in nitrobenzene, and final removal of sulfonic acid group by hydrolysis (70% yield (2)) see (2).]

C is sol. in Na₂CO₃ soln. (1). [For study of ionization const. see (6).]

Č on nitration (no details) gives 2,6-dichloro-4-nitrophenol [Beil. VI-241], colorless ndls. from aq., m.p. 125° (7).

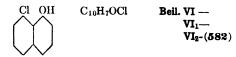
 \bar{C} dislvd. in aq. alk. and shaken with $(CH_3)_2SO_4$ yields (1) (2) the methyl ether, 2,6-dichloroanisole, b.p. 105-106° at 20 mm. (2), m.p. 10.1° (1).

[For study of rearr. of ethers (8) or esters (9) of C see indic. refs.]

- **2.6-Dichlorophenyl benzoate:** m.p. 74.0-74.5° (9).
- 2,6-Dichlorophenyl p-nitrobenzoate: unreported.
 - ____ 2,6-Dichlorophenyl 3,5-dinitrobenzoate: unreported.
- --- 2,6-Dichlorophenyl benzyl ether: m.p. 39.5-40° (10).
- **2.6-Dichlorophenyl** p-nitrobenzyl ether: unreported.
- 2,6-Dichlorophenoxyacetic acid: ndls. from aq., m.p. 134.5-135.0° cor. (9).
 Vith chloroacetic acid (3·1370) + aq. alk. (9)
- ---- 2,6-Dichlorophenyl N-phenylcarbamate: unreported.
- **2,6-Dichlorophenyl** $N-(\alpha-naphthyl)$ carbamate: unreported.
- 2,6-Dichlorophenyl N-(β-naphthyl)carbamate: unreported.

3:1595 (1) Holleman, Rec. trav. chim. 37, 96-103 (1918). (2) Huston, Neeley, J. Am. Chem. Soc. 57, 2177 (1935). (3) Seifart, Ann. Suppl 7, 203 (1870). (4) Richardson, J. Chem. Soc. 1937, 1364. (5) Blicke, Snith, Powers, J. Am. Chem. Soc. 54, 1468 (1932). (6) Murray, Gordon. J. Am. Chem. Soc. 57, 110-111 (1935). (7) Tarugi, Gazz. chim. ital. 30, II 490-491 (1900). (8) Tarbell, Wilson, J. Am. Chem. Soc. 64, 1068-1069 (1942). (9) Tarbell, Fanta, J. Am. Chem. Soc. 65, 2172 2173 (1943). (10) Huston, Eldridge, J. Am. Chem. Soc. 53, 2262-2263 (1931).

3:1610 8-CHLORONAPHTHOL-1



M.P. 67° (1)

Ndls. from aq. — Volatile with steam.

[For formn. of C from 8-chloro-1-nitronaphthalene [Beil. V-556] by merely refluxing with aq. see (1).]

Č is sol. in aq. alk. giving orange-colored soln. which couples with solns. of diazonium salts (1).

[For reactn. of \bar{C} with benzotrichloride (3:6540) yielding 4-benzoyl-8-chloronaphthol-1, m.p. 121°, used in prepn. of triphenylmethane dyes see (2); with o-nitrophenylsulfenyl chloride see (3); for coupling of \bar{C} with diazotized 2-hydroxynaphthylamine-1 (or its relatives) yielding o-hydroxyazo cpds. see (4).]

3:1610 (1) Woroshtzow, Koslow, Ber. 69, 412-415 (1936). (2) Soc. Chem. Ind. Basel, Ger. 378,908, Aug. 7, 1923, Ger. 378,909, Aug. 11, 1923, Swiss 98,559, April 2, 1923; Cent. 1923, IV 594. (3) Akt.-Ges. Anilin-Fabrikation, Ger. 402,642; Sept. 17, 1924; Cent. 1924, II 2505. (4) Soc. Chem. Ind. Basel, Brit. 180,433, June 22, 1922; Cent. 1922, IV 841.

M.P. 67.0-67.5° (1) 66-67° (2) 67° (3) 66.2-66.5° (4) (5) 66° (6) (7)

[See also a-chlorocrotonic acid (3:2760).]

Ndls. from aq. (2) (4) (5); note, however, that from aq. solns. of salts acidification first ppts. \bar{C} as an oil. — \bar{C} is more sol. aq. than its stereoisomer; e.g., \bar{C} is sol. in 15.3 pts. aq. at 19° (8). — \bar{C} is much more volatile with steam than its stereoisomer (3:2760) (4) (5). — \bar{C} is spar, sol. cold but eas. sol. hot lgr. (8).

Preparation. [For prepn. of \bar{C} from lower-melting form (m.p. 63°) of α,β -dichloro-n-butyric acid (3:1375) with excess 10% aq. NaOH at not above 10° see (4) (5) cf. (9).]

Chemical behavior. \bar{C} on htg. in s.t. at 150-160° for 12 hrs. (10), or with pyridine hydrochloride in pyridine 7 days at room temp. or rapidly at 100° (2), or even slowly on steam distillation (11) is converted to the stereoisomeric α -chlorocrotonic acid (3:2760), m.p. 99°.

Č on reduction with Na/Hg in aq. is dehalogenated yielding (12) (4) crotonic acid (1:0425), m.p. 72°; whether any isocrotonic acid (1:1045), b.p. 169°, m.p. 15°, is formed at all is uncertain.

 \bar{C} with Cl_2 in CS_2 adds 1 mole halogen yielding (13) the same α, α, β -trichloro-n-butyric acid (3:1280), m.p. 59.5-60°, also obtd. by like treatment of α -chlorocrotonic acid (3:2760). — The behavior of \bar{C} with Br_2 appears to be unreported.

 $\ddot{\mathbf{C}}$ behaves as a monobasic acid; dissociation const. at 25° is 1.58 \times 10⁻³ (14); Neut. Eq. 120.5.

Salts. [K \overline{A} , ndls. from alc. in which it is much more sol. (viz., 1 pt K \overline{A} in 22 pts. 99.5% alc. at 16.5° (4)) than its stereoisomer (use in sepn. (2) (9)), eas. sol. aq., Ba $\overline{A}_2.31/2H_2O$, eas. sol. aq. but spar. sol. alc. (8); Pb $\overline{A}_2.H_2O$, ppt. (8).]

[For study of rate of reactn. of C with K₃AsO₃ see (3)]

The acid chloride of C is unreported.

- Methyl α-chloroisocrotonate: unreported. [However, for study of rate of esterification of C with MeOH see (15).]
- Ethyl α-chloroisocrotonate: oil; see 3:9368. [Note also that C in EtOH with conc. H-SO₄ at 100° gives only (7) the stereoisomeric ethyl α-chlorocrotonate (3:8523).]
- ---- α-Chloroisocrotonamide: unreported.
- α -Chloroisocrotonanilide: unreported.
- α -Chloroisocroton- α -naphthalide: unreported.

3:1615 (1) Stelling, Z. physik. Chem. B-24, 423 (1934). (2) Pfeiffer, Ber. 43, 3045 (1910). (3) Backer, van Oosten, Rec. trav. chim. 59, 57-58 (1940). (4) Wislicenus, Ann. 248, 288, 290 (1888). (5) Wislicenus, Ber. 20, 1008-1010 (1887). (6) von Auwers, Ber. 56, 724 (1923). (7) von Auwers, Ann. 432, 62 (1923). (8) Michael, Browne, Am. Chem. J. 9, 284 (1887). (9) Michael, Schulthess, J. prakt. Chem. (2) 46, 255-256 (1892). (10) Michael, Pendleton, J. prakt. Chem. (2) 38, 4 (1888).

4 (1888).
 Wislicenus, Ann. 248, 337 (1889).
 Wisling, Chem. 3, 244 (1889).
 Wisland, Z. physik. Chem. 3, 244 (1889).

Michael, Oechslin, Ber. 42, 322 (1909).

White cryst. from MeOH, EtOH, lgr., or CHCl₃ by addn. of lt. pet. — Note that on distillation under reduced press. \bar{C} goes over with only slight decompn. as a green vapor which condenses to a green liquid; on solidification much of this color is lost and recrystallization yields colorless \bar{C} . — \bar{C} is quite stable in dark; in sunlight, however, it turns brown and decomposes.

65.5°

 65°

(10)

(11) (12)

PREPARATION OF C

[For prepn. of \bar{C} from benzoin (1:5210) with SOCl₂ in pyridine (yield 74-79% (9)) (5) or with SOCl₂ directly (yield 90% (6)) (2) (3) (10) (13) see indic. refs. — Note that l-benzoin with SOCl₂ undergoes racemization (7) yielding \bar{C} .]

[For form. of \bar{C} from α,α -dichlorobenzyl phenyl ketone (ms,ms-dichlorodesoxybenzoin) [Beil. VII-436, VII₁-(234)] by partial dehalogenative reduction using H_2 + platinum oxide cat. (65% yield (1)) or AcOH + Fe powder at 70-80° (15) see indic. refs.; from 1,2-diphenyl-1,2-epoxyethylene (diphenyloxene) with conc. HCl in s.t. at 120° for 2 hrs. see (11); from benzoyl-phenyl-diazomethane (azibenzil) [Beil. VII₁-(395)] in ether with HCl gas see (12)]

CHEMICAL BEHAVIOR OF C WITH INORGANIC REAGENTS

Reduction. [C̄ in alc. soln. with H₂ + platinum oxide cat. (1), or in AcOH with Fe powder on protracted treatment (14), gives benzyl phenyl ketone (desoxybenzoin) (1:5165).]

Oxidation. [C̄ with conc. HNO₃ on warming gives (14) dibenzoyl (benzil) (1:9015).]

Halogenation. [C with Br₂ (1 mole) in AcOH at 100° for ½-hr. gives (10) α-bromo-α-chlorobenzyl phenyl ketone, m.p. 85°.]

Behavior with alkalies and alkali carbonates. (For alc. alkalies see below under organic reactants.) — $[\bar{C}$ with powdered KOH (3 moles) in toluene refluxed 2 hrs. loses HCl and rearranges giving (20% yield (11)) 1,2-diphenyl-1,2-epoxyethylene (diphenyloxene), b.p. 174-180° at 18 mm., m.p. 52°; note, however, that two later workers (15) (29) have been unable to duplicate this report. — Note, however, that \bar{C} with powdered KOH in dry ether gives (15) a mixt. of benzoic acid (1:0715), diphenylacetic acid (1:0765), desoxybenzoin (1:5165), and benzil (1:9015).]

[C with excess ignited Na₂CO₃ at 200° without solvent for 1 hr. gives (11) a mixt. (yield not stated) of both stereoisomeric 1,2-dibenzoyl-1,2-diphenylethylenes (dibenzoylstilbenes): higher-melting isomer [Beil. VII-844], m.p. 232°; lower-melting isomer [Beil. VII-843, VII₁-(453)], m.p. 212-214°.]

[Č with NaSH in alc. soln. in cold gives (16) benzoyl-phenyl-carbinyl mercaptan (desylthiol), m.p. 42-44° (benzoyl ester, m.p. 110-112° (16)), accompanied by two forms of didesyl sulfide, one of m.p. 168-169°, the other of m.p. 128-129° (16).

Behavior with metals. [\bar{C} with Na in C_6H_6 evolves H_2 and on warming gives a mixt. which with aq. followed by dil. acid gives (2) a mixt. of benzoic acid (1:0715) + benzilic acid (1:0770) together with an unidentified neutral oil.]

Behavior with other inorganic reactants. [Č with moist silver oxide in ethylene glycol at 100° for 3 hrs., then boiled 2 hrs., gives (29) 1,2-dibenzoyl-1,2-diphenylethane (bidesyl) [Beil. VII-841, VII₁-(452)], m.p. 254-255° (29).]

CHEMICAL BEHAVIOR OF C WITH ORGANIC REACTANTS

Behavior with arom. hydrocarbons + AlCl₃. $[\bar{C} \text{ with } C_6H_6 (1:7400) + AlCl_3 \text{ gives } (78\% \text{ yield } (17)) (18) (19) \omega, \omega-\text{diphenylacetophenone } (ms-\text{phenyldesoxybenzoin} = \text{triphenyl-vinyl alc.})$ [Beil. VII-522, VII₁-(291)], m.p. 137° (19), 135–136° (17) (18). $-\bar{C}$ with toluene (1:7405) + AlCl₃ gives (77% yield (17)) ω -phenyl- ω -(p-tolyl)acetophenone (α -(p-tolyl)desoxybenzoin), m.p. 97–98° (17). $-\bar{C}$ with mesitylene (1:7455) + AlCl₃ in CS₂ gives (13) ω -phenyl- ω -mesitylacetophenone (α -mesityldesoxybenzoin), m.p. 111–112° (13).] (See also below under reactn. of \bar{C} with RMgX cpds.)

Behavior with organic hydroxy or mercapto compounds. With alcohols (or alkoxides). [Č in MeOH with MeOH/NaOMe gives (80% yield (11)) 1,2-diphenyl-1-methoxy-1,2-epoxyethane, b.p. 194–196° at 16 mm., accompanied by some cis + trans dibenzoylstilbene (see above).]

[Č in EtOH with EtOH/NaOEt gives similarly a prod., b.p. 188° at 12 mm., regarded (11) as 1,2-diphenyl-1-ethoxy-1,2-epoxypropane. — Note, however, that $\bar{\mathbb{C}}$ in EtOH/NaOEt or with alc. NaOH at 25° gives (5) cf. (1) benzoin (1:5210) and that under certain conditions an apparently intermediate benzoin diethylacetal $C_6H_5CH(OH).C(OC_2H_5)_2.-C_6H_5$, m.p. 66-67°, can be isolated (5).]

With phenols (or alkali phenates). [C with phenol + anhydrous K₂CO₃ in acetone refluxed 5 hrs. (20) or C with Na phenate (21) gives (59% yield (20)) desyl phenyl ether (the phenyl ether of benzoin), m.p. 85.5° (21), 85° (20); note that this prod. is isomeric with, but different from, ms-phenylbenzoin [Beil. VIII-211], whose m.p is almost the same; note also that desyl phenyl ether on attempted distillation at ord. press. undergoes a fission into phenol and a cpd. regarded (21) as 2,2,4,4-tetraphenylcyclobutanedione-1,3, m.p. 244-245°.]

With mercaptans. $[\bar{C} + \alpha$ -mercaptoacetic acid (thioglycolic acid) at 100° for 6 hrs. evolves HCl and yields (22) S-desylthioglycolic acid, m.p. 105° (corresp. oxime, m.p. 123°; corresp. semicarbazone, m.p. 178° (22)). — \bar{C} with β -mercaptopropionic acid at 100° for 6 hrs. evolves HCl and yields (16) β -(desylthio)propionic acid, m.p. 108-109°.]

[Č with thiophenol in EtOH/NaOEt gives in good yield (16) desyl phenyl sulfide, m.p. 83-84° (16), 81° (23). — Č in MeOH with aq. sodium thiosalicylate gives (22) S-desylthiosalicylic acid, m.p. 189°.]

Behavior with carbonyl compounds. [For behavior of \bar{C} with cyclohexanone + sodium in di-n-butyl ether see (24).]

Behavior with organic acids (or their salts). [\bar{C} with anhydrous NaOAc in excess Ac₂O refluxed 1 hr. yields (11) mainly the β -stereoisomer, m.p. 153°, of 1,2-diacetoxy-1,2-diphenylethylene [Beil. VI-1026, VI₁-(499)], accompanied by some of the more sol. α -stereoisomer, m.p. 118°.]

 $[\ddot{\mathbf{C}} + \mathbf{K}$ thiobenzoate in abs. alc. boiled 10 min. gives (100% yield (16)) desyl thiobenzoate, m.p. 110-112°.]

[C in aq. alc. KCN does not directly eliminate KCl and give the corresp. desyl cyanide

(ms-cyanodesoxybenzoin) [Beil. X-755, X_1 -(360)] which might be expected although this compd., m.p. 90-92° (25), 89-90° (26), is well known and preparable (yields 60% (25), 47% (26)) from benzyl cyanide + ethyl benzoate and otherwise. — Instead Č in aq. alc. KCN loses HCl and gives (27) (28) 1-cyano-1,2-diphenyl-1,2-epoxyethane (α -cyano- α , β -diphenyl-ethylene oxide) which obviously can exist in two geometrically stereoisomeric forms: one has m.p. 74° (27), 77-78° (28); the other has m.p. 52° (27); for much further detail especially with reference to further reactn. prods. of these epoxynitriles see (27) (28).

Behavior of \tilde{C} with RMgBr reactants. (See also above under behavior of \tilde{C} with hydrocarbons + AlCl₃.)

[\bar{C} with C_6H_6MgBr (2 moles) gives (29) (21) the prod. normally to be expected, viz., 1,1,2,2-tetraphenylethanol-1 [Beil. VI-732, VI₁-(364)], m.p. 236° (21) (30), 230.5° (29); the intermediate ketone, viz., ms-phenyldesoxybenzoin (for consts. see above reference) may sometimes (21) be formed, but for discussion of possible alternative mechanisms see (21) (29).]

Č with the three tolyl MgBr reactants has been studied, but the reaction is complex and shows no tendency to go way through to the expected tetraarylethanols (only one of which has been reported by any means). — [Č with o-tolyl MgBr (2 moles) gives (29) a mixt. of prods., including the expected intermediate ketone, viz, ms-(o-tolyl)desoxybenzoin, m.p. 56-57° (32); note, however, that the 1,2-diphenyl-1,2-di-(o-tolyl)ethanol-1 which should be the end prod. is unknown. — Č with m-tolyl MgBr gives (29) similarly a mixt. of prods. including the intermediate ketone, viz., ms-(m-tolyl)desoxybenzoin, m.p. 83-84° (32), 82.5-83.5° (29), 82-83° (33), but again the ultimate 1,2-diphenyl-1,2-di-(m-tolyl)ethanol-1 is unknown. — Č with p-tolyl MgBr (2 moles) gives (31) the ketone ms-(p-tolyl)desoxybenzoin, m.p. 97-98° (17), 96-97° (31); the ultimate 1,1-diphenyl-1,2-di-(p-tolyl)ethanol-1, m.p. 195-196°, has been obtd. by other means (29).]

Behavior of \bar{C} with amines. With primary amines. $[\bar{C}$ (1 mole) with aniline (2 moles) in alc. at room temp. for 24 hrs. gives (6) N-(desyl)aniline (benzoin anil =ms-anilinodesoxybenzoin) [Beil. XIV-103, XIV₁-(395)], mp. 99°; note that \bar{C} with aniline at 140–150° for 1hr. (34) ppts. aniline hydrochloride and leaves a mixt. contg. benzoin-anil = anilide (cf. (35)) since with benzaldehyde at 150-160° for 1 hr. under CO_2 it yields pentaphenyldihydroimidazole (34). — \bar{C} with p-toluidine in alc. at room temp. for 24 hrs. gives (3) similarly N-(desyl)-p-toluidine (ms-(p-toluidino)desoxybenzoin), m.p. 145°.]

[For corresp. reactns. of \bar{C} with *m*-chloroaniline, *p*-chloroaniline, *m*-bromoaniline, *p*-iodoaniline, *p*-aminophenol, *p*-phenetidine, *p*-aminoacetanilide, or ethyl *p*-aminobenzoate see (3); for study of rate of this group of reactns. see (4); note that o-toluidine, o-chloroaniline, and o-anisidine do not undergo this reactn. (3).]

With secondary amines. [C̄ with Me₂NH (2-3 moles) in alc. in s.t. at 100-110° gives (36) ms-(dimethylamino)desoxybenzoin, m.p. 59-61° (36).]

[\overline{C} (1 mole) with N-methylaniline (2 moles) in alc. refluxed $2\frac{1}{2}$ hrs. gives (47% yield (3)) ms-(N-methyl-N-phenylamino)desoxybenzoin, m.p. 100°; if reactants in alc. are stood at room temp. for 100 days, yield is 61% (3).]

[\bar{C} with piperidine at 100° for 20 min. gives (8) ms-(piperidino)desoxybenzoin [Beil. XX₁-(14)], m.p. 85–86° (8).]

With phenylhydrazine. C (1 mole) with phenylhydrazine (2 moles) in abs. alc. at room temp. for 3 days ppts. phenylhydrazine hydrochloride and yields (37) benzil bis-(phenylhydrazone) = benzil-phenylosazone, m.p. 233° dec. (37) [cf. under benzil (1:9015)].

N-Desylphthalimide [Beil. XXI-480, XXI₁-(374)]: pale yel. cryst. from AcOH. m.p. 157-158° (38), 155-156° (39). [From C with K phthalimide at 100° for 2 hrs, (24% yield (39)); note that C + potassium phthalimide in nitrobenzene at 150-160°

for 1½ hrs. gives a mixt. of N-desylphthalimide with the lower-melting stereoisomer of dibenzovlstilbene (1,2-dibenzovl-1,2-diphenylethylene) [Beil. VII-843, VII₁-(453)], m.p. 208° (39) (see also above).

3:1618 (1) Buck, Ide, J. Am. Chem. Soc. 54, 4363 (1932). (2) Schroeter, Caspar, Ber. 42, 2348-2349 (1909). (3) Cameron, Nixon, Basterfield, Trans. Roy. Soc. Canada (3) 25, III 145-156 (1931); Cent. 1932, I 2032; C.A. 26, 3250 (1932). (4) Cameron, Nixon, Basterfield, Trans. Roy. Soc. Canada (3) 25, III 157-169 (1931), Cent. 1932, I 2033; C.A. 26, 3251 (1932). (5) Ward, J. Chem. Soc. 1929, 1541-1553. (6) Cameron, Trans. Roy. Soc. Canada (3) 23, III 53-60 (1929); Cent. 1930, I 1133, C.A. 24, 610 (1930). (7) McKenzie, Wren, J. Chem. Soc. 97, 481-482 (1910). (8) Henley, Turner, J. Chem. Soc. 1931, 1185. (9) Ward, Org. Syntheses, Coll. Vol. 2 (1st ed.) 159-160 (1943), 12, 20-21 (1932). (10) Taylor, Forscey, J. Chem. Soc. 1930, 2276.

(11) Madelung, Oberwegner, Ann. 194, 224-234 (1931). (12) Curtius, Lang, J. prakt. Chem. (2) 44, 548-549 (1891). (13) Maxwell, Adams, J. Am. Chem. Soc. 52, 2970 (1930). (14) Lachowicz, Ber. 17, 1163 (1884). (15) Richard, Compt. rend. 197, 1432-1434 (1933). (16) Schönberg, Iskander, J. Chem. Soc. 1942, 93-94. (17) Koelsch, J. Am. Chem. Soc. 54, 2051 (1932). (18)Richard, Compt. rend. 200, 754 (1935). (19) Anschutz, Forster, Ann. 368, 93-94 (1909). Bradsher, Rosher, J. Am. Chem. Soc. 61, 1525 (1939).

(21) Richard, Compt. rend. 198, 1242-1244 (1934). (22) Behaghel, Schneider, Ber. 68, 1590, 1593 (1935). (23) Mitchell, Smiles, J. Chem. Soc. 1933, 1529. (24) Allen, Can. J. Research 4, 271-272 (1931). (25) Kohler, Blatt, J. Am. Chem. Soc. 50, 507-508 (1928). (26) Howk, McElvain, J. Am. Chem. Soc. 54, 286 (1932). (27) Kohler, Brown, J. Am. Chem. Soc. 55, 4299-4304 (1933). (28) Richard, Compt. rend. 198, 943-945 (1934). (29) Roger, McGregor, J. Chem. Soc. 1934, 1850-1853. (30) Wegler, Ber. 67, 35-39 (1934).

(31) McKenzie, Roger, McKay, J. Chem. Soc. 1932, 2603. (32) Roger, McKay, J. Chem. Soc. 1933, 336. (33) Roger, McGregor, J. Chem Soc. 1932, 443. (34) Langenbeck, Hutschenreuter, Juttemann, Ann. 485, 54, 57-58 (1931). (35) Strain, J. Am. Chem. Soc. 50, 2221 (1928). (36) Thomson, Stevens, J. Chem. Soc. 1932, 1937. (37) Bodforss, Ber 71, 481 (1939). (38) Neumann, Ber. 23, 995 (1890). (39) McKenzie, Barrow, J. Chem. Soc. 103, 1333 (1913).

3:1620 2,4,5-TRICHLOROPHENOL

$$\begin{array}{c|c} \text{OH} & \text{C}_6\text{H}_3\text{OCl}_3 & \text{Beil. VI} -\\ \text{Cl} & \text{VI}_1-\\ \text{VI}_{2^-}(180) \end{array}$$

Colorless ndls. from alc. or lgr. — Volatile with steam. — Sublimes.

[For prepn. of C from 1,2,4,5-tetrachlorobenzene (3:4115) with MeOH/NaOH in s.t. at 160° for 7 hrs. (yields: 85% (5), 80% (10)) (note that by this method \bar{C} is sometimes sole product (5), at others is accompanied (7) (10) by some of its methyl ether (2,4,5trichloroanisole) (see below)) see indic. refs.; from 2,4,5-trichloroaniline via diazotization in conc. H₂SO₄ as directed followed by htg. at 170-180° (65% yield (9)) see indic. refs.: from 2,4,5-trichloro-1-fluorobenzene with NaOMe see (6); from 3,5,6-trichloro-2-hydroxybenzoic acid by htg. with soda-lime at 185° see (3); from 2,4-dichloro-5-aminophenyl oamino-p-toluenesulfonate via diazotization, use of Cu₂Cl₂ reactn., and subsequent hydrolysis as directed see (4); from 2,5-dichlorophenol (3:1190) with Cl₂ in AcOH (9) or in AcOH + NaOAc (4) see indic. refs.l

 \bar{C} behaves as a weak monobasic acid (ioniz. const. at $25^{\circ} = 4.3 \times 10^{-8}$ (2)) but can be titrated with N/10 aq. NaOH; Neut. Eq. calcd. 197.5, found 197.1 (1). — C forms a spar. sol. K salt (4). — \bar{C} in toluene treated with MeOH/NaOH yields (11) anhydrous Na salt; from aq. this prod. cryst. as pentahydrate (12). — [For prepn. of Na, K, or Li salts see (12), of Ca or Ba salts see (13), of Zn salt see (14). — For use of these salts as fungicides see (11) (12) (13) (14) (15); for use of \bar{C} with triphenyl phosphate as wood preservative see (16).]

Č with Br₂ in AcOH (9) or with excess Br₂/aq. (17) yields 6-bromo-2,4,5-trichlorophenol, cryst. from AcOH or lt. pet., m.p. 81-82° (17), 81° (9) (corresp. benzoate, m.p. 116-117° (9)). — Č with Br₂ in pres. of Fe powder yields (9) 3,6-dibromo-2,4,5-trichlorophenol, ndls. from AcOH, m.p. 195° (9) (corresp benzoate, m.p. 176° (9)).

 \bar{C} treated below 10° with conc. HNO₃ (D=1.43) in AcOII gives (90% yield (5)) 6-nitro-2,4,5-trichlorophenol, pale yel. lfts. from lgr., m.p. 92-93° (5), 81° (9).

Č dislvd. in 20% NaOH refluxed with Me₂SO₄ gives (78.5% yield (5)) (9) corresp. methyl ether (2,4,5-trichloroanisole), ndls. from alc., m.p. 75° (5), 77.5° (9).

- ① 2,4,5-Trichlorophenyl benzoate: ndls. from alc, m.p. 92-93° (9), 91-92° (4), 89-90° (3). [From C in dil. alk. by shaking with benzoyl chloride (9).]
- ② 2,4,5-Trichlorophenoxyacetic acid: m.p. 153° (see 3:4335).

3:1620 (1) Tiessens, Rec. trav. chim. 50, 114 (1931). (2) Tiessens, Rec. trav. chim. 48, 1068 (1929). (3) Farinholf, Stuart, Twiss, J. Am chem Soc. 62, 1240 (1940). (4) Groves, Turner, Sharp, J. Chem. Soc. 1929, 516-517. (5) Harrison, Peters, Rowe, J. Chem. Soc. 1943, 235-237. (6) de Crauw, Rec. trav. chim. 48, 1064-1065 (1929). (7) Holleman, Rec. trav. chim. 39, 736-738 (1920). (8) A G F A, Ger. 349,794, March 9, 1922, Cent. 1922, IV 45. (9) Kohn, Fink, Monatsh 58, 83-86 (1931). (10) A.G F A, Ger. 411,052, March 23, 1925, Cent. 1925, I 2411.

(11) Mills (to Dow Chem Co), U.S. 1,955,080, April 17, 1934, Cent 1934, II 1991. (12) Mills (to Dow Chem Co), U.S. 1,991,329, Feb. 12, 1935, Cent. 1935, II 2430. (13) Mills (to Dow Chem Co), U.S. 2,039,431, May 5, 1936, Cent 1937, I 984 (14) Mills (to Dow Chem Co), U.S. 1,994,002, March 12, 1935, Cent 1935, II 2431 (15) Ellis (to Insulte Co.), U.S. 2,161,654, June 6, 1939, Cent 1939, II 4620 (16) Norton (to Dow Chem. Co), U.S. 2,304,013, Dec. 1, 1942, C.A. 37, 2908 (1943). (17) Fox, Turner, J. Chem. Soc. 1930, 1863

3:1625 1,4,6-TRICHLORONAPHTHALENE

M.P. 69° (4)

68° (1)

65° (2) (3) (5) (7)

58° (1)

56° (2) (3) (7) (8) see text

Ndls. from alc.; spar. sol. boilg. alc. (2). — Volatile with steam. — Sublimes.

 \bar{C} shows the double m.p. phenomena also exhibited by several of its isomers; if the fused \bar{C} in a m.p. tube is allowed to cool and then withdrawn from the bath it soon solidifies to a translucent mass which upon immediate reimmersion melts at 58°, but if left for a short time in the air it becomes opaque and then shows m.p. 68°; the translucent form rarely persists more than 20 min. (1).

[For prepn. of \bar{C} from 5,8-dichloronaphthylamine-2 [Beil. XII-1310] via diazotization and use of Cu_2Cl_2 reactn. see (4); for prepn. of \bar{C} from 1,6-dichloro-4-nitronaphthalene [Beil. V-556] (5) (2), from 4,6-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-162] (6), from 4,7-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-163] (7), from 1,4-dichloronaphthalenesulfonyl chloride-7 [Beil. XI-183] (8) (6), from 1-chloro-4-nitronaphthalene-

sulfonyl chloride-6 [Beil XI-189] (9), from 1-chloro-4-nitronaphthalenesulfonyl chloride-7 [Beil. XI-188] (9), from 1-chloronaphthalene-4,6-bis-(sulfonyl chloride) [Beil. XI-215] (3), or from 1-chloronaphthalene-4,7-bis-(sulfonyl chloride) [Beil. XI-214] (2), each with PCl₅ as directed, see indic. refs.]

[Č treated with ClSO₃H in CS₂ and reaction prod. converted to salts as directed (1) yields sodium 1,4,6-trichloronaphthalenesulfonate-X (corresp. sulfonyl chloride, m.p. 144° (1)).]

[C on oxidn. with dil. HNO₃ in s.t. at 150-160° for several days (8) yields a dichloro-nitro-phthalic acid not further characterized.]

3:1625 (1) Turner, Wynne, J. Chem. Soc. 1941, 247, 254. (2) Armstrong, Wynne, Chem. News 61, 94 (1890). (3) Armstrong, Wynne, Chem. News 62, 162-163 (1890). (4) Claus, Jack, J. prakt. Chem. (2) 57, 3-4 (1898). (5) Cleve, Bull. soc. chim. (2) 29, 500 (1878). (6) Armstrong, Wynne, Chem. News 61, 273, 275 (1890). (7) Cleve, Ber. 24, 3479 (1891). (8) Widman, Ber. 12, 962 (1879). (9) Cleve, Chem. Zig. 17, 398 (1893).

3:1655 1,4-DICHLORONAPHTHALENE

$$\begin{array}{c} \text{Cl} & \text{Cl}_{10}\text{H}_6\text{Cl}_2 & \text{Beil. V - 542} \\ & & \text{V}_{1^-}(262) \\ & & \text{V}_{2^-}(445) \end{array}$$

M.P.	68-69°	(1)		B.P. 2	86-28 7 °	at 740 mm.	(7)
	68°	(2)	(14)	14	47°	at 12 mm.	(2)
		(16)	(22)				
		(24)	(36)				
	67-68°	(3)	(30)				
	67.5°	(15)	(33)				
	67°	(17)					
	67.4-68°	(4)					
	66.6-67°	(5)					
	66.5°	(6)					
	66-67°	(7)	(18)				
	65.5-66.5°	(8)					
	65-66°	(9)					
	63-64°	(10)					

Ndls. from alc.; spar. sol. alc., more sol. AcOH, very eas. sol. acetone.

[For sepn. of \bar{C} from mixts, with α -chloronaphthalene (3:6878) via sulfonation of the latter sec (11); for use of \bar{C} as wood impregnant see (12).]

[For prepn. of \bar{C} from 1-aminonaphthalenesulfonic acid-4 (naphthionic acid) [Beil. XIV-739, XIV₁-(732)] via convn. to diazonium salt and htg. with PCl₅ (13) in POCl₃ (7) (3) (6) see indic. refs.; from 1,4-dichloronaphthylamine-7 [Beil. XII-1310] via diazotization and reactn. with alc. see (14); for prepn. of \bar{C} from 4-chloronaphthalenesulfonyl chloride [Beil. XI-160] with PCl₅ (yields: 65–70% (5), 49% (4)) (15) (16) see indic. refs.; from K 4-bromonaphthalenesulfonate-1 [Beil. XI-164] (17), from naphthalene-1,4-bis-(sulfonyl chloride) [Beil. XI-212] (9), from 4-nitronaphthol-1 [Beil. VI-615] (18), from 1-chloro-4-nitronaphthalene [Beil. V-555, V₁-(264)] (18), with PCl₅ as directed see indic. refs.]

[For prepn. of \tilde{C} from naphthalene (1:7200) with SOCl₂ in s.t. at 170-180° (10), with 2 moles SO₂Cl₂ at 140-160° (19), with Cl₂ + FeCl₃ in CCl₄ at 0° (together with other products) (20), or with HOCl (8) see indic. refs.; from 1-chloronaphthalene (3:6878) with SO₂Cl₂ at 100-180° (21) or with Cl₂ (together with other products) (1) see indic. refs.; for formn.

of \bar{C} from naphthalene 1,2,3,4-tetrachloride (3:4750) on htg. at b.p. (22) or by actn. of alc. KOH (23) (24) (25) (26) (33).]

[\tilde{C} with benzoyl chloride (3:6240) + AlCl₃ in CS₂ yields (27) 1,4-dichloro-8-benzoyl-naphthalene, m.p. 104–105° (27), which with alc. gives (28) isoviolanthrone; for reactn. of \tilde{C} with phthalic anhydride see (29).]

[\bar{C} on mononitration with HNO₃ (D=1.45) yields (30) 1,4-dichloro-8-nitronaphthalene Beil. V-556, V-1(264)], m.p. 92° (30), 93° (31); note that the isomeric 1,4-dichloro-2-nitronaphthalene, m.p. 116.5°, has been obtd. only by indirect means (32).]

[Č on monosulfonation with fumg. H₂SO₄ at 160°, with sulfuric acid monohydrate at ord. temp. (34), or with ClSO₃H in CS₂ (33) yields 1,4-dichloronaphthalenesulfonic acid-6 [Beil. XI-183, XI₁-(41)] (corresp. sulfonyl chloride, m.p. 132° (33), corresp. sulfonamide, m.p. 244° (33)).]

 \bar{C} on oxidn. with boilg. dil. HNO₃ (D=1.3) yields (35) 3,6-dichlorophthalic acid (3:4870); \bar{C} on oxidn. with CrO₃/AcOH yields (36) 5,8-dichloronaphthoquinone-1,4 [Beil. VII-730], yel. ndls. from alc., m.p. 173-174° (36), together with 4,7-dichlorophthalide [Beil. XVII-312], m.p. 163° (36).

3:1655 (1) Turner, Wynne, J. Chem. Soc. 1941, 245. (2) von Auwers, Frühling, Ann. 422, 195 (1921). (3) Weissberger, Sangewald, Hampson, Trans. Faraday Soc. 30, 890 (1934). (4) Beattie, Whitmore, J. Am. Chem. Soc. 55, 1546-1548 (1933). (5) Zil'bermann, Rashevskaya, Martyntseva, J. Applied Chem. (U.S.S.R.) 9, 1832-1840 (1936); Cent. 1937, I 4786, C.A. 31, 2597 (1937). (6) Wahl, Vermeylen, Compt. rend. 184, 334-336 (1927). (7) Erdmann, Ann. 247, 351-352 (1888). (8) Klingstedt, Wiese, Rudback, Acta Acad. Aboensis Math. et Phys. 4, No. 2, 1-36 (1927); Cent. 1928, I 504; C.A. 23, 1309 (1929). *(9) Ferrero, Bolliger, Helv. Chim. Acta 11, 1146-1147 (1928). (10) Meyer, Monatsh. 36, 728-729 (1915).

(11) Holscher (to Deutsche Solvay-Werke), Ger. 695,690, Aug. 1, 1940; C.A. 35, 5519 (1941). (12) Röchling'sche Eisen und Stahlwerke, Ger. 415,228, June 16, 1925, Cent. 1925, II 1239. (13) Cleve, Ber. 10, 1723-1724 (1877). (14) Claus, Philipson, J. prakt. Chem. (2) 43, 60 (1891). (15) Cleve, Bull. soc. chim. (2) 26, 242-243 (1876). (16) Cleve, Arnell, Bull. soc. chim. (2) 39, 62 (1883). (17) Cleve, Jolin, Bull. soc. chim. (2) 28, 516 (1877). (18) Atterberg, Ber. 9, 1187 (1876). (19) Farbwerke Meister Lucius Brüning, Ger. 286,489, Oct. 22, 1913, Cent. 1915, II 677, C.A. 10, 1912 (1916). (20) B.A.S.F., Ger. 234,912, May 26, 1911; Cent. 1911, II 63.

(21) Armstrong, Chem. News 66, 189 (1892).
(22) Krafft, Becker, Ber. 9, 1089 (1876).
(23) Faust, Saame, Ann. 160, 66, 70 (1871).
(24) Widman, Ber. 15, 2161 (1882).
(25) Cleve, Ber. 23, 954 (1890).
(26) Armstrong, Wynne, Chem. News 58, 264 (1888).
(27) I.G., French 664,016, Aug. 28, 1929, Cent. 1930, I 1221.
(28) I.G., Brit. 303,123, Feb. 20, 1929, Cent. 1929, I 2705.
(29) Waldmann, J. prakt. Chem. (2) 131, 80 (1931).
(30) Widman, Bull. soc. chim. (2) 28, 509 (1877).

(31) Friedlander, Karamessinis, Schenk, Ber. 55, 46, 50 (1922). (32) Hodgson, Crook, J. Chem. Soc. 1936, 1500-1503. (33) Armstrong, Wynne, Chem. News 61, 273, 284 (1890). (34) B.A.S.F., Ger. 229, 912, Jan. 11, 1911, Cent. 1911, I 358. (35) Atterberg, Bull. soc. chim. (2) 27, 409 (1877), Ber. 10, 547 (1877). (36) Guareschi, Ber. 19, 1155 (1886).

3:1670 3,5-DICHLOROPHENOL

Cryst. (from pet. eth. (1)). — Spar. sol. cold aq., fairly eas. sol. hot aq. (2). Volatile with steam (3). [For study of dissociation const. see (7).]

[For prepn. from 3,5-dichloroaniline [Beil. XII-626] via diazo reaction see (1) (2) (3) (4); for prepn. from 1,3,5-trinitrobenzene via 3-amino-5-chloroanisole see (5) or via 3,5-dichloroanisole see (6).]

 \bar{C} is readily nitrated; e.g., \bar{C} (16 g.) dislvd. in a soln. of NaNO₃ (12 g.) in aq. (180 ml.), treated during 1 hr. at 90–100° by grad. addn. of dil. H₂SO₄ (1:5; 48 ml.), htd. 2 hrs. then steam-distd., gave (3) in distillate 3,5-dichloro-2-nitrophenol (5 g.), lemon-yel. ndls. from pet. ether m.p. 51°, and by repeated hot dil. HCl extraction of tarry residue 3,5-dichloro-4-nitrophenol (6 g.) pale yel. ndls. from aq., m.p. 150° (3). [This latter product also results from the action of nitrous acid (3).]

C dislyd. in 4 pts. AcOH and treated with 3 pts. fumg. HNO₃ for ¾ hr. at 70° (2) gives (60% yield (2)) of 3,5-dichloro-2,4,6-trinitrophenol, pale yel. pr. from AcOH, m.p. 139-140° cor. (2).

C dislyd in 5 pts. AcOH gives with Br₂ (as specified (4)) 100% yield of 3,5-dichloro-2,4,6-tribromophenol, cryst. from AcOH, m.p. 189° (4).

C dislyd in aq. NaOH and shaken with (CH₃)₂SO₄ gives the methyl ether, 3,5-dichloroanisole, m.p. 39° (6). [The value of 68° given in Ref. 6, p. 104, is probably erroneous.]

- ① 3,5-Dichlorophenyl acetate: m.p. 38° (5).
- (5) 3.5-Dichlorophenyl benzoate: m.p. 55° (5).

3:1670 (1) Blanksma, Rec. trav. chim. 27, 29-30 (1908). (2) Willstatter, Schudel, Ber. 51, 784-787 (1918) (3) Hodgson, Wignall, J. Chem. Soc. 1927, 2217-2218. (4) Kohn, Pfeifer, Monatsh.
 48, 237-239 (1927). (5) Hodgson, Wignall, J. Chem. Soc. 1926, 2077-2079. (6) Holleman, Rec. trav. chim. 37, 103-107, 201 (1918). (7) Murray, Gordon, J. Am. Chem. Soc. 57, 110-111 (1935).

M.P.	69.5°	(1)	B.P. 246°	at 760 mm. (1)
	69° u.c.	(2)	245°	(8)
	69°	(3) (4)	243.5-244.5°	(12)
	68°	(5) (6) (7) (8)	242-246°	at 748 mm. (9)
	67-68°	(9) (10) (11)		
		(12) (23)		
	67.0°	(13)		
	67°	(14)		
	66.7°	(15)		
	66-67° cor.	(16)		

Colorless cryst. from lgr. — Ndls. with 1 mole solvate from AcOH, latter lost over CaO (17).

 $\bar{\mathbf{C}}$ is almost insol. aq.: 1000 g. aq. at 11.2° dis. 0.51 g. $\bar{\mathbf{C}}$ {14}; at 25.4°, 0.858 g. $\bar{\mathbf{C}}$ {14}; at 96°, 2.43 g. $\bar{\mathbf{C}}$ {14}. — $\bar{\mathbf{C}}$ is volatile with steam, but not from alk. soln (difference and sepn. from o-chlorophenol (3:5980) or p-chlorophenol (3:0475) {18}). — $\bar{\mathbf{C}}$ is eas. sol. alc. or ether.

Binary systems contg. \bar{C} . — \bar{C} + nitrobenzene: this system forms a 1:1 molecular compound, m.p. 31°; this compd. forms with \bar{C} a cutectic, m p 28 7° contg. 65 wt. % \bar{C} , and with nitrobenzene a cutectic, m p. + 2.0° contg. 15 5 wt. % \bar{C} ; for data and f p./compn. diagram see (13). — \bar{C} + diphenylamine: for partial f p./compn. data and diag. see (19). — \bar{C} + 2,4,6-tribromophenol: for f.p./compn. data and diag. see (20). — \bar{C} + $\alpha,\alpha,\alpha,\alpha'$ -tetramethylphthalan: for study of this system see (15). — \bar{C} + 2,4,6-trinitroresorcinol (styphnic acid): forms no mol. cpd. but gives a cutectic, m.p. 60° contg. 91.8% \bar{C} (21).

PREPARATION OF C

From phenol. By direct action of chlorine. [For prepn. of \tilde{C} from phenol (1:1420) with Cl_2 see (3) (for very old initial work of (22) (12)); with Cl_2 + aq. alk. (i.e., with NaOCl) see (23) (16) (24).]

By indirect action of chlorine. [For prepn. of \bar{C} from phenol (1:1420) by chlorination with ethyl N,N-dichlorocarbamate (25), with N,N'-dichlorourea (26), with conc. HCl + 30% H₂O₂ (27), or with HCl + KClO₃ (28) (29) see indic. refs]

From other phenols or their relatives. [For formn. of \bar{C} from 2,4,6-trichloro-3-hydroxybenzaldehyde (6) by elimination of the aldehyde group with 50% aq. KOH at 60-70° for 4 hrs. (89.9% yield) see (6); from 2,4,6-trichloro-3-bromophenol (see below) or from 2,4,6-trichloro-3,5-dibromophenol (see below) by replacement of Br by H through use of Zn + AcOH see (9); from 2,4,6-tribromophenol [Beil. VI-203, VI₁-(107)] by replacement of all bromine by chlorine using Cl₂ in AcOH see (30).]

[For form. of \tilde{C} from phenol-p-sulfonic acid [Beil. XI-241, XI₁-(55)] (10) or its alkali salts (31) (32) in aq. soln. with Cl_2 (100% yield (10)) see indic. refs.; from aq p-hydroxyazobenzene [Beil. XVI-96, XVI₁-(233)] (75% yield (11)), from benzyl phenyl ether [Beil. YI-432, VI₁-(220)] (33), from o-hydroxybenzyl alcohol (saligenin) (1:1490) (34) with Cl_2 see indic. refs.; from dipotassium salt of salicylic acid (1:6780) with aq. KOCl (4 moles) see (8).

From other miscellaneous sources. [For formn. of \tilde{C} from aniline in HCl soln. with Cl₂ see (35); from 2,4,6-trichloroamline via diazotization and subsequent hydrolysis as directed see (7); from indigo [Beil. XXIV-417, XXIV₁-(370)] in aq. suspension with Cl₂ see (36) (37); from benzene (1:7400) with Cl₂O see (38); from 2,4,6-trichlorophenyl hypochlorite (see below) by warming with acids or alkalies see (75).]

USES OF C (OR ITS SALTS)

Although the topic cannot here be exhaustively pursued, the bactericidal, fungicidal, and general antiseptic action of \bar{C} or its salts has attracted much attention [for examples of useful articles in this general connection, see (39) (40) (41) (42) (43) (44) (45) (46); for patents on use of \bar{C} or its salts in the indicated fields see the following: for use of \bar{C} (with triaryl phosphates) as wood preservative (47), as preservative for glue (48), as insecticide and fungicide for board-like compns. from vegetable fibers (49), as bactericide (50) (51), as Na \bar{A} for anti-mildew treatment of textiles (52), as textile asst. in mercerization (53); for various complexes contg. \bar{C} and intended for use as insecticides, etc., see (54) (55) (56)].

CHEMICAL BEHAVIOR OF C

Reduction of \bar{C} . [The catalytic hydrogenation of \bar{C} apparently has not been extensively studied, but it is said (57) to be more stable toward $H_2 + PdCl_2$ than the corresponding 2,4,6-tribromophenol.]

Oxidation of \bar{C} . \bar{C} on oxidn. gives various products according to circumstances [e.g., \bar{C} in 2 N H₂SO₄ on electrolytic oxidn. gives (58) 2,6-dichlorohydroquinone (3:4600); \bar{C} on oxidn. with CrO₃/AcOH (59) (60) (61) (62) (63), with cold fumg. HNO₃ (12) (63), with HNO₃/H₂SO₄ (64), with NO + NO₂ in alc. (65) (66) or AcOH (61), or with PbO₂ in AcOH or C₆H₆ (61) gives (yields: 69% (59), 45% (60), 27% (61)) 2,6-dichlorobenzoquinone-1,4 (3:3750) (note that this product may be accompanied (61) by more or less 2-chloro-6-(2',4',6'-trichlorophenoxy)benzoquinone-1,4, m.p. 134-135°, and 2,6-bis-(2',4',6'-trichlorophenoxy)benzoquinone-1,4, m.p. 245°, which resemble the main prod. in appearance, composition, and behavior (61))].

[C on oxidn. with boilg. mixt. of conc. HNO₃ + HCl gives (16) 2,3,5-trichlorobenzoquinone-1,4 (3:4672).]

[\bar{C} on oxidn. with ClSO₃H (67), with Cl₂ + fumg. H₂SO₄ followed by ClSO₃H (68), with aqua regia (69) (70) (72), with HCl + KClO₃ (28) (16), with CrO₃/AcOH (71) or K₂Cr₂O₇/H₂SO₄ (71) gives (90% yield (68)) 2,3,5,6-tetrachlorobenzoquinone-1,4 (chloranil) (3:4978).]

[For study of oxidn. potential of C see (73).]

Nuclear substitution of \bar{C} . Chlorination. $[\bar{C}$ in HCl suspension with Cl₂ (74) or in AcOH soln. with Ca(OCl)₂ (75) gives 2,4,6-trichlorophenyl hypochlorite (2,4,4,6-tetrachlorocyclohexadien-2,5-one-1) [Beil. VII-147, VII₁-(96)], scales from ether/pet. ether, m.p. 122° (75) (10), 121-122° (76), 119° (74)]

[\tilde{C} with $Cl_2 + SbCl_5$ at not above 130° gives (77) 2,3,4,4,5,6-hexachlorocyclohexadien-2,5-one-1 ("hexachlorophenol") (3:3180), m.p. 107°.]

[$\bar{\mathbb{C}}$ with Cl_2 (3) in pres. of I_2 at 40° (78), or $\bar{\mathbb{C}}$ with Cl_2 in CCl_4 in pres. of FeCl₃ (79), or $\bar{\mathbb{C}}$ with Cl_2 in pres. of SbCl₃, I_2 , or FeCl₃ at 70–75° (80), gives 2,3,4,6-tetrachlorophenol (3:1687), m p. 69°.]

[C with Cl₂ in pres. of SbCl₃, I₂, or FeCl₃ at 135-140° gives (81) pentachlorophenol (3:4850), m.p. 190°.]

[C with FeCl₃ (no details) yields (14) 1,2,3,5-tetrachlorobenzene (3:0915), m.p. 51°.]

Bromination. [C with Br₂/aq. KBr soln. as directed (82) (83) gives a monobromo derivative of C frequently designated as "trichlorophenol bromide"; which of the three structures 4-bromo-2,4,6-trichlorocyclohexadien-2,5-one-1, or 2,4,6-trichlorophenyl hypobromite should be assigned to this prod. has never been decisively settled (83); however, on oxidn. with fumg. HNO₃ it gives (82) 2,6-dichlorobenzoquinone-1,4 (3:3750) and with cone. H₂SO₄ at 100° isomerizes (82) to 3-bromo-2,4,6-trichlorophenol, m.p. 73° (9) (corresp. benzoate, mp 117° (82))]

[C with Br₂ (large excess) + Fe powder at room temp. for 24 hrs. gives (100% yield (84)) cf. (85) 3,5-dibromo-2,4,6-trichlorophenol, cryst. from AcOH, m.p. 204° cor. (corresp. methyl ether, m.p. 127°; corresp. benzoate, m.p. 196° (84)).]

Nutration. [The direct nitration of \bar{C} has not been reported, presumably because nitration reagents readily oxidize free \bar{C} to 2,6-dichlorobenzoquinone-1,4 (3:3750) (see above under oxidn. of \bar{C}). — However, both possible nitration products have been obtained by indirect means: for 3-nitro-2,4,6-trichlorophenol, m.p. 71-72°, see (86); for 3,5-dinitro-2,4,6-trichlorophenol, m.p. 165-167°, see (87).]

Sulfonation. [C with fumg. H₂SO₄ (65% SO₃) at 50° gives (93% yield (88) 2,4,6-tri-chlorophenolsulfonic acid-3.]

Miscellaneous [Č with SCl₂ + AlCl₃ in CS₂ or CCl₄ gives (89) a product, m.p. 285°, which may be 3,3'-dihydroxy-2,4,6,2',4',6'-hexachlorodiphenyl sulfide]

Reactions of the phenolic group of C. (See also under O's below.)

Acidic character of \tilde{C} . \tilde{C} in aq. behaves as an acid and can be titrated with N/10 aq. NaOH (3); Neut. Eq. = 197 5. — [Data on dissoc. const. of \tilde{C} include the following: in aq. at 25° 1.0×10^{-7} (90), 3.9×10^{-7} (2) cf. (91) (92). — For study of acid strength of \tilde{C} in formamide see (93). — For study of exchange reaction of \tilde{C} with heavy water see (94).]

Salts of \bar{C} . [NH₄ \bar{A} : spar. sol. cold aq., eas. sol. hot aq. (22), somewhat spar. sol. alc. (24); loses NH₃ in air (12). — K \bar{A} , ½H₂O: (24) (12). — Na \bar{A} : prepn. (95), behavior with I₂ in various solvents (95) (96), behavior with chloroacetone (3:5425) giving acctonyl 2,4,6-trichlorophenyl ether, m.p. 75° (96).]

 $Mg\bar{A}.2H_2O$: eas. sol. aq. (12). — $Ba\bar{A}_2.4H_2O$: spar. sol. aq. (12). — $Pb\bar{A}_2$ (12).

AgA.H₂O: yellow (97) [study of decompositions (98) (96) (99)].

Etherification of \bar{C} . (See also below under \mathbb{O} 's.)

[\bar{C} with 1,2-dibromoethane (ethylene dibromide) in alk. soln. gives (100) β -bromoethyl 2,4,6-trichlorophenyl ether, m.p. 47–48°. — \bar{C} with ethylene oxide (1:6105) in alc. NaOEt gives (101) β -hydroxyethyl 2,4,6-trichlorophenyl ether, m.p. 77° (101) (for study of rate of this reaction see (102)). — \bar{C} (as Na \bar{A}) with benz-o-chlorophenylimino-chloride gives (103) N-(o-chlorophenyl)benzimino 2,4,6-trichlorophenyl ether, m.p. 99–100°, which at 250–270° for 2 hrs. rearr. (103) to the N-benzoyl derivative (m.p. 131–132°) of 2,4,6,2'-tetrachloro-diphenylamine. — \bar{C} with 2,4,6-trichlorobenzyl chloride + NaOH gives (104) 2,4,6-trichlorobenzyl 2,4,6-trichlorophenyl ether, m.p. 101–103°.]

Esterification of \bar{C} . (See also below under \mathbb{D} 's.)

- [\bar{C} with SOCl₂ in pyridine + C₆H₆ gives (4) bis-(2,4,6-trichlorophenyl) sulfite, cryst. from C₆H₆, m p. 87-88°; note, however, that this prod. is unstable and even within a few hours reverts to \bar{C} .]
- [\bar{C} with PCl₅ in C₆H₆ gives (105) bis-(2,4,6-trichloropnenoxy)phosphoryl chloride, (C₆H₂OCl₃)P(O)Cl, cryst. from C₆H₆, m.p. 126-129° (105). (Note that \bar{C} with PCl₅ in s.t. at 200-300° gives also (106) some 1,2,3,5-tetrachlorobenzene (3:0915).) \bar{C} (3 moles) with POCl₃ (1 mole) refluxed several days gives (107) tris-(2,4,6-trichlorophenyl) phosphate, m.p. 201° (107).]
- [\overline{C} (2 moles) with COCl₂ (3:5000) in aq. alk. gives (108) bis-(2,4,6-trichlorophenyl) carbonate, m.p. 153-154° (109).]
 - ② 2,4,6-Trichlorophenyl methyl ether (2,4,6-trichloroanisole) [Beil. VI-192]: cryst. from alc., m.p. 61-62° (9), 60° (110) (111), 59.5° (112); b.p. 240° cor. at 738 mm. (110) cf. (87). [From C with Me₂SO₄ + 15% KOH (87); for crystallographic data see (82); for attempted cleavage with pyridine or piperidine see (113); for nitration see (87).]
 - 2,4,6-Trichlorophenyl ethyl ether (2,4,6-trichlorophenetole) [Beil. VI-192, VI₁-(104)]:
 m.p. 43-44° (12), b.p. 246° (12). [From K\(\bar{A}\) + EtI (12) or from Ag\(\bar{A}\) + EtI (98).]
 - —— 2,4,6-Trichlorophenyl acetate: oil, b.p. 261-262° (114). [From C with AcCl (114).] D 2,4,6-Trichlorophenyl benzoate [Beil. IX-117]: m.p. 75.5° (9). 74° (115), 73-74° (6),
 - (115), 73-74 (15), 73-74 (15), 70° (14). [From C with benzoyl chloride (3:6240) in pres. of aq. NaOH (115) (9); for study of rate of benzoylation of C at 25° and 85° see (116).]
 - ---- 2,4,6-Trichlorophenyl o-nitrobenzoate: unreported.
 - 2,4,6-Trichlorophenyl m-nitrobenzoate: unreported.
 - 2,4,6-Trichlorophenyl p-nitrobenzoate: m.p. 106° (115).
 - ---- 2,4,6-Trichlorophenyl 3,5-dinitrobenzoate: unreported.
 - **D 2,4,6-Trichlorophenyl benzenesulfonate:** m.p. 66° (117). [From C with benzenesulfonyl chloride in aq. alk. (117).]
 - D 2,4,6-Trichlorophenyl o-nitrobenzenesulfonate: m.p 142° (118). [From $\ddot{\textbf{C}}$ with o-nitrobenzenesulfonyl chloride + $\textbf{K}_2\textbf{CO}_3$ in acetone (118)]
 - 2.4.6-Trichlorophenyl p-toluenesulfonate: unreported.
 - --- 2,4,6-Trichlorophenyl phenyl ether: unreported.
 - 2,4,6-Trichlorophenyl 2,4-dinitrophenyl ether: m.p. 136° (119). [From C with 2,4-dinitrochlorobenzene in alc. alk. (119).]
 - ---- 2,4,6-Trichlorophenyl benzyl ether: unreported.
 - 2,4,6-Trichlorophenyl p-nitrobenzyl ether: unreported.
 - 2,4,6-Trichlorophenoxyacetic acid: m.p. 177° (120).
 - 2,4,6-Trichlorophenyl N-phenylcarbamate: unreported.
 - D 2,4,6-Trichlorophenyl N-(p-bromophenyl)carbamate: pl. from C₆H₆ + EtOAc, m.p. 162-164° cor. (121). [From C with p-bromobenzazide (121) in lgr. (121).]
 - **D** 2,4,6-Trichlorophenyl N-(p-iodophenyl)carbamate: m.p. 172-173° (122). [From \bar{C} with p-iodobenzazide (122) in lgr. (122).]

- **D 2,4,6-Trichlorophenyl** N-(m-nitrophenyl)carbamate: white rods from lgr., m.p. 165-167° u.c.; 169-170° cor. (123). [From \bar{C} with m-nitrobenzazide (123) in lgr. (123).]
- **② 2,4,6-Trichlorophenyl** N-(p-nitrophenyl) carbamate: pale yel. rods from lgr., m.p. 166° cor. (124). [From \bar{C} with p-nitrobenzazide (124) in lgr. (124).]
- ---- 2,4,6-Trichlorophenyl N-(3,5-dinitrophenyl)carbamate: unreported.
- Q 2,4,6-Trichlorophenyl N-(3,5-dinitro-4-methylphenyl)carbamate: yel. pr. from lgr. or EtOAc, m.p. 195-196° u.c., 201-202° cor. (125). [From C with 3,5-dinitro-4-methylbenzazide (125) in lgr. (125)]
- **2.4.6-Trichlorophenyl** $N-(\alpha-naphthyl)$ carbamate: unreported.
- **D 2,4,6-Trichlorophenyl** $N-(\beta-\text{naphthyl})$ carbamate: pr. from lgr., m.p. 157-158° u.c., 161-162° cor. (126). [From \bar{C} with β -naphthyl isocyanate (126) or β -naphthazide (126) in lgr. (126)]
- **D 2,4,6-Trichlorophenyl** N,N-diphenylcarbamate: m.p. 143° (127). [From $\bar{\mathbf{C}}$ with N,N-diphenylcarbamyl chloride (127).]
- 3:1673 (1) Jaeger, Z. anory. allgem. Chem. 101, 129 (1917).
 (2) Tiessens, Rec. trav. chim. 48, 1068 (1929).
 (3) Tiessens, Rec. trav. chim. 50, 115-116 (1931).
 (4) Richter, Ber. 49, 2344 (1916).
 (5) Hassel, Naeshagen, Z. physik. Chem. B-12, 86 (1931).
 (6) Lock, Monatsh. 55, 312 (1930).
 (7) Cain, Norman, J. Chem. Soc. 89, 23-24 (1906).
 (8) Lassar-Cohn, Schultze, Ber. 38, 3301 (1905).
 (9) Kohn, Fink, Monatsh. 58, 76, 87-89 (1931).
 (10) Datta, Mitter, J. Am. Chem. Soc. 41, 2032 (1919).
- (11) Schmidt, J. prakt. Chem. (2) 85, 237-238 (1912). (12) Faust, Ann. 149, 149-155 (1869). (13) Hrynakowski, Szmyt, Z. physik Chem. A-182, 111, 114-115 (1938). (14) Daccomo, Ber. 18, 1163-1164 (1885). (15) Bennett, Wain, J. Chem. Soc. 1936, 1118. (16) Leger, Compt. rend. 146, 696 (1908), Bull. soc. chim. (4) 3, 578-582 (1908). (17) van Erp, Rec. trav. chim. 30, 281 Note (1911). (18) Takagi, Ishimasa, J. Pharm. Soc. Japan 1925, No. 517, 17-18, Cent. 1926, 182; C.A. 20, 2669 (1926). (19) Giua, Cherchi, Gazz. chim. ital. 49, II 269, 282 (1919). (20) Kuster, Wurfel, Z. physik. Chem. 50, 74-80 (1904).
- (21) Efremov, Ann. inst. anal. phys-chim. (U.S.S.R.) 5, 75-141 (1931), Cent. 1934, I 3734; C.A. 27, 277 (1933). (22) Laurent, Ann. chim. (2) 63, 27-33 (1836), (3) 3, 206-211 (1841), Ann. 23, 60-71 (1837); 43, 209-212 (1842). (23) Chulkov, Parini, Statoselets, Org. Chem. Ind. (U.S.S.R.) 3, 97-101 (1937); Cent. 1938, I 1419; C.A. 31, 4967 (1937). (24) Chandelon, Bull. soc. chim. (2) 38, 116-124 (1882). (25) Chabrier de la Saulmere, Ann. chim. (11) 17, 353-370 (1942); C.A. 38, 3256 (1944); Compt. rend. 213, 400-402 (1941); C.A. 37, 2010 (1943). (26) Likhosherstov, J. Russ. Phys.-Chem. Soc. 61, 1019-1023, 1025-1028 (1929); Cent. 1930, I 1924; C.A. 24, 836 (1930). (27) Marsh, J. Chem. Soc. 1927, 3164. (28) Hofmann, Ann. 52, 57, 62 (1844). (29) Graebe, Ann. 146, 8, 12 (1868). (30) Renedikt, Schmidt, Monatsh. 4, 604 (1883).
- (31) Tanaka, Kutani, J. Pharm. Soc. Japan No. 541, 196-199 (1927), Cent. 1927, II 51, C.A. 21, 2255 (1927). (32) Vogel, J. prakt. Chem. (1) 94, 449-450 (1865). (33) Sintenis, Ann. 161, 338 (1872). (34) Piria, Ann. 56, 47 (1845). (35) Hofmann, Ann. 47, 68 (1843), 53, 8, 35 (1845). (36) Erdmann, J. prakt. Chem. (1) 19, 330, 335 (1840). (37) Laurent, Ann. chim. (3) 3, 500 (1841); J. prakt. Chem. (1) 25, 472 Note (1842). (38) Scholl, Norr, Ber. 33, 726 (1900). (39) Mel'nikov, Avetesyan, Rokitskaya, Compt. rend. acad. sci. U.R S.S. 31, 123-124 (1941); Cent. 1942, II 2055; C.A. 37, 950-951 (1943). (40) Ordal, Proc. Soc. Expt. Biol. Med. 47, 387-389 (1941); C.A. 35, 6061 (1941).
- (41) Thorburn, Vincent, J. Australian Inst. Agr. Sci. 7, 29-31 (1941); C.A. 35, 7719 (1941). (42) Lebduska, Pidra, Zent. Bakt. Parasitenk. I Abt., Orig. 145, 425-438 (1940), C.A. 35, 8008 (1941). (43) Richardson, Hide and Leather 99, No. 19, 28, 38 (1940), C.A. 34, 4605 (1940). (44) Caius, Kamat, Naidu, Indian J. Med. Research 15, 327-332 (1927); Cent. 1928, I 1538; C.A. 23, 1926 (1929). (45) Caius, Naidu, Jang, Indian J. Med. Research 15, 117-134 (1927); Cent. 1929, II 56; C.A. 21, 3922 (1927); 22, 4562 (1928). (46) Iwanowski, Turski et al., Przemysł Chem. 16, 205-221 (1932); Cent. 1933, I 867; C.A. 27, 3796 (1933). (47) Norton (to Dow Chem. Co.), U.S. 2,304,013, Dec. 1, 1942; C.A. 37, 2908 (1943). (48) Britton, Mills (to Dow Chem. Co.), U.S. 1,946,057, Feb. 6, 1934; Cent. 1934, I 3162; [C.A. 28, 2568 (1934)]. (49) Ellis (to Insulite Co.), U.S. 2,161,654, June 6, 1939; Cent. 1939, I (4620; [C.A. 33, 7568 (1939)]. (50) I.G., French 709,788, Aug. 13, 1931; Cent. 1932, I 1804; C.A. 26, 1060 (1932).
- (51) I.G., Austrian 126,151, Feb. 11, 1932; Cent. 1932, II 426; not in C.A. (52) British Dyestuff Corp., Renshaw, Fairbrother, Brit. 259,690, Nov. 11, 1926; Cent. 1927, I 667; C.A. 21, 3433

- (1927). (53) Brodersen, Waldmüller, Ger. 576,384, May 10, 1933; Cent. 1933, II 473; C.A. 27, 3833 (1933). (54) Urbschat, Heckmanns (to I.G.), Ger. 552,150, June 11, 1932; Cent. 1932, II 1500; C.A. 26, 4427 (1932). (55) Heckmanns, Urbschat (to I G.), Ger. 545,642, March 4, 1932; Cent. 1932, II 759, C.A. 26, 3610 (1932). (56) Brodersen, Ext (to I G.), Ger. 442,432, March 28, 1927, Cent. 1927, II 487; not in C.A. (57) Mladenovic, Bull. soc. chum. roy. Yougoslav. 4, 187-195 (1933), Cent. 1934, II 2354; [C.A. 28, 5426 (1934)]. (58) Fichter, Stocker, Ber. 47, 2016 (1914). (59) Conant, Fieser, J. Am. Chem. Soc. 45, 2202 (1923). (60) Hunter, Morse, J. Am. Chem. Soc. 55, 3701, 3704 (1933).
- (61) Hunter, Morse, J. Am. Chem. Soc. 48, 1615-1624 (1926). (62) Kehrmann, Tiessler, J. prakt. Chem. (2) 40, 481 (1889). (63) Ling, J. Chem. Soc. 61, 559 (1892). (64) Guareschi, Daccomo, Ber. 18, 1170 (1885). (65) Weselsky, Ber. 3, 646 (1870). (66) Lampert, J. prakt. Chem. (2) 33, 381 (1886). (67) Schuloff, Pollak, Chem. Ztq. 56, 569-570 (1932); Cent. 1932, II 1510; [C.A. 26, 5086 (1932)]. (68) Heimberg, Ger. 511,209, Nov. 7, 1930; Cent. 1931, I 1360; C.A. 25, 1266 (1931). (69) Kempf, Mochrke, Ber. 47, 2619-2620 (1914). (70) Kempf, Mochrke, Ger. 256,034, Feb. 4, 1913, Cent. 1913, I 758, C.A. 7, 2096-2097 (1913).
- (71) Levy, Schultz, Ann. 216, 160 (1881).
 (72) Datta, Chatterjee, J. Am. Chem. Soc. 38, 1819 (1916).
 (73) Fieser, J. Am. Chem. Soc. 52, 5234 (1930).
 (74) Benedikt, Monatsh. 4, 233-235 (1883).
 (75) Zincke, Schaum, Bcr. 27, 545-546 (1894).
 (76) King, McCombie, J. Chem. Soc. 103, 226 (1913).
 (77) Barral, Bull. soc. chim. (3) 11, 559-560 (1894).
 (78) Kohn, Pfeifer, Monatsh. 48, 233-244 (1927).
 (79) Michael, Buschmann, Ger. 527,393, June 19, 1931, Cent. 1931, II 2785, [C.A. 25, 4556 (1931)].
 (80) Barral, Grosfillex, Bull. soc. chim. (3) 27, 1175-1176 (1902).
- (81) Barral, Jambon, Bull. soc. chim. (3) 23, 822-825 (1900) (82) Kohn, Rabinowitsch, Monatsh. 48, 347-356 (1927). (83) Lauer, J. Am. Chem. Soc. 48, 442-451 (1926). (84) Kohn, Dömötor, Monatsh. 47, 212-214 (1926). (85) Korczynski, Reinholz, Schmidt, Roczniki Chem. 9, 731-740 (1929); Cent. 1930, I 2076, [C.A. 24, 1858 (1930)]. (86) Fox, Turner, J. Chem. Soc. 1930, 1860. (87) Kohn, Heller, Monatsh. 46, 95 (1925). (88) Weiler, Better (to I.G.), Ger. 583,055, Aug. 24, 1931, Cent. 1932, II 2370-2371; C.A. 27, 735 (1933). (89) Muth (to I.G.), Ger. 583,055, Aug. 28, 1933, Cent. 1933, II 3883, C.A. 28, 179 (1934). (90) Hantzsch, Ber. 32, 3070 (1899).
- (91) Ogston, J. Chem. Soc. 1936, 1713.
 (92) Murray, Gordon, J. Am. Chem. Soc. 57, 110-111
 (1935).
 (93) Verhoek, J. Am. Chem. Soc. 58, 2581 (1936).
 (94) Small, Wolfenden, J. Chem. Soc. 1936, 1814.
 (95) Hunter, Seyfried, J. Am. Chem. Soc. 43, 154-159 (1921).
 (96) Hunter, Whitney, J. Am. Chem. Soc. 54, 1167-1173 (1932).
 (97) Hantzsch, Scholtze, Ber. 40, 4879 (1907).
 (98) Hunter, Olson, Daniels, J. Am. Chem. Soc. 38, 1761-1771 (1916).
 (99) Hunter, Rathmann, J. Gen. Chem. 7, 2230-2234 (1937). Cent. 1938, I 3331, C. A. 32, 518 (1938).
 (100) Jacobs, Heidelberger, J. Biol. Chem. 21, 442 (1915).
- (101) Boyd, Marle, J. Chem. Soc. 105, 2136 (1914). (102) Boyd, Thomas, J. Chem. Soc. 115, 1242 (1919). (103) Chapman, J. Chem. Soc. 1929, 570 (104) Holt (to du Pont Co.), U.S. 2,073,010, March 9, 1937; Cent. 1937, I 5058; C.A. 31, 3065 (1937). (105) Anschütz, Boedeker, Ann. 454, 106-107 (1927). (106) Zeharia, Cent. 1896, I 100 (107) Breusch, Keskin, Rev. faculté sci. univ. Istanbul 7-A, 182-189 (1942), C.A. 38, 1483 (1944). (108) Barral, Morel, Bull. soc. chim. (3) 21, 724-726 (1899). (109) Barral, Compt. rend. 138, 911 (1904). (110) Hugounenq, Ann. chim. (6) 20, 521-524 (1890).
- (111) Durrans, J. Chem. Soc. 123, 1426 (1923). (112) Lock, Monatsh. 62, 185 (1933). (113) Cahn, J. Chem. Soc. 1931, 1122. (114) Fischer, Ann. Suppl. 7, 184–185 (1870). (115) Raiford, Taft, Lankelma, J. Am. Chem. Soc. 46, 2056 (1924). (116) Bernouilli, St. Goar, Helv. Chim. Acta 9, 756–757 (1926). (117) Minovici, Bul. soc sci. Bucuresci 2, 131 (1893). (118) Tozer, Smiles, J. Chem. Soc. 1938, 2056. (119) Bost, Nicholson, J. Am. Chem. Soc. 57, 2368–2369 (1935). (120) Bischoff, Ber. 33, 1605 (1900).
- (121) Sah, Cheng, Rec. trav. chim. **58**, 592-593 (1939). (122) Sah, Young, Rec. trav. chim. **59**, 357-363 (1940), C.A. **35**, 4363 (1941). (123) Sah, Woo, Rec. trav. chim. **58**, 1013-1015 (1939). (124) Sah, Cheng, Rec. trav. chim. **58**, 595-597 (1939). (125) Sah, Rec. trav. chim. **58**, 587, 589 (1939). (126) Sah, Rec. trav. chim. **58**, 454-458 (1939). (127) Korczynski, Gazz. chim. ital. **53**, 96-97 (1923).

Beil. II - 210

II1--

 Π_2 —

3:1676 DECACHLORODIETHYL ETHER

(bis-(Pentachloroethyl) ether; Cl₃C
"Perchloroether")

M.P. 69° (1)

 $D_{-}^{14.5} = 1.900 (2)$

[For crystallog. data see (3).]

[For prepn. of C from abs. diethyl ether (1:6110) with excess dry Cl₂ in direct sunlight see (1).]

 $\bar{\mathbf{C}}$ on boilg. decomposes (2) into trichloroacetyl chloride (3:5420) and hexachloroethane (3:4835).

 \bar{C} with conc. H₂SO₄ at 240° is slowly attacked yielding (2) trichloroacetyl chloride (3:5420).

C with alc. K₂S loses 2 atoms of chlorine yielding (2) di-(trichlorovinyl) ether (3:6373).

Č with metallic potassium on htg. detonates; in this behavior Č behaves toward alkali metals like many other highly halogenated compounds.

Note that all these data on \bar{C} are very old; no later studies of \bar{C} are reported in the literature.

3:1676 (1) Regnault, Ann. 34, 27-29 (1840). (2) Malaguti, Ann. chim. (3) 16, 13-28 (1846). (3) Nickles, Ann. chim. (3) 22, 29 (1848).

3:1685 CHLOROPROPIOLIC ACID Cl.C=C.COOH C3HO2Cl

Beil. II - 478 II₁---

 II_{2} -(451)

M.P. 69-70° (1)

Colorless cryst. from pet. eth.; eas. sol. ether; eas. vol. (even in desiccator). Very irritating and poisonous; salts extremely toxic (1). — Stable in dry state at room temperature.

[For prepn. from propiolic ac. [Beil. II-477] by actn. of KOH/KOCl soln. at 0° see (1) (2).]

 $\ddot{\mathbf{C}}$ on htg. with Ba(OH)₂ soln. yields chloroacetylene (3:7000) + BaCO₃ while acidification and ether extraction of the aq. layer yields malonic ac. (1:0480), m.p. 133-134° (1). [An alk, soln. of $\ddot{\mathbf{C}}$ on stdg. is also partly converted to malonic ac. (1).]

3:1685 (1) Straus, Kollek, Heyn, *Ber* **63**, 1876–1877 (1930). **(2)** Brit. 333,946, Sept. 18, 1930; *Cent.* **1931**, I 523.

3:1687 2.3.4.6-TETRACHLOROPHENOL

 $\begin{array}{cccc} \text{OH} & \mathrm{C_6H_2OCl_4} & \text{Beil. VI - 193} \\ & & & & & & & \\ \mathrm{Cl} & & & & & & \\ \mathrm{Cl} & & & & & & \\ \mathrm{Cl} & & & & & & \\ \end{array}$

M.P.	70°	(1) (2) (3)	B.P.	164°	at 23 mm. (4)
	69-70°	(4)		160.5°	at 21 mm. (4)
	68-69°	(5) (6)		159°	at 20 mm. (4)
	67.5-68°	(7)		157°	at 19 mm. (4)
	67-69°	(8)		155°	at 18 mm. (4)
	67-68°	(9)		152.5°	at 17 mm. (4)
	67°	(10) (11)		150°	at 16 mm. (4)
	65.5°	(12)			
	65–66°	(13)			

Ndls. from lgr., AcOH, or ether. — Almost insol. cold aq.; spar. sol. hot aq.; but volatile with steam. — Eas. sol. alc., C_6H_6 , $CHCl_3$, CS_2 , lgr.; fairly sol. hot pet. eth. — Odorless at ord. temp.

PREPARATION OF C

[For prepn. of \bar{C} from phenol (1:1420) with Cl₂ at 80° for 14 days (7) or with Cl₂ in pres. of 2-3% I₂ or 4-5% SbCl₃ or 5-6% FeCl₃ for shorter periods (7), from sodium phenolate with SO₂Cl₂ (13), or from 2,4,6-trichlorophenol (3:1673) with Cl₂ (1) in pres. of I₂ at 40° (8) or with Cl₂ in CCl₄ soln. in pres. of FeCl₃ (14), see indic. refs.]

[For form. of \tilde{C} from 3,5,6-trichloro-2-hydroxybenzoic acid (3,5,6-trichlorosalicylic acid) (5) with Cl₂ in 30% AcOH see (5); from 2,4,5,6-tetrachloro-3-hydroxybenzoic acid [Beil. X-144] (11) by htg. with lime see (11); from 2,4,5,6-tetrachloro-3-hydroxybenzalde-hyde (6) with 50% aq. KOH at 100° for 2 hrs. (the CO group being eliminated as K formate) see (6); from o-(2,4,5,6-tetrachloro-3-hydroxybenzoyl)benzoic acid (3) by cleavage with conc. H₂SO₄ see (3).]

[For formn. of C from 1,2,4,4,5,6,6-heptachlorocyclohexen-1-one-3 [Beil. VII-51] by reduction with SnCl₂/HCl/AcOH (4) or with KI/AcOH or Na₂SO₃/AcOH see (12); from "6-hydroxyphenylene diazosulfide" with Cl₂ in AcOH followed by reduction with SnCl₂ see (10).]

USES OF C (OR ITS SALTS)

[For patents on use of \bar{C} (or its salts) as bactericide (15) (16) in preservation of rubber latex (17), as insecticide (18), or in triphenyl phosphate as wood preservative (19) see indic. refs.]

[For general articles on \bar{C} (or its salts) as bactericides (20), fungicides (21) (27) for paint (22) or leather (23) (24) (25) (26), or in preservation of brine samples for analysis (28) see indic. refs.]

PHYSIOLOGICAL EFFECTS OF C (OR ITS SALTS)

[For studies on dermatitis from \bar{C} or its salts see (29) (30); for report on toxicity of \bar{C} in leather see (31).]

CHEMICAL BEHAVIOR OF C

Action of chlorine. [C with Cl₂ in AcOH gives (4) (12) 1,2,4,4,5,6,6-heptachlorocyclo-hexen-1-one-3 [Beil. VII-51].]

Action of bromine. \ddot{C} with Br₂ (1 mole) in pres. of Fe powder gives (8) 5-bromo-2,3,4,6-tetrachlorophenol [Beil. VI₁-(106)], cryst. from AcOH, m.p. 197° (8) (32), 192° (33) (corresp. acetyl deriv., m.p. 144° (33); corresp. benzoyl deriv., m.p. 169° (33)).

Action of nitric acid. [C with fumg. HNO₃ (5 wt. parts) is oxidized (70% yield (4)) (12) to 2,3,5-trichlorobenzoquinone-1,4 (3:4672). — Note, however, that the mononitro deriv. of C, viz., 5-nitro-2,3,4,6-tetrachlorophenol, ndls. from C₆H₆, m.p. 122°, has been obtd. (8) by HBr cleavage of the corresp. methyl ether (see below).]

Behavior of \bar{C} as an acid. \bar{C} in aq. behaves as an acid, K at $25^{\circ} = 4.2 \times 10^{-6}$ (2) cf. (34), and can be titrated with N/10 aq. NaOH (1); Neut. Eq. = 232. — [For prepn. of alk. salts of \bar{C} by neutralization in mixtures of org. solvents see (35); for uses of salts of \bar{C} see above.]

Miscellaneous reactions of C. [C (as KA) in conc. aq. soln. with COCl₂ (3:5000) in toluene gives (36) bis-(2,3,4,6-tetrachlorophenyl) carbonate, m.p. 155-156° (36).]

- ② 2,3,4,6-Tetrachlorophenyl methyl ether (2,3,4,6-tetrachloroanisole): ndls. from MeOH, m.p. 64-65° (4), 60° (8), b.p. 266-270° u.c. at 244 mm. (8). [From C with MeI in MeOH/NaOMe soln. (4) cf. (8).— Note that this prod. on nitration with 7-8 wt. pts. fumg. HNO₃ gives 5-nitro-2,3,4,6-tetrachloroanisole, m p. 58° (8).]
- 2,3,4,6-Tetrachlorophenyl ethyl ether (2,3,4,6-tetrachlorophenetole): ndls. from alc.,
 m.p. 59-60° (4), 55° (6). [From C with EtI in EtOH/NaOEt soln. (4); also indirectly (6).]
- D 2,3,4,6-Tetrachlorophenyl acetate: cryst. from alc., m.p. 66° (5), 65-66° (4), 59° (12). [From C with Accol (4) or with Accol (12).]
- **D** 2,3,4,6-Tetrachlorophenyl N-phenylcarbamate: ndls. from alc., m.p. 141-142° (4). [From \tilde{C} with phenyl isocyanate in C_6H_6 24 hrs. at room temp. (4)]

3:1687 (1) Tiessens, Rec. trav. chim. 50, 116, 119 (1931). (2) Tiessens, Rec. trav. chim. 48, 1068 (1929). (3) Fries, Auffenberg, Bcr. 53, 24, 28 (1920). (4) Biltz, Giese, Bcr. 37, 4013-4017 (1904). (5) Farinholt, Stuart, Twiss, J. Am. Chem. Soc. 62, 1239, 1241 (1940). (6) Lock, Nottes, Monatsh. 67, 323 (1936). (7) Barral, Grosfillex, Bull soc. chim. (3) 27, 1174-1178 (1902) (8) Kohn, Pfeifer, Monatsh. 48, 233-236 (1927). (9) Holleman, Rec. trav. chim. 40, 318-319 (1921). (10) Fries, Vorbrodt, Siebert, Ann. 454, 190 (1927).

(11) Zincke, Walbaum, Ann. 261, 239-246 (1891). (12) Zincke, Schaum, Ber. 27, 549 (1894). (13) Durrans, J. Chum. Soc. 121, 47 (1922). (14) Michel, Buschmann (to I.G.), Ger. 527,393, June 19, 1931; Cent. 1931, II 2785; C.A. 25, 4556 (1931). (15) I.G., French 685,331, July 9, 1930, Cent. 1930, II 2732, C.A. 24, 5928 (1930). (16) I.G., French 709,788, Aug. 13, 1931, Cent. 1932, I. 1804; C.A. 26, 1060 (1932). (17) Monsanto Chem. Co., Brit. 530,836, Jan. 16, 1941, Cent. 1942, I. 2831, C.A. 36, 1207 (1942). (18) Ellis (to Insulte Co.), U.S. 2,161,654, June 6, 1939; Cent. 1939, II 4620, C.A. 33, 7568 (1939). (19) Norton (to Dow Chem. Co.) U.S. 2,304,013, Dec. 1, 1942; C.A. 37, 2908 (1943). (20) McInikor, Arctesyan, Rokitskaya, Compt. rend. acad. sci. U.R.S.S. 31, 123-124 (1941), Cent. 1942, II 2055, C.A. 37, 950-951 (1943).

(21) Mallman, Michael, Mich State Coll. Agr Expt Sta, Tech. Bull. 174 (1940); C.A. 35, 7560 (1941). (22) Partansky, Ind. Eng. Chem., Anal. Ed. 14, 527-531 (1942). (23) Richardson, Hide and Leather 99, No. 19, 28, 38 (1940); C.A. 34, 4605 (1940). (24) Richardson, Shoe Leather Reptr. 221, No. 3, 17-21 (1941), C.A. 35, 3475 (1941). (25) Itollar, J. Am. Leather Chem. Assoc. 39, 179-190 (1944); C.A. 38, 4827 (1944). (26) Greene, Lollar, J. Am. Leather Chem. Assoc. 39, 209-218 (1944; C.A. 38, 6595 (1944). (27) Wellmann, Heald, Phytopathology 30, 638-648 (1940); Cent. 1942, I 2545; C.A. 34, 8165 (1940). (28) Veldhuis, Fruit Products J. 18, 6-7 (1938), Cent. 1939, I 1091; C.A. 32, 9321 (1938). (29) Butler, Arch. Dermatol. Syphilol. 35, 251-264 (1937); Cent. 1937, II 435; C.A. 31, 5360 (1937). (30) Stingily, Southern Med. J. 33, 1268-1272 (1940); C.A. 36, 847 (1942).

(31) Lollar, J. Am. Leather Chem. Assoc. 39, 203-209 (1944), C A 38, 6594 (1944). (32) Kohn, Zandmann, Monatsh. 47, 372-373 (1926). (33) McCombie, Ward, J. Chem. Soc. 103, 2005 (1913). (34) Murray, Gordon, J. Am. Chem. Soc. 57, 110-111 (1935). (35) Mills (to Dow Chem. Co.), U.S. 1,955,080, April 17, 1934; Cent. 1934, II 1991 C.A. 28, 3743 (1934). (36) Barral, Compt. rend. 138, 981 (1904).

3:1690 2,6-DICHLOROBENZALDEHYDE $C_7H_4OCl_2$ Beil.

$$C_7H_4OCl_2$$

$$Cl$$

$$CHO$$

$$CHO$$

$$C_1$$

$$Reil. VII - 237$$

$$VII_1-(134)$$

M.P. 71° (1) 70-71° (2) 70° (3) 69-70° (4) (5) Colorless cryst. from pet. ether (b.p. 40-60°) or lgr.

[For prepn. of \bar{C} from 2,6-dichlorotoluene (3:6270) by oxidn. with MnO₂ + H₂SO₄ see (2); for prepn. of \bar{C} from 2,6-dichlorobenzaldehyde diethylacetal (see below) by hydrolysis on shaking with dil. HCl see (6).]

[Č on reduction would presumably yield 2,6-dichlorobenzyl alc., but this prod. is unreported in the literature.]

 \bar{C} in alk. suspension on oxidn. with air gives (7) 2,6-dichlorobenzoic acid (3:4200), m.p. 144° .

[\bar{C} (fused) with Cl₂ in brilliant artificial light gives (58% yield (8)) 2,6-dichlorobenzoyl chloride, b.p. 126-128° at 18 mm. — \bar{C} with PCl₅ at 160° gives (90% yield (9)) (4) (5) 2,6-dichlorobenzal (di)chloride (3:9398) oil, b.p. 124-126° at 16 mm. (9), accompanied in some preparations (4) (5) by some bis-(α ,2,6-trichlorobenzyl) ether, m.p. 180-185° (4) (5).]

[\bar{C} with alkali sulfite (1 mole) under press, reacts at one of the two halogen atoms giving (2) 6-chlorobenzaldehydesulfonic acid-2 [Beil. XI-324] — \bar{C} with alkali sulfite (2 moles) under press, gives (2) benzaldehyde disulfonic acid-2,6 [Beil. XI-326].]

 \bar{C} disslvd. in 7–8 wt. pts cone. H₂SO₄, and at 10–15° mononitrated with a mixt. of fumg. HNO₃ + cone. H₂SO₄, poured into aq. gives (yield not stated (10)) (2) 2,6-dichloro-3-nitrobenzaldehyde [Beil. VII-263], pl. from CS₂ (10) or lfts from C₆H₆ (2), m p. 76° (10), 76–77° (2) (corresp. α-oxime, m p. 156–157° (10), β-oxime, m p. 154–155° (10); note that a mixt of the two oximes melts 128–130° (10)) — [Note that no dintro-2,6-dichlorobenzaldehyde has been reported; also that the mp.'s of certain of the isomeric mononitrodichlorobenzaldehydes are very close to the above mononitration prod.: e g., 2,4-dichloro-6-nitrobenzaldehyde (from 2,4-dichlorobenzaldehyde 3:1800) has m.p. 74–75°; 2,5-dichloro-3-nitrobenzaldehyde (from 2,5-dichlorobenzaldehyde 3:1145) has m.p. 66.5–67°; 3,4-dichloro-6-nitrobenzaldehyde (from 3,4-dichlorobenzaldehyde 3:0550) has m.p. 73°.]

[C on sulfonation gives (2) 2,6-dichlorobenzaldchydesulfonic acid-3 [Beil XI-325].]

[\bar{C} with 50% KOH at 100° for 5 hrs. under N₂ undergoes cleavage of the aldehyde group giving (84% yield (11)) *m*-dichlorobenzene (3:5960) q.v. and the corresp. K formate.]

 $[\bar{C}]$ with aq. alc. hydrazine sulfate gives (86% yield (18)) 2,6-dichlorobenzaldazine, m.p. 153° cor.; but this prod or \bar{C} with hydrazine hydrate refluxed 5 hrs. gives 2,6-dichlorobenzaldehyde hydrazone, m.p. 134°, which by Wolff-Kishner reduction gives (80% yield (18)) 2,6-dichlorotoluene (3:6270).]

[\tilde{C} with EtOH contg. 1½ wt. % dry HCl refluxed 24 hrs. gives (13.6% yield (6)) 2,6-dichlorobenzaldehyde dicthylacetal, oil, b.p. 142-144° at 10 mm., m.p. -1° (6); this prod. with dil HCl readily hydrolyzes back to \tilde{C} + EtOH.]

[\bar{C} with β -naphthol (2 moles) in AcOH with 30% HBr in AcOH at 100° for 2 hrs. or at room temp. for 24 hrs. condenses and ring-closes giving (88% yield (8)) 9-(2,6-dichlorophenyl)-1,2,7,8-dibenzoxanthane ($C_{27}H_{16}OCl_2$), cryst. from lgr., m.p. 264-265° (8). — Note that \bar{C} with β -thionaphthol (2 moles) under similar conditions yields a prod. $C_{27}H_{18}S_2Cl_2$, of unknown structure.]

 \bar{C} with anhydrous NaOAe + Ac₂O in Perkin synthesis (12) (13) (1), or \bar{C} with malonic acid in AcOH (13) gives (yields: 81-83% (12), 80% (1), 18% (13)) 2,6-dichlorocinnamic acid [Beil. IX₁-(239)], cryst. from AcOH, m.p. 196° (12), 193° (13), 183° (1); note that in this reaction some 2,6-dichlorobenzal diacetate [Beil. VII₁-(134)], ndls. from lgr., m.p. 85° (1), is sometimes formed.

C appears to behave normally with RMgX reactants [e.g., C with MeMgI in dry ether followed by usual hydrolysis gives (68.6% yield (14)) 2,6-dichlorophenyl-methyl-carbinol,

m.p. 34-35°, b.p. 137-138° at 17 mm., 134-136° at 13 mm. (corresp. benzoate, m.p. 77°); \tilde{C} with C_6H_6MgBr similarly gives in good yield (1) 2,6-dichlorophenyl-phenyl-carbinol, m.p. 57° (corresp. acetate, m.p. 105°)]. [For conversion of \tilde{C} to 2,6-dichlorostyrene (16) (17) via formn. of 2,6-dichlorophenyl-methyl-carbinol (above) and dehydration of latter with KHSO₄ (31.5% yield (16)) see indic. refs]

Č with aniline readily condenses yielding (1) 2,6-dichlorobenzaldehyde anil, m.p. 64-65°.

- **② 2,6-Dichlorobenzaldoxime:** colorless ndls. from C_6H_6 (10) or lgr. (1), m.p. $149-150^\circ$ (10), $146-147^\circ$ (1). [From \tilde{C} with NH₂OH.HCl + Na₂CO₃ in dil. alc. at 100° for 5 hrs. (10) cf. (1); with cold Ac₂O this prod. gives an acetyl deriv., m.p. 51° (10); with boilg. Ac₂O for 5 min. the oxime loses H₂O giving (1) 2,6-dichlorobenzonitrile [Beil. IX-343, IX₁-(141)], ndls. from lgr. or by sublimation, m.p. 143° (1), $144.5-146.5^\circ$ (15).]
- ---- 2,6-Dichlorobenzaldehyde phenylhydrazone: unreported.
- --- 2,6-Dichlorobenzaldehyde o-nitrophenylhydrazone: m p. 154° (1).
- --- 2,6-Dichlorobenzaldehyde p-nitrophenylhydrazone: unreported.
- ---- 2,6-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.
- ---- 2,6-Dichlorobenzaldehyde p-bromophenylhydrazone: m.p. 142° (1).
- --- 2,6-Dichlorobenzaldehyde semicarbazone: unreported.

3:1696 (1) Reich, Salzmann, Kawa, Bull. soc. chim. (4) 21, 217-225 (1917). (2) Geigy and Co., Ger. 199,943, July 4, 1908; Cent. 1908, II 363-364; [C.A. 2, 3000 (1908)]. (3) Lock, Ber. 66, 1530 (1933). (4) Olivier, Weber, Rec. trav. chim. 52, 169-174 (1933). (5) Olivier, Weber, Rec. trav. chim. 53, 882 (1934). (6) Lock, Ber. 72, 303 (1939). (7) Hans (to I.G.), Ger. 506,438, Sept. 4, 1930; Cent. 1930, II 3850; C.A. 25, 304 (1931). (8) Dilthey, Quint, Heinen, J. prakt. Chem. (2) 152, 68-72 (1939). (9) Lock, Asinger, Monatsh. 59, 157 (1932). (10) Meisenheimer, Theilacker, Beisswenger, Ann. 495, 254 (1932).

(11) Lock, Ber. 66, 1530 (1933). (12) Bock, Lock, Schmidt, Monatsh. 64, 401-402, 407-408 (1934). (13) Willstadt, Ber. 64, 2692 (1931). (14) Lock, Bock, Ber. 70, 921 (1937). (15) Norris, Klemka, J. Am. Chem. Soc. 62, 1433 (1940). (16) Marvel, Overberger, Allen, Johnston, Saunders, Young, J. Am. Chem. Soc. 68, 863 (1946). (17) Michalek, Clark, Chem. & Eng. News 22, 1559-1563 (1945). (18) Lock, Stach, Ber. 76, 1252-1256 (1943).

Beil. VI - 648 3:1700 1-CHLORONAPHTHOL-2 C₁₀H₇OCl VI₁---VI₂-(603) M.P. 72° (1) 71° (2) 70-71° (3) 70° (4) (11) (20) (27) 68-69° (5) 68° (8)

Ndls. from hot aq., ndls. from lgr., pr. from CHCl₃; eas. sol. alc., AcOH, C₆H₆, CHCl₃, boilg. lgr. — For crystallographic constants see (4). — Volatile with steam.

[For prepn. of \bar{C} from β -naphthol (1:1540) with Cl_2 in AcOH (80% yield (21)) (3) (4) (6), with SO_2Cl_2 in CS_2 (7) or with $C_6H_5ICl_2$ (84% yield (2)) see indic. refs.; from sodium β -naphtholate in CS_2 suspension on treatment with Cl_2 (8) or in cold aq. with NaOCl (84% yield (5)) (9) see indic. refs.; for formn. of \bar{C} from β -naphthol (1:1540) as by-prod. of its

oxidn. with FeCl₃ to β -dinaphthol (2,2'-dihydroxybinaphthyl-1,1') see (10) (11) (the proportion of \bar{C} increases with increasing acidity (11)); for formn. of \bar{C} from β -naphthol as by-prod. of react. with SeOCl₂ see (20).]

 \bar{C} with 1 mole Cl_2 in AcOH soln. gives (12) 1,6-dichloronaphthol-2 (3:3600), m.p. 119.5° (12); \bar{C} with 1 mole Br_2 yields (7) (13) 6-bromo-2-chloronaphthol-2 [Beil. VI-651], ndls. from AcOH with 1 mole solvent, m p. 92°, anhydrous ndls. by sublimation, m.p. 101° (7). [Note, however, that \bar{C} in AcOH + NaOAc with 1 mole Br_2 yields (1) "1-bromo-1-chloro-2-oxonaphthalenedihydride-1,2," pale yel. pr. from lgr., m.p. 90° when pure but on short stdg. soon becoming lower.]

[$\bar{\mathbf{C}}$ in AcOH with conc. HI (D=1.5) boiled 5 hrs. gives (79% yield (5)) β -naphthol (1:1540), m.p. 121° (5); note, however, that $\bar{\mathbf{C}}$ is unaffected by SnCl₂ either in acid or alk. even after protracted refluxing, but in AcOH/HCl in s.t. 8 hrs. at 100° (1) reduces to β -naphthol.]

[C in alk. soln. treated with p-nitrobenzenediazonium chloride soln. loses its halogen atom and yields (14) (15) (16) cf. (21) 1-(p-nitrobenzeneazo)naphthol-2 ("Para Red") [Beil. XVI-165, XVI₁-(255)], red ndls. from pyridine, m.p. 246-247° u.c. (14), from AcOH, m.p. 250° cor. (15). (Note, however, that as much as 40% of a light yel. by-prod., m.p. 125° dec., is also formed (16).)]

[\bar{C} melted with PCl₅ and then treated with aq. (4), or \bar{C} in alk. soln. shaken with POCl₃ (17), or sodium salt of \bar{C} shaken in xylene with POCl₃ (18), yields *tris*-(1-chloronaphthyl-2) phosphate, ndls. from alc., m.p. 152° (4) (note that by the second method (above) *bis*-(1-chloronaphthyl-2) phosphoric acid, ndls. from alc. + HCl, m.p. 251° (4), is also formed (4)).]

[Č (2 moles) with Na₂S (1 mole) htd. in aq. under N₂ gives (97.5% yield (19)) bis-(2-hydroxynaphthyl-1) sulfide [Beil. VI-976, Vl₁-(470)], colorless cryst. from AcOH, m.p. 226° cor. (19).]

[C on refluxing a few hrs. with aniline (best under N₂ (23)) yields (22) 1-anilinonaphthol-2 [Beil. XIII-678], ndls. from lgr., m.p. 153-154° (22), 155-156° (23); for corresp. reactn. with many other monamines (22) (23) and diamines (24) see indic. refs.]

Č under many circumstances yields ethers with difficulty and small yields; e.g., Č with MeOH + conc. H₂SO₄ (25) or p-toluenesulfonic acid (26) gives only 2-7% methyl ether; however, Č in MeOH/KOH htd. with MeI in s.t. at 100° for 5 hrs. (25), or Č in 15% KOH shaken with Me₂SO₄ for ½ hr. (91% yield (5)), gives 1-chloro-2-methoxynaphthalene, pr. from alc., m.p. 70-71° (5), 68° (25), 78° (27); this methyl ether on protracted htg. with conc. HCl in s.t. at 200-250° yields Č + MeCl (17) (27). — Č with EtOH + conc. H₂SO₄ (25) gives only 0.5-10% ethyl ether, but Č with EtOH/KOH + EtBr htd. 3 hrs. at 100° (25) gives 1-chloro-2-ethoxynaphthalene, lfts. from alc., m.p. 58° (25).

- ① 1-Chloro-2-naphthyl acetate: tbls. from alc., m.p. 42-43° (3). [From C with AcCl (3).]
- ① 1-Chloro-2-naphthyl benzoate: lfts. from alc., m.p. 101° (27). [From C in alk. soln. by shaking with BzCl (27).]

3:1700 (1) Fries, Schimmelschmidt, Ann. 484, 293, 296-297 (1930). (2) Neu, Ber. 72, 1511 (1939). (3) Zincke, Ber. 21, 3384-3385 (1888). (4) Cleve, Ber. 21, 895-896 (1888). (5) Franzen, Stauble, J. prakt. Chem. (2) 103, 379-380 (1921/22). (6) Clifford (to Goodyear Tire and Rubber Co.), Brit. 302,147, Feb. 6, 1929; Cent. 1929, 1 1867. (7) Armstrong, Rossiter, Chem. News 59, 225 (1889), Ber. 24, Referate, 705 (1891). (8) Schall, Ber. 16, 1901 (1883). (9) Kalle and Co., Ger. 168,824, March 16, 1906; Cent. 1906, I 1307. (10) Ioffe, J. Gen. Chem. (U.S.S.R.) 7, 2715-2718 (1937); Cent. 1939, II 4475; C.A. 32, 2931 (1938). (11) Ioffe, Kuznetzov, Litovskii, J. Gen. Chem. (U.S.S.R.) 5, 1685-1686 (1935); Cent. 1937,

I 2589; C.A. 30, 3426 (1936). {12} Ruggli, Knapp, Merz, Zimmermann, Helv. Chim. Acta 12, 1051 (1929). {13} Armstrong, Rossiter, Chem. News 63, 136 (1891); Ber. 24, Referate, 719 (1891). {14} Hewitt, Mitchell, J. Chem. Soc. 89, 1172 (1906). {15} Wahl, Lantz, Bull. soc. chim. (4) 33, 103 (1923). {16} Ioffe, J. Gen. Chem. (U.S.S.R.) 7, 2637-2638 (1937); Cent. 1938, I 3042; C.A. 32, 2110 (1938). {17} Autenrieth, Ber. 30, 2379-2380 (1897). {18} Akt.-Ges. fur Anilinfabrikation, Ger. 246,871, May 11, 1912, Cent. 1912, I 1875. {19} Ringeissen, Compt. rend. 198, 2182 (1934); Cent. 1934, II 2677; C.A. 28, 5432. {20} Morgan, Burstall, J. Chem. Soc. 1928, 3269.

(21) Pollak, Gebauer-Fulnegg, Monatsh. 50, 317 (1928). (22) Wahl, Lantz, Ger. 365,367, Dec. 13, 1922; Brit. 182,084, Aug. 16, 1922, French 548,440, Jan. 15, 1923, Cent. 1923, II 997, 998. (23) Wahl, Lantz, Compt. rend. 175, 171-174 (1922); Cent. 1922, III 1294. (24) Wahl, Lantz, Compt. rend. 194, 464-467 (1932); Cent. 1932, I 2464. (25) Davis, J. Chem. Soc. 77, 33-40 (1900). (26) Fieser, Lothrop, J. Am. Chem. Soc. 57, 1460 (1935). (27) Autenrieth, Arch. Pharm. 233, 34-37 (1895).

01 01 (1000).

M.P. 71.5-72° (1) B.P. 235-236° (1)

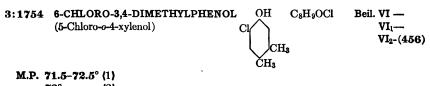
 \bar{C} is volatile with steam. — The products of m.p. 45-46° (2) and m.p. 58° (3) formerly supposed to have been \bar{C} are now regarded (1) as 2,4,6-trichloro-3-methylphenol (3:0618) and 2,4-dichloro-3-methylphenol (3:1205) respectively

[For prepn. of \bar{C} from 6-amino-4-chloro-3-methylphenol (1) via diazotization and use of Cu_2Cl_2 reaction see (1); from 4,6-diamino-3-methylphenol (1) via tetrazotization and use of Cu_2Cl_2 reaction see (1); for formn. of \bar{C} (together with other isomers) from 4-chloro-3-methylphenol (3:1535) or from 6-chloro-3-methylphenol (3:0700) in CHCl₃ with Cl_2 (1 mole) see (1).]

 \bar{C} in CHCl₃ with 1 mole Cl₂ gives alm. quant. yields (1) 2,4,6-trichloro-3-methylphenol (3:0618), m.p. 46° (1).

- 4,6-Dichloro-3-methylphenyl benzoate: mats of very fine ndls. from alc., m.p. 57.5°
 (1). [From C with BzCl in pyridine (1)]
- **4.6-Dichloro-3-methylphenyl benzenesulfonate:** thin lustrous plates from alc., m.p. 86° (1). [From \tilde{C} + benzenesulfonyl chloride in pyridine (1).]
- **4.6-Dichloro-3-methylphenyl** p-toluenesulfonate: very fine ndls. from alc., m.p. $104-105^{\circ}$ (1). [From $\tilde{C} + p$ -toluenesulfonyl chloride in pyridine (1).]

3:1745 (1) Huston, Chen, J. Am. Chem. Soc. 55, 4216-4218 (1933). (2) von Walther, Zipper, J. prakt. Chem. (2) 91, 374 (1864). (3) Tanaka, Morikowa, Sakamoto, J. Chem. Soc. Japan 51, 275-277 (1930); C.A. 26, 706-707 (1932).



72° (2) 71° (4) Ndls. from lt. pet. - Volatile with steam.

[For prepn. of \bar{C} from 6-amino-3,4-dimethylphenol (5-amino-o-4-xylenol) [Beil. XIII-629, XIII₁-(244)] (1) via diazotization and use of Cu₂Cl₂ reaction (yield not stated) see (1); from 3,4-dimethylphenol (o-4-xylenol) (1.1453) with SO₂Cl₂ in CHCl₃ (23% yield) see (4) cf. (2) (3).]

[For studies on bactericidal action of C see (2) (3).]

C with Cl2 does not (1) give a trichloro derivative.

Č with HNO₃ in AcOH soln, as directed gives (5) 2-nitro-6-chloro-3,4-dimethylphenol (5-chloro-3-nitro-o-4-xylenol), yel. pl. from C₆H₆, m.p. 127.5° (5); note, however, that neither the isomeric mononitro deriv. nor the corresp. dinitro deriv. is known.

C does not (5) couple with benzenediazonium chloride.

[For behavior of \bar{C} with sulfur chloride + AlCl₃ in CS₂ see (6).]

- —— 6-Chloro-3,4-dimethylphenyl acetate: unreported.

 ① 6-Chloro-3,4-dimethylphenyl benzoate: m.p. 43° (1).
- 3:1754 (1) Hinkel, Collins, Ayling, J. Chem. Soc. 123, 2973 (1923). (2) Heicken, Angew. Chem. 52, 263-265 (1939). (3) Lockemann, Kunzmann, Angew Chem. 46, 296-301 (1933). (4) McClement, Smiles, J. Chem. Soc. 1937, 1019. (5) Hinkel, Ayling, Bevan, J. Chem. Soc. 1928, 2530-2531. (6) Dvorkovitz, Smiles, J. Chem. Soc. 1938, 2026.

[See also 4-chloro-2-phenylphenol (3:8980).]

Important Note. Through the year 1944 (and perhaps in some cases beyond) the chlorophenylphenol of m.p. 72° (\tilde{C}) has been regarded as having the structure 4-chloro-2-phenylphenol = 5-chloro-2-hydroxybiphenyl = "p-chloro-o-phenylphenol." In 1945, however, this view was corrected by the paper of Weissberger and Salminen (1); in this text, therefore, expression of the facts is reported in the light of their paper. Particular care is, therefore, required in consulting reference prior to it since such material is universally expressed in the reverse sense of the present view.

[For prepn. of \bar{C} from 2-hydroxybiphenyl (1:1440) with Cl_2 (note that 4-chloro-2-phenylphenol (3:8980) is also formed) see (2) (4); for prepn. of \bar{C} from 3-amino-2-hydroxybiphenyl (5) by diazotization and use of Cu_2Cl_2 reaction (45% yield (1)) see indic. refs.]

 \bar{C} is sol. in aq. 25% NaOH at 60°, but resultant salt is more sol. than corresp. prod. from the isomeric 4-chloro-2-phenylphenol (3:8980) (for use in sepn. of \bar{C} from the latter see (4)); note that sodium salt of \bar{C} cryst. as trihydrate, i.e., Na \bar{A} .3H₂O (4), and that anhydrous Na \bar{A} dec. at 316° without melting (4).

The calcium salt of \bar{C} is very spar. sol. aq. (use in sepn. of \bar{C} from the isomeric 4-chloro-2-phenylphenol (3)).

[For reaction of C with methallyl chloride (3:7145) in pres. of alk. see (10).]

C on mononitration with HNO₃ in AcOH at 15-19° as directed gives (31% yield (1)) 3-chloro-2-hydroxy-5-nitrobiphenyl, tan needles, m.p. 130-131° (1), 129-131° (6).

[\tilde{C} (?) on condensation with formaldehyde + ethanolamine as directed (9) gives a prod., m.p. 182-183°; for similar condens. of \tilde{C} (?) with formaldehyde + morpholine see (7).]

3:1757 (1) Weissberger, Salminen, J. Am. Chem. Soc. 67, 58-60 (1945). (2) Britton, Bryner (to Dow Chem. Co.), U.S. 1,969,963, Aug. 14, 1934, C.A. 28, 6160 (1934). (3) Rittler, Heller (to Chem. Fabrik von Heyden), Ger. 615,133, June 27, 1935, Cent. 1936, I 8k4; C.A. 29, 6247 (1935). (4) Britton, Bryne (to Dow Chem. Co.), U.S. 1,921,727, Aug. 8, 1933; Cent. 1934, I 128-129, C.A. 27, 5086 (1933): Brit. 396,251, Aug. 24, 1933; Cent. 1934, I 128-129, CA. 28, 578 (1934). (5) Vorozhtsov, Troshchenko, J. Gen. Chem. (U.S.S.R.) 8, 431-437 (1938); Cent. 1940, II 2152; C.A. 32, 7907 (1938). (6) Vorozhtsov, Troshchenko, J. Gen. Chem. (U.S.S.R.) 9, 59-64 (1939), Cent. 1940, 2153-2154; C.A. 33, 6281 (1939). (7) Bruson (to Röhm and Haas Co.), U.S. 2,040,039, May 5, 1936; Cent. 1936, II 1386-1387; C.A. 30, 4177 (1936). (8) Harris, Christiansen, J. Am. Pharm. Assoc. 24, 553-557 (1935). (9) Bruson, J. Am. Chem. Soc. 58, 1743 (1936). (10) Coleman, Moore (to Dow Chem. Co.), U.S. 2,170,990, Aug. 29, 1939; Cent. 1939, II 4592; C.A. 34, 1098 (1940).

This compd. is known in two diastereoisomeric forms, one solid (\bar{C}) , and one liquid (3:9082) q.v.

Č cryst. from alc. (1) or CCl4 (3) in colorless pr. with strong camphoraceous odor.

[For preparation of \bar{C} from butadiene-1,3 by treatment in cold with Cl₂ (4) (6) (7) in CS₂, CCl₄, CHCl₃, or lgr. soln. (4), or with SCl₂ in pet. ether (1) see indic. refs.; for prepn. from 1,2,3,4-tetrahydroxybutane (erythritol) (1:5825) with PCl₅ in CS₂ see (3); for formn. from acetylene + HCl in electric discharge see (2).] [The proportion of solid (\bar{C}) and liq. (3:9082) isomers formed varies with conditions.]

C on warming with Zn dust in alc. yields (4) butadiene-1,3, b.p. -4.8°.

Č with MeOH/KOH at 10-18° loses 2 HCl yielding (8) 2,3-dichlorobutadiene-1,3 (3:5220), b.p. 39-40° at 80 mm., and other products.

3:1760 Backer, Strating, Rec. trav. chim. 54, 55-56 (1935). (2) Losanitch, Cent. 1913, II 754. (3) Henninger, Ann. chim. (6) 7, 229 (1886). (4) Muskat, Northrup, J. Am. Chem. Soc. 52, 4053-4055 (1930). (5) Ssorokin, Bjelikow, Cent. 1926, II 801. (6) Muskat (to du Pont), U.S. 2,038,593, April 28, 1936; Cent. 1936, II 3359; C.A 30, 3912 (1936). (7) Ruys, Edwards (to Shell Development Co.), U.S. 2,099,231, Nov. 16, 1937; Cent. 1938, I 3387; C.A. 32, 190 (1938). (8) Berchet, Carothers, J. Am. Chem. Soc. 55, 2007 (1933).

3:1775 3.4-DIMETHYLPHENACYL C₁₀H₁₁OCl Beil. VII - 323 CHLORIDE VII₁-(172) CO.CH₂Cl CH₃ (ω-Chloro-3,4-dimethyl-CH₃

M.P. 73°

acetophenone)

[For prepn. from o-xylene (1:7430) + chloroacetyl chloride (3:5235) + AlCl₃ see (1) (2).

C on oxidn, with alk, KMnO₄ gives 4-methylisophthalic ac. [Beil, IX-863], m.p. 332° cor. (corresp. dimethyl ester, ndls. from MeOH, m.p. 80°).

3:1775 (1) Kunckell, Ber. 30, 1713 (1897). (2) Jörlander, Ber. 50, 1459 (1917).

White ndls. with strong odor like ordinary benzaldehyde. — Volatile with steam (1). [For prepn. of C from 2,4-dichlorotoluene (3:6290) via bromination at 180-200° to 2,4dichlorobenzal (di)bromide and hydrolysis with conc. H₂SO₄ at 100° (92% yield) see (1); for analogous prepn. via 2,4-dichlorobenzal (di)chloride and its hydrolysis see (2) (4): for prepn. of C from 2-chloro-4-aminobenzaldehyde via diazo/CuCl reactn. see (3).

C on oxidn. with KMnO4 yields 2,4-dichlorobenzoic acid (3:4560), mp. 162°. — C on htg. with MeOH/NaOMe in s.t. at 183° for 8 hrs. undergoes Cannizzaro reactn. vielding 2,4-dichlorobenzyl alc., m.p. 58-59° (2), and 2,4-dichlorobenzoic ac. (3:4560), m.p. 161-162° (2).

C on mononitration as specified (6) yields 2,4-dichloro-6-nitrobenzaldehyde [Beil, VII-263], cryst. from lgr., m.p. 74-75° (6). [Note that 2,4-dichloro-5-nitrobenzaldehyde [Beil. VII₁-(144)], m.p. 74°, has also been prepd. indirectly.]

For conversion of C to 2.4-dichlorostyrene (7) (8) via reaction with MoMgI giving (63% yield (1)) 2,4-dichlorophenyl-methyl-carbinol, b.p. 130-134° at 11 mm. (1), 127° at 7 mm. (corresp. p-nitrobenzoate, m.p. 113° (1)), and dehydration of latter with KHSO₄ (33% yield (7)) see indic. refs.]

- ① 2,4-Dichlorobenzaldoxime: ndls., m.p. 136-137° (4). [The oxime hydrochloride has m.p. 133.5° but on treatment with Na₂CO₃ yields oxime (4).
- 2.4-Dichlorobenzaldehyde phenylhydrazone: unrecorded.
- 2,4-Dichlorobenzaldehyde p-nitrophenylhydrazone: unrecorded.
- 2.4-Dichlorobenzaldehyde 2.4-dinitrophenylhydrazone: unrecorded.
- ---- 2.4-Dichlorobenzaldehyde semicarbazone: unrecorded.
- 3:1800 (1) Lock, Böck, Ber. 70, 923 (1937). (2) van der Lande, Rec. trav. chim. 51, 103, 109 (1932). (3) Blanksma, Chem. Weekblad 6, 899-913 (1909), Cent. 1910, I 261. (4) Erdmann, Schwechten, Ann. 260, 68-69 (1890). (5) Seelig, Ann. 237, 169 (1887). (6) Geigy and Co., Ger. 198,909; Cent. 1908, II 214. (7) Marvel, Overberger, Allen, Johnston, Saunders, Young. J. Am. Chem. Soc. 68, 862-863 (1946). (8) Michalek, Clark, Chem. & Eng. News 22, 1559-1563 (1945).

3:1815 5-CHLORO-2-METHYLPHENOL OH C₇H₇OCl (5-Chloro-o-cresol)

$$\begin{array}{c|cccc} \text{OH} & \text{C}_7\text{H}_7\text{OCl} & \textbf{Beil. VI} - \\ & & & \text{VI}_1\text{-}(\textbf{174}) \\ & & & \text{VI}_2\text{-}(\textbf{332}) \end{array}$$

M.P. 73-74° (1) (4)

Long white hard ndls. from pet. eth.; eas. sol. alc., AcOH; less sol. pet. eth. (1). Č is eas. sol. alk. (1).

[For prepn from 5-chloro-2-methylandine [Bed. XII-835] see (1) (4)]

 \bar{C} on mononitration (2) in AcOH with fumg. HNO₃ at 5° gives mixt. of two mononitration products: 6-nitro-5-chloro-2-methylphenol, volatile with steam, golden-yel. pr. from peteth., m.p. 54.5-55° (2), and 4-nitro-5-chloro-2-methylphenol, not volatile with steam, cryst. from aq. or C_6H_6 , m.p. 144-145° (2).

 \bar{C} on nitration (3) with 3 pts. HNO₃ (D=1 48) at 0° gives a dinitro compd., 4,6-dinitro-5-chloro-2-methylphenol [Beil. VI₁-(181)], yel. ndls., from pet. eth., m.p. 146° (3); acetyl deriv., m.p. 109-110° (3).

[For action of HNO_2 on \bar{C} see (4).]

D 5-Chloro-2-methylphenyl benzoate: from $\ddot{C}+BzCl+aq.$ alk., white lfts. from alc., m.p. $53-54^{\circ}$ (1).

3:1815 (1) Zincke, Ann. 417, 207-208 (1918). (2) von Auwers, Schornstein, Cent. 1924, II 2269. (3) Zincke, Ann. 418, 234 (1918). (4) Hodgson, Moore, J. Chem. Soc. 1926, 2037.

3:1820 1,1,1-TRICHLORO-2-(o-CHLOROPHENYL)-2-(p-CHLOROPHENYL)ETHANE ("o,p'-DDT")

 $CI \longrightarrow CII--CCl_3$ Beil. S.N. 479

M.P. 74.0-74.5° (4) cor. (6) **73-74°** (5)

This compound is the so-called o,p-isomer of "DDT" (3:3298). Although known to be a substantial contaminant (e.g., 18% (1) -19% (5)) of technical "DDT," very little information is at present available regarding it.

Cryst. from MeOH.

[For prepn. of \bar{C} from 2,2,2-trichloro-1-(o-chlorophenyl)ethanol (5) with chlorobenzene (3:7903) in pres. of conc. H_2SO_4 at 60° (64% yield) see (5).]

C on dinitration with fumg. HNO₃ at 50° for 1 hr gives (5) a dinitro deriv., cryst. from 95% alc., m.p. 148.0-148.5° cor. (5); note that this prod. has same m.p. as corresp. deriv. from "DDT" but that m.p. of a mixt. of the two dinitro compds. is depressed.

 \bar{C} on tetranitration with a mixt. (1:1 by volume) of fumg. HNO₃ + conc. H₂SO₄ at 100° for 1 hr. gives (2) a prod., m.p. 229.5-230° cor.; note that the corresp. prod. from "DDT" has m.p. 223.5-224.5° cor. (2).

C with anhydrous AlCl₃ (1 mole) + large excess C₆H₆ at ord. temp. evolves HCl and gives (10% yield (3)) 1,1,2,2-tetraphenylethane, m.p. 211°; in this connection see corresp. behavior of "DDT" (3:3298).

 \tilde{C} with alc. KOH loses 1 HCl giving (97% yield (5)) (7) 1,1-dichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)ethylene (3:1925), accompanied by a little o_pp' -dichlorodiphenylacetic acid, m.p. 106-107.5° cor. (7), the proportion of which may be increased by reaction of \tilde{C} with Ba(OH)₂ in ethylene glycol at 175° (7).

3:1820 (1) Gunther, J. Chem. Education 22, 239 (1945). (2) Schechter, Haller, J. Am. Chem. Soc. 66, 2129-2130 (1944). (3) Fleck, Preston, Haller, J. Am. Chem. Soc. 67, 1419-1420 (1945). (4) Cristol, Hayes, Haller, Ind. Eng. Chem., Anal. Ed. 17, 470-473 (1945). (5) Haller, Bartlett, Drake, Newman, Cristol, et al., J. Am. Chem. Soc. 67, 1591-1602 (1945). (6) Cristol, J. Am. Chem. Soc. 67, 1498 (1945). (7) Cristol, Haller, J. Am. Chem. Soc. 67, 2222-2223 (1945).

M.P. 74-75° (1) 74° (2)

Ndls. from lgr.

[For prepn. of \tilde{C} from 2,5-dimethylphenol (p-xylenol) (1:1473) by chlorination with SOCl₂ in CHCl₃ (1) or AcOH (2) see indic. refs]

[For studies of bactericidal action of C see (2) (3).]

[For behavior of \bar{C} with o-mitrosulfenyl chloride see (4) cf. (5); behavior of \bar{C} with sulfur chloride in CS₂ see (1).]

- ---- 4-Chloro-2,5-dimethylphenyl acetate: unreported.
- ---- 4-Chloro-2,5-dimethylphenyl benzoate: unreported.

3:1822 (1) Lesser, Gad, Ber. 56, 977 (1923) (2) Heicken, Angew. Chem. 52, 264-265 (1939). (3) Lockemann, Kunzmann, Angew. Chem. 46, 296-301 (1933). (4) Learmonth, Smiles, J. Chem. Soc. 1936, 327-328. (5) McClement, Smiles, J. Chem. Soc. 1937, 1019-1021.

M.P. 73-75° (1)

Cryst. with sharp odor suggesting chloroacetic acid. — Sol. in 20 pts. aq. — $\tilde{\mathbf{C}}$ blisters skin. — $\tilde{\mathbf{C}}$ in small amts. (5 g.) can (with care) be distilled, but attempts to distil larger units lead to decomposition with loss of HCl (2).

[For prepn. of \tilde{C} from α,α,γ -trichloro-n-butyraldehyde (3:9094) by odixn. with fumg. HNO_3 in cold see (1).]

C does not react with Zn dust in aq. or with aq. KI even at 100° (2); C does not react with NH₂OH (2).

 \ddot{C} on boilg. with aq. (100 pts.) for 4 days yields (2) a soln. which is strongly acid, reduces Fehling soln. and hot NH₄OH /AgNO₃, and presumably conts. HOCH₂.CH₂.CO.COOH.

 \tilde{C} with aq. Na₂CO₃ loses one of its three chlorine atoms (probably that in γ position) and upon acidification gives a soln. presumably contg. a lactone; for details see (2).

The acid chloride corresp. to C is unreported.

- Methyl α, α, γ -trichloro-n-butyrate: unreported.
- Ethyl α,α,γ -trichloro-n-butyrate: unreported.
- α,α,γ -Trichloro-n-butyramide: unreported.
- α,α,γ -Trichloro-n-butyranilide: unreported.
- ---- α, α, γ -Trichloro-n-butyr- α -naphthalide: unreported.

3:1831 (1) Natterer, Monatsh. 4, 551-553 (1883). (2) Natterer, Monatsh. 5, 258-265 (1884).

3:1840
$$\alpha,\beta,\beta$$
-TRICHLOROACRYLIC Cl C₃HO₂Cl₃ Beil. II - 402 Π_1 -(187) Π_2 -(388) M.P. 76° (1) (2) (13) B.P. 221-223° at 760 mm. (5) 74-75° (3) 133° cor. at 30 mm. (5) 73° (4) 72.9° (5)

236

Pr. from CS₂ or dry ether. — $\bar{\rm C}$ is very eas. sol. hot aq. but spar. sol. cold aq.; at 25° its satd. aq. soln. conts. 6.4% $\bar{\rm C}$ (1), at 20° 6% $\bar{\rm C}$ (2). — $\bar{\rm C}$ with aq. within certain limits forms two liq. layers; for thermal anal. of the system see (5); note that $\bar{\rm C}$ with aq. forms a compd. of compn. $\bar{\rm C}$ + 2.5 H₂O, m.p. -0.6°, and that $\bar{\rm C}$ with this compound forms a eutectic, m.p. 17° (5). — $\bar{\rm C}$ is very sol. in alc., ether, or CHCl₃.

[C is usually prepd. from hexachloropropylene (3:6370) by direct or indirect hydrolysis of its terminal —CCl₃ group to —COOH; for prepn. of C from hexachloropropylene by such hydrolysis with 90% H₂SO₄ in pres. of Al₂(SO₄)₃ at not above 130° (5) (1) cf. (6) (7) (81% yield (13)) or with boilg. aq. susp. of BaCO₃ (isolated as BaĀ₂ in 92% yield (1)) see indic. refs.; for prepn. of C from hexachloropropylene (3:6370) via conversion with alc. NaOEt to triethyl orthotrichloroacrylate and subsequent quantitative hydrolysis with alc. KOH see (4).]

[For form. of \bar{C} from hexachlorocyclopentanedione-1,3 [Beil. VII-553] by hydrolytic cleavage with 10% NaOH (3), or from β -bromo- α,β,β -trichloropropionic acid (see below) by elimination of HBr on stdg. several days with aq. Ba(OH)₂ (2), see indic. refs.]

 \bar{C} on reduction with H_2 in pres. of Pd cat. at ord. temp. and press. absorbs 4 moles H_2 yielding (8) propionic acid (1:1025).

 \bar{C} with Cl_2 in CCl_4 soln. in sunlight adds 1 mole halogen giving (9) (8) pentachloropropionic acid (3:4895).

[\bar{C} with HBr might be expected to yield β -bromo- α,β,β -trichloropropionic acid, but this reaction is unreported although the expected prod. [Beil. II-257], m.p. 83-84° has been prepd. by other means and with Ba(OH)₂ loses HBr giving \bar{C} (2).]

 \ddot{C} with half its wt. of PCl₅ at 80° loses H₂O between two molecules giving (4) trichloro-acrylic acid anhydride, cryst., insol. aq., m.p. 39-40° (4) (5); this product is also formed during the distillation of \ddot{C} even at reduced press. (5).

Č with excess SOCl₂, however, gives (80-90% yield (1)) (13) trichloroacryloyl chloride (3:5845) q.v.

Salts of \bar{C} . [Na \bar{A} (conductivity of aq. solns.) (10); K \bar{A} , spar. sol. cold aq. (2); Ag \bar{A} , spar. sol. cold aq. but recryst. from hot aq. without decompn. (2) (4); Mg \bar{A}_2 .3½H₂O, sol. aq. (10); Ca \bar{A}_2 .3½H₂O, sol. aq. (10) (2); Sr \bar{A}_2 .5H₂O, sol. aq. (10); Ba \bar{A}_2 .3½H₂O, sol. aq. (10) (2) (note that this salt on htg. in atm. of H₂ gives (11) dichloroacetylene (3:5010)); Zn \bar{A}_2 .6H₂O and Zn \bar{A}_2 .3½H₂O (10); Cd \bar{A}_2 .2H₂O (10); Hg \bar{A}_2 (no crystal aq.) (10).]

- Methyl α, β, β -trichloroacrylate: unreported.
- Ethyl α,β,β -trichloroacrylate: b.p. 192–194°; 112–114° at 50 mm.; $D_4^{20} = 1.2183$; $n_D^{20} = 1.4649$ (4). [Prepd. indirectly from triethyl orthotrichloroacrylate (itself obtd. from hexachloropropylene with NaOEt) by shaking with conc. HCl (4).]
- Φ α,β,β -Trichloroacrylamide: m.p. 97° (12), 96–97° (4), 96° (2). [From trichloroacryloyl chloride (3:5845) with conc. NH₄OH (4) or from ethyl trichloroacrylate (above) with alc. NH₃ (12).]
- α,β,β-Trichloroacrylanilide: m.p. 98° (13). [From trichloroacryloyl chloride (3:5845) with aniline in CHCl₃ at 0° (77% yield) (13).]

3:1849 (1) Böeseken, Dujardin, Rec. trav. chim. 32, 98-101 (1913). (2) Maberry, Am. Chem. J.
 9, 3-6 (1887). (3) Zincke, Rohde, Ann. 299, 380 (1898). (4) Fritsch, Ann. 297, 315-318 (1897).
 (5) Böeseken, Carriere, Rec. trav. chim. 34, 179-186 (1915). (6) Prins, J. prakt. Chem. (2) 89, 416 (1914). (7) Prins, Ger. 261,689, July 2, 1913; Cent. 1913, II 394-395; C.A. 7, 3641 (1913).
 (8) Böeseken, van der Weide, Rec. trav. chim. 35, 272-273 (1927). (9) Boeseken, Rec. trav. chim. 46, 844-846 (1927).

(11) Bösseken, Carriere, Verslag Akad. Wetenschappen 22, 1186-1188 (1914). (12) Gilta, Bull soc. chim. Belg. 39, 587-588 (1930). (13) Bergmann, Haskelberg, J. Am. Chem. Soc. 63, 1438 (1941).

M.P. 76° (1)

Colorless cryst. from CS₂ + CHCl₃; fairly sol. aq.

[For prepn. of \bar{C} from α,β -dichloroacrylic acid (3:2265) in CS₂ with dry Cl₂ in sunlight see (1).]

Salts: KA; AgA (readily dec. to AgCl on warming aq. soln.); CaA2; BaA2 (1).

3:1850 (1) Maberry, Smith, Ber. 22, 2659-2660 (1889).

M.P. 76-77° (1) (2) (3) (Also see text.)

Ndls. from pet. ether or by sublimation. — \bar{C} is spar. sol. aq. but very eas. sol. ether or CHCl₃. — \bar{C} on htg. above its m.p. (e.g., to 120°), then rapidly cooled to 60° or below remelts at 63-64° (2) (3); on standing, however, \bar{C} finally reverts to the form of m.p. 76-77°. — \bar{C} decomposes on attempted distn.

[For prepn. of \tilde{C} from propiolic acid (acetylene-carboxylic acid) [Beil. II-477] by conversion to chloropropiolic acid (3:1685) and subsequent addr. of 1 HCl by htg. with a large excess cone. HCl at 100° for 5 hrs. (77% overall yield from propiolic acid) see (1); for formn. from "chloralide" (3:3510) by reduction with Zn + HCl in alc. soln. see (2) (3).]

The behavior of C toward hydrogenation has not been reported.

Neither C nor its ethyl ester (see below) adds Br₂ (3).

 $[\bar{C} \text{ with aq. Ba}(OH)_2 \text{ on boilg. splits both HCl and CO}_2 \text{ yielding chloroacetylene (3:7000);}$ the formn. of this highly explosive substance probably accounts for the ignition and detonation sometimes observed cf. (2) (1).]

Salts: $K\bar{A}$ (3); $Ag\bar{A}$ (3); $Ca\bar{A}_2.2H_2O$ (2); $Ba\bar{A}_2.2H_2O$ (2); $Zn\bar{A}_2.2H_2O$ (3).

 $\ddot{\mathbf{C}}$ with PCl₅ gives (3) β,β -dichloroacryloyl chloride, b.p. above 145°; this prod. with EtOH or $\ddot{\mathbf{C}}$ in EtOH with dry HCl gives (3) ethyl β,β -dichloroacrylate, b.p. 173–175°.

—— β₂β-Dichloroacrylamide: ndls. from CHCl₃, m.p. 112-113° (3). [From the above acid chloride with dry NH₃ (3).]

3:1875 (1) Straus, Kollek, Heyn, Ber. 63, 1876-1877 (1930). (2) Wallach, Ann. 283, 83-94 (1880). (3) Wallach, Ann. 193, 6-8, 19-28 (1878).

Beil. S.N. 474

3:1890 1,1-DICHLORO-2-(o-CHLOROPHENYL)-2-(p-CHLOROPHENYL)ETHANE ("o,p-DDD")

$$\begin{array}{c|c} C_{14}H_{10}Cl_{4} \\ \hline Cl & Cl \\ C-CH \\ Cl & II & Cl \\ \end{array}$$

M.P. 76-78° (1)

Colorless cryst. from MeOH or from pentane. — Note that \tilde{C} is a minor impurity in technical grade "DDT" (3:3298).

[For prepn. of \bar{C} from 2,2-dichloro-1-(o-chlorophenyl)ethanol (1) with chlorobenzene (3:7903) in pres of H_2SO_4 (39% yield) see (1).]

 \bar{C} with alc. KOH loses 1 HCl giving (1) 1-chloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)-ethylene (not described) which upon oxidn. with $CrO_3/AcOH$ gives (1) 2,4-dichlorobenzo-phenone (3:1565).

3:1890 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., J. Am. Chem. Soc. 67, 1600 (1945).

M.P. 77° (1) (4) B.P. 176.6° at 5 mm. (5)

 \bar{C} is sol. in NaOH. [For prepn. of Na \bar{A} using solns. of \bar{C} in org. solv. such as McOH, ether, or toluene see (2).]

Č htd. with NaOH/Na₂CO₃ soln. under press for 3 hrs. at 290–300° gives 4-phenyl-pyrocatechol [Beil. VI-990], m p. 145°; diacetate, m.p. 77 5–78° (3).

C in CCl₄ stood 5 days with 1 mole Br₂ gave (44% yield) 6-bromo-2-chloro-4-phenylphenol, wh. pr. (from CHCl₃), m p. 84-86° cor. (4); C in AcOH (25% yield) or in CS₂ (56% yield) stood 2 days with 2 moles Br₂ gave 6-bromo-4'-(p-bromophenyl)-2-chlorophenol, coarse wh. ndls., m.p. 143-146° cor. (4)

C in AcOH treated with 1 mole HNO₃ in AcOH gave 38% yield of 2-chloro-6-nitro-4-phenylphenol, thick yel. pl. (from CCl₄), m.p. 89-90° cor. (5).

 \overline{C} with $(CH_3)_2SO_4 + NaOH$ (1) or $CH_3I + aq$. KOH (5) yields the corresp. Me ether, 2-chloro-4-phenylanisole, m.p. $91-92^\circ$ (1), 93° cor. (5).

- 0 2-Chloro-4-phenyl-phenyl acetate: m.p. 68° (7). [From $\ddot{C} + Ac_2O + NaOAc$ in 92% yield (7).]
- 2-Chloro-4-phenyl-phenyl benzoate: from C + BzCl + aq. alk. in 80% yield (4); cryst. from AcOH (4), m.p. 95-97° cor. (4), 110-111° (6).
- 2-Chloro-4-phenyl-phenyl benzenesulfonate: m.p. 59-60° (8). [From C + benzenesulfonyl chloride + aq. 10% NaOH (8).]
- ② 2-Chloro-4-phenyl 2,4-dinitrophenyl ether: from C + 2,4-dinitrochlorobenzene in conc. aq. KOH refluxed for several hrs.; yield, 70%; m.p. 109-111°C. (4).

3:1900 (1) Grether (to Dow Chem. Co.), U.S. 1,832,484, Nov. 17, 1931; Cent. 1932, I 740. (2) Mills (to Dow Chem. Co.), U.S. 1,955,080, Apr. 17, 1934, Cent. 1934, II 1991. (3) Harvey (to Squibb and Sons), U.S. 1,952,755, Mar. 27, 1934; Cent. 1934, II 1846. (4) Colbert, Meigs, Mackin, J. Am. Chem. Soc. 56, 202-204 (1934). (5) Colbert, Meigs, Stuerke, J. Am. Chem. Soc. 56, 2129 (1934). (6) Harris, Christiansen, J. Am. Pharm. Assoc. 24, 553-557 (1935). (7) Savoy, Abernathy, J. Am. Chem. Soc. 64, 2220 (1942). (8) Savoy, Abernathy, J. Am. Chem. Soc. 64, 2720 (1942).

3:1903
$$\alpha,\beta$$
-DICHLORO- n -BUTYRIC H H $C_4H_6O_2Cl_2$ Beil. II -279 ACID (high-melting isomer) (lsocrotonic acid dichloride) CH_3 — C — C —COOH II_1 — II_2 —

[See also α, β -dichloro-n-butyric acid (low-melting isomer) (crotonic acid dichloride) (3:1375).]

Colorless cryst. from pet. ether $-\bar{C}$ is very eas. sol. alc., ether, much less sol. ag.

[For prepn. of \bar{C} from α -chlorocrotonic acid (3:2760) by addn. of 1 HCl using conc. aq. HCl (satd. at 0°) in s.t. at 100° for 50 hrs. see (2) (4); from either α -chloro- β -hydroxy-n-butyric acid of m.p. 62° [Beil. III-309] (4) or from β -chloro- α -hydroxy-n-butyric acid of m.p. 125° [Beil. III-306] (3) by htg. with conc. aq. HCl (satd. at 0°) in s.t. at 100° for 40 hrs. see indic. refs.; for formn of \bar{C} by (partial) isomerization of the lower-melting isomer (crotonic acid dichloride) (3:1375) with conc. HCl in s.t. at 100° see (5); from the amide (see below) corresp. to \bar{C} with HNO₂ see (1)]

 \bar{C} behaves as an acid but is slightly weaker than its isomer; ionization const. of \bar{C} is 6.1×10^{-3} (5); its reported salts include AgA, spar sol. aq (4); BaA2.3H2O (4): and ZnA2 (4).

 \bar{C} with ale. KOH loses 1 mole HCl giving (2) (4) mainly α -chlorocrotonic acid (3:2760) accompanied by some α -chloro-isocrotonic acid (3:1615).

The acid chloride corresp to C is unreported.

- —— Methyl α,β -dichloro-n-butyrate: unreported.
- —— Ethyl α, α -dichloro-n-butyrate: unreported.
- —— α,β-Dichloro-n-butyramide: m p 125° (1). [Prepd. indirectly but with HNO₂ gives C (1)]

3:1903 (1) Rambaud, Bull. soc. chim. (5) 1, 1339 (1934). (2) Michael, Schulthess, J. prakt. Chem. (2) 46, 259-262 (1892). (3) Melikoff, Petrenko-Kritschenko, Ann. 266, 371-374 (1891). (4) Melikoff, Ann. 234, 201-204 (1886). (5) Michael, Bunge, Ber. 41, 2911 (1908).

3:1905
$$\alpha,\alpha,\beta$$
-TRICHLORO- n -BUTYR- Cl C₄H₇O₂Cl₃ Beil. I - 664
ALDEHYDE HYDRATE | CH₃ CH₋C-CH_.OH | I₁-C_.(725)

[See also α,α,β -trichloro-n-butyraldehyde (butyrchloral) (3:5910).]

Lfts. from aq. or alc. — Spar. sol cold but fairly eas. sol hot aq.; very eas. sol. alc. — For crystallographic data see (3) (5). — Note that because of tendency to dissociate on htg. into butyrchloral (3:5910) + aq. the m.p. observed for \bar{C} varies according to rate of htg. (3). — Note also that \bar{C} is isomeric with chloral ethylalcoholate (3:0860) with which it must not be confused; for distinction of \bar{C} from chloral hydrate (3:1270) see (9) (10).

Č is employed in medicine as a sedative; from the body it is excreted in the urine as urobutyrochloralic acid [Beil 1-664], which upon hydrolysis yields (4) 2,2,3-trichlorobutanol-1 (3:1336) + glucuronic acid [Beil. III-884, III₁-(306)].

[For prepn. of C from butyrchloral (3:5910) by reactn. with aq. see (1) (2) (6).]

 $[\bar{C}$ is reduced by fermenting yeast giving (7) dextrorotatory 2,2,3-trichlorobutanol-1, m.p. 62°; for actn. of \bar{C} on alc. fermentation see (8).

 $\tilde{\mathbf{C}}$ on oxidn. with 3 wt. pts. fumg. HNO₃ (D=1.504) at 30-35° for $1\frac{1}{2}$ hrs. then stood at room temp. for 24 hrs. gives (95% yield (11)) α,α,β -trichloro-n-butyric acid (3:1280).

C on distn. with half its wt. of Ac₂O (12), or shaking with conc. H₂SO₄ (13), or on distn. with CHCl₃ (14), or on htg. alone loses its combined aq. yielding butyrchloral (3:5910), b.p. 165°.

 \overline{C} with conc. H₂SO₄ (at least 6 wt. pts.) at room temp. for 2 days trimerizes to a mixt. (80% yield (12)) of two parabutyrchlorals: these are colorless crystn., sharp-melting solids, sol. in org. solvents, but insol. aq.; the less sol. α -parabutyrchloral, rhombic cryst. from boilg. AcOH or boilg. EtOH, has m.p. 180°; the more sol. β -parabutyrchloral (stereoisomer?), cryst. from boilg. AcOH or boilg. EtOH, has m.p. 157°; these polymers can be distilled at 15 mm. but attempts to distill them at ord. press. result in complete dissociation to butyrchloral (3:5910).

Č with aq. KOH or NaOH evolves heat and yields (1) (15) 1,1-dichloropropene-1 (3:5120) + the salt of formic acid (1:1005).

[$\bar{\mathbf{C}}$ with conc. aq. HCN fails (16) to react, but upon addn. of alc. and subsequent digestion (16), or $\bar{\mathbf{C}}$ (1 mole) with aq. KCN (2 moles) at 40° (17), gives (20% yield (17)) α,α,β -trichloro-n-butyraldehyde cyanohydrin [Beil. III-322, III₂-(226)], pl. from aq., m.p. 101-102° (17) (18), accompanied by (61% yield (17)) α -chlorocrotonic acid (3:2760), m.p. 98.5-99° (17). — Note that $\bar{\mathbf{C}}$ (1 mole) in alc. treated gradually with powdered KCN (2 moles) below 15° over a 3-4 hr. period gives (90% yield (17)) ethyl α -chlorocrotonate (3:8523); in this reactn. the intermediate ethyl α,β -dichloro-n-butyrate readily loses HCl and is generally not isolated; use of alcs. other than EtOH gives good yields of the corresp. alkyl α -chlorocrotonates (17). — Note that for $\bar{\mathbf{C}}$ with KCN in $\mathbf{C}_6\mathbf{H}_6$ the reaction takes a different course (17). — Finally, note that $\bar{\mathbf{C}}$ (1 mole) in cone. aq. NH₄OH first dissolves, then ppts. butyrchloral-ammonia as a heavy oil; the mixt. on satn. with dry NH₃ gas in cold followed by treatment at 10° with powdered KCN (1 mole) evolves heat and gives (93% yield (17)) α -chlorocrotonamide, m.p. 113.5° (17).]

[$\bar{\mathbf{C}}$ undergoes condensation with various org. systems: e.g., $\bar{\mathbf{C}}$ with phenyl isocyanide (1 mole) in ether for 4–5 days gives (53% yield (19)) α -hydroxy- β , β , γ -trichloro-valeranilide, tbls. from alc., $\mathbf{C}_6\mathbf{H}_6$, or CHCl₃, m.p. 156–158° (19). — $\bar{\mathbf{C}}$ (1 pt.) with malonic acid (1:0480) (1 pt.) in pyridine (1 pt.) at 100° for 3 hrs. evolves CO₂ and gives (20) β -hydroxy- γ , γ , δ -trichloro-n-caproic acid, cryst. from hot aq., m.p. 102° (20). — $\bar{\mathbf{C}}$ (1 mole) with nitromethane (1½ moles) in dil. alc. in pres. of Na₂SO₃ at 60° gives (100% yield (21)) 1-nitro-3,3,4-trichloropentanol-2, b.p. 156° at 4 mm., m.p. abt. 20° (21); $\bar{\mathbf{C}}$ (1 mole) with nitroethane (1 mole) in 50% alc. in pres. of Na₂SO₃ + K₂CO₃ at 70° gives (22) 2-nitro-4,4,5-trichlorohexanol-3, b.p. 138° at 0.75 mm. (22).]

[$\bar{\mathbf{C}}$ forms with various org. substances molecular cpds. of pharmaceutical interest: e.g., $\bar{\mathbf{C}}$ (1 mole) with quinine (base) (1 mole) in abs. alc. at 75° for 1 hr. gives 1:1 cpd., m.p. 139° (note that the corresp. cpd. from chloral (3:5210) + quinine has m.p. 149° (23}). — $\bar{\mathbf{C}}$ (1 mole) with 2,3-dimethyl-1-phenylpyrazolone-5 ("Antipyrine") (1 mole) (m.p. 112°) rubbed together and recrystd. from aq. gives (24) 1:1 molecular cpd., colorless pr., m.p. 72° (for f.p./compn. data and diagram of this system see (24)). — $\bar{\mathbf{C}}$ with 2,3-dimethyl-4-dimethylamino-1-phenylpyrazolone-5 ("Pyramidone") (m.p. 107.5°) on fusion or in aq. or $\bar{\mathbf{C}}_6\mathbf{H}_6$ (25) (26) gives a 1:1 mol. cpd. ("Trigemin"), cryst. from $\bar{\mathbf{C}}_6\mathbf{H}_6$, m.p. 85–86° (26), long ndls. from aq., m.p. 84° (24) (for f.p./compn. data and diagram on this system see (24)); for stabilization of "Trigemin" by addn. of 5–10% hexamethylenetetramine (27) or 2% MgO (28) see indic. refs.]

[\bar{C} with various org. hydroxy acids in pres. of conc. H₂SO₄ condenses to give prods. of the chloralide type: e.g., for reactn. of \bar{C} with citric acid (1:0505), malic acid (1:0450), or tartaric acid (1:0525) see (29); with gallic acid (1:0875) (and numerous other phenolic acids) see (30).]

 \bar{C} with conc. aq. NH₄OH first dissolves then ppts. a heavy oil of butyrchloral-ammonia (17); cryst. m.p. 62° (see also above for its reaction with KCN).

[Č with excess dry NH₄OAc on moderate htg. for several hrs., then pouring into aq., gives (18) α,α,β -trichloro-n-butyraldimine, cryst. from C₆H₆, m.p. 169-170° (31), 164-165° (18); observe that this m.p. is notably close to that of the condensation prod. of butyr-chloral (3:5910) with acetamide, and that latter is readily formed from NH₄OAc by dry htg.; this matter, however, seems to have received no further attention.]

 \bar{C} with aq. NH₂OH.HCl on htg. readily yields (32) α,α,β -trichloro-n-butyraldoxime (first separating as an oil), cryst. from lgr., m.p. 65° (32).

The reaction of \tilde{C} with arylhydrazines is of special interest and has been extensively studied. With phenylhydrazine the reaction is extremely vigorous (33) (34) and unless carefully controlled (35) may become almost explosively violent yielding only tar. With nuclear-substituted phenylhydrazines, however, the reaction is milder, and their study has shown that all arylhydrazines react in the same general pattern although this comprises several different courses according to the solvent used. The pattern will be illustrated here only by the case of 2,4-dichlorophenylhydrazine (see below); for details of the analogous reaction of \tilde{C} with phenylhydrazine (33) (34), o-, m-, and p-tolylhydrazines (34), 2,5-dichlorophenylhydrazine (35) (36), 3,5-dichlorophenylhydrazine (35), 2,4,5-trichlorophenylhydrazine (36), p-bromophenylhydrazine (37), 4,5-dibromophenylhydrazine (35), and 2,4,6-tribromophenylhydrazine (35) see indic. refs.

[The reactn. of $\tilde{\mathbb{C}}$ (1 mole) with 2,4-dichlorophenylhydrazine hydrochloride (1 mole) first gives the expected butyrchloral 2,4-dichlorophenylhydrazone (A) which, however, cannot be isolated because of immediate further reaction in two different modes according to the solvent employed. In dil. aq. HCl contg. NaOAc (A) loses HCl in two different ways leading on one hand to α,β -dichlorocrotonaldehyde 2,4-dichlorophenylhydrazone (B), long yel. pr. from alc. or AcOH, m.p. 112° (33), and on the other (simultaneously and with rearr. of unsatd. linkages) to the crimson 1-(2,4-dichlorobenzeneazo)-2,3-dichlorobutene-1 (C) (in most instances the last is not isolatable in pure form although it has been in the case (37) of $\tilde{\mathbb{C}}$ with 2,4-dibromophenylhydrazine); in MeOH, EtOH, or AcOH, however, the two α -chlorine atoms of the initial arylhydrazone (A) undergo hydrolysis with consequent formn. of β -chloro- α -keto-n-butyraldehyde 2,4-dichlorophenylhydrazone (D), pale yel. pr. from alc., m.p. 129° (33).]

[This last type of cpd. (D) can be caused to undergo two further important types of reaction: e.g., (D) with further 2,4-dichlorophenylhydrazine in MeOH soln. not only undergoes conventional condensation of its α -keto grouping but also has the β -chlorine atom replaced by methoxyl so that the product obtd. is β -methoxy- α -keto-n-butyraldehyde bis-(2,4-dichlorophenyl)osazone (E), bright yel. pr. from pyridine or C_0H_0 , m.p. 196° dec. (33) (this reaction occurs so readily in MeOH that from C + 2,4-dichlorophenylhydrazine hydrochloride both (D) and (E) are formed and may be separated by fractional crystn.); on the other hand, (D) with alc. NaOEt on htg. loses HCl and ring-closes (38) to 1-(2,4-dichlorophenyl)-4-hydroxy-5-methylpyrazole (F), colorless cryst. from boilg. alc., m.p. 184° (38) (this type of reactn. comprises a general synthesis of 4-hydroxypyrazoles).]

3:1905 (1) Krämer, Pinner, Ber. 3, 383-390 (1870). (2) Moureu, Murat, Tampier, Bull. soc. chim. (4) 29, 33 (1921). (3) Lieben, Zeisel, Monatsh. 4, 534-538 (1883). (4) Mering, Z. physiol. Chem. 6, 491-496 (1882). (5) von Lang, Z. Krist. 25, 521-522 (1896). (6) Pinner, Ann. 179,

26-29 (1875), (7) Rosenfeld, Biochem. Z. 156, 54-57 (1925); Cent. 1925, I 2301; C.A. 19, 2683 (1925). (8) Neuberg, Ehrlich, Biochem. Z. 101, 239-275 (1920); Cent. 1920, I 534; C.A. 14, 2007 (1920). (9) Gabutti, Boll. chim. farm. 42, 777-778 (1903); Cent. 1904, I 480. (10) Ware, Chemist and Druggist 123, 282 (1935), Cent. 1936, I 1667; C.A. 30, 983 (1936).

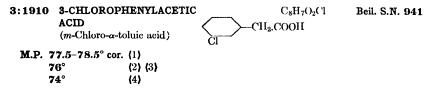
(11) Roberts, J. Chem. Soc. 1938, 779. (12) Chattaway, Kellett, J. Chem. Soc. 1928, 2709-2714. (13) Willcox, Brunel, J. Am. Chem. Soc. 38, 1837 (1916). (14) Engel, Moitessier, Compt. rend. 90, 1075-1077 (1880). (15) Pinner, Ann. 179, 44 (1875). (16) Pinner, Bischoff, Ann. (17) Chattaway, Irving, J. Chem. Soc. 1929, 1043-1047. (18) Pinner, **179.** 97–99 (1875) Klein, Ber. 11, 1488, 1491 (1878). (19) Passermi, Gazz chim ital. 52, 435 (1922). (20) Riedel,

Straube, Ann. 367, 44 (1909).

(21) Chattaway, Witherington, J. Chem. Soc. 1935, 1178-1179. (22) Chattaway, Drewitt, Parkes, J. Chem. Soc. 1936, 1294. (23) Chemisch-Pharmazeutische A.G., Bad Homburg, Ger. 590,312, Dec. 29, 1933, Cent 1934, I 1353. (24) Pfeiffer, Seydel, Z. physiol. Chem. 178, 102-103, 106-107 (1928). (25) Polish 13,363, May 12, 1931; Cent. 1932, II 925. (26) M L.B., Ger. 150,799, April 25, 1904; Cent. 1904, I 1379. (27) Chemisch-Phalmazeutische A.G., Bad Homburg, Ger. 438,984, Dec. 29, 1926, Cent. 1927, I 1068. (28) Altwegg (to Soc. Chim. des Usines du Rhone), Brit. 294,092, Aug. 9, 1928, Cent. 1929, I 1049. (29) Shah, J. Indian Chem. Soc. 16, 285-286 (1939). (30) Katrah, Meldrum, J. Indian Chem. Soc. 9, 121-125 (1932).

(31) Schiff, Ber 11, 2167 (1878) (32) Schiff, Tarugi, Gazz. chim. ital. 21, II 8-9 (1891). (33) Chattaway, Irving, J. Chem. Soc. 1930, 87-94. (34) Chattaway, Irving, J. Chem. Soc. 1931, 751-753. (35) Chattaway, Irving, J. Am. Chem. Soc. 54, 263-271 (1932). (36) Chattaway, Adair, J. Chem. Soc. 1933, 1488-1490. (37) Irving, J. Chem. Soc. 1940, 813-817. (38)

Chattaway, Irving, J. Chem. Soc. 1931, 786-794.



Colorless and best recrystd. from commercial n-heptane (Skellysolve "C") (1); Ifts, from aq. alc. (4). - Very spar. sol. aq., quite sol. alc. or C6H6, misc. with other. [For study of ionization const. see (3).] — [For study of fate of \bar{C} in animals see (5).]

[For prepn. of C from m-chlorobenzyl bromide (mp. 15-15.5° cor., bp. 103-105° at 8 mm., $D_{25}^{25} = 1.5652$ (1)) via conversion to m-Cl.C₆H₄.CH₂MgBr and subsequent carbonation (65-75% yield) see (1); from m-aminophenylacetic acid [Beil. XIV-456, XIV₁-(588)] via diazotization and use of Cu₂Cl₂ reactn. (but no details reported) (5); from m-chlorophenylpyruvic acid (4) in dil. aq. NaOH with 30% H₂O₂ (57% yield) see (4); from mchlorophenylacetonitrile, m.p. 11.5°, bp 261° at 757 mm. (2), by hydrolysis in H₂SO₄/ .AcOH /aq. see (2).]

[For reactn. of closely related m-Cl.C₆H₄.CH₂.COOMgX with large excess of various RMgX cpds. see (6) and also under m-chlorobenzyl chloride (3:6445).]

[C with SOCl2 yields (5) m-chlorophenylacetyl chloride, yel.-green liq., b.p. 52° at 16 mm. (5); this prod. with aminoacetic acid (glycine) in dil. aq. NaOH yields (5) m-chlorophenylacetaminoacetic acid (m-chlorophenylaceturic acid), colorless ndls. from aq., m.p. 144-145° (5).1

[C converted to its Pb salt, latter dried at 110° and distilled, yields (2) 3,3'-dichlorodibenzyl ketone, colorless ndls. from alc., m.p. 89° (2) (corresp. oxime, m.p. 73° (2), semicarbazone, m.p. 121° (2)).]

- Methyl 3-chlorophenylacetate: unreported.
- Ethyl 3-chlorophenylacetate: unreported.
- (3-Chlorophenylacet)anilide: thin white pl. from dil. alc., m.p. 130° cor. (1). [From

Č with 1 mole aniline on htg. at 180-190° for 2 hrs. (1), or indirectly from m-chlorobenzyl phenyl ketoxime by Beckmann rearr. with PCl₅ in ether (64-82% yield (1)).]

(3-Chlorophenylacet)-m-chloroanilide: white ndls. from dil. alc., m p. 120° cor. (1). [From C with m-chloroaniline (1 mole) on htg at 180-190° for 2 hrs. (1), or indirectly from m-chlorobenzyl m-chlorophenyl ketoxime by Beckmann rearr. with PCl₅ in ether (64-82% yield (1)).]

3:1910 (1) Jenkins, J. Am. Chem. Soc. 55, 2898-2899 (1933). (2) Kenner, Morton, J. Chem. Soc. 1934, 679-680 (3) Dippy, Williams, J. Chem. Soc. 1934, 1888-1892. (4) Buck, Ide, J. Am. Chem. Soc. 54, 3307-3309*(1932). (5) Muenzen, Cercedo, Sherwin, J. Biol. Chem. 68, 508-510 (1926). (6) Ivanov, Pchnénitchny, Bull. soc. chm. (5) 1, 231-232 (1934).

Colorless cryst. from alc. (0.8 ml./g. (5)); somewhat less sol in alc. than isomeric 2-chlorobiphenyl (3:0300). — Volatile with steam. — [For f p./compn. curves of systems: \bar{C} + biphenyl (1:7175), \bar{C} + 4-fluorobiphenyl, or \bar{C} + 4-bromobiphenyl, see (7)]

[For prepn. of \bar{C} from biphenyl (1:7175) with Cl_2 in pres. of Fe (30% yield (5)) (14) (16) (17), or SbCl₅ (12), see indic. refs. (2-chlorobiphenyl (3:0300) is also formed; for use of mixt. for transformer oil see (18); for sepn. of mixt. see (19)); for prepn. of \bar{C} from p-aminobiphenyl via diazotization and use of Cu_2Cl_2 reactn. see (2) (7).]

[For prepn. of \bar{C} from p-chloroaniline [Beil. XII-607, XII₁-(604)] via diazotization and coupling of resultant diazonium salt with C_6H_6 in aq. NaOH suspension (yields: 41% (1), 40% (6)) cf. (21) (23) or in aq. NaOAc (yield = 35% (6)), or by formn. of p-chlorobenzene-diazonium chloride/ZnCl₂ cpd. and reactn of latter with C_6H_6 in AcOH + NaOAc (yield = 34% (20)) see indic. refs.: from N-nitroso-acet-p-chloroanilide with C_6H_6 in CHCl₃ for a few days at room temp see (13).]

[For formn. of \bar{C} from decompn. of dibenzoyl peroxide (1:4930) in boilg. chlorobenzene see (22); from decompn. of benzoyl *p*-chlorobenzoyl peroxide see (23); from di-(*p*-chlorobenzoyl) peroxide in C_6H_6 see (24)(4) (3); for formn. of \bar{C} from 4-hydroxybiphenyl (1:1585) with PCl₅ see (10); from *p*-xenylselenium trichloride on htg. see (25); from *p*-chloroiodobenzene + Cu powder see (2)]

[\bar{C} with aq. 15–30% NaOH at 300–400° under pressure (26) in pres. of Cu (27), or \bar{C} with aq. Na₂CO₃ + Cu at 300° (28), or \bar{C} with aq. vapor over cat. at 525–600° (29) gives (75% yield (26)) 4-hydroxybiphenyl (1:1585) (28) (29) or its mixt. with 3-hydroxybiphenyl (1:1475) (27)]

[\bar{C} with conc. aq. NH₄OH + cat. under press. as directed (30) (31) gives p-aminobiphenyl.]

[\bar{C} with Li in dry ether under N₂ gives (32) Li p-xenyl. — \bar{C} with Na sand in C₆H₆ at 110–120° under press. followed by carbonation with CO₂ gives (65–67% yield (33)) biphenyl-4-carboxylic acid (p-phenylbenzoic acid) [Bcil. IX-671, IX₁-(280)]. — \bar{C} with Na

+ diethyl carbonate (1:3150) in C_6H_6 as directed gives (yields: 42% (35), 35–40% (36), 39% (37), 23% (38)) tri-(p-xenyl)carbinol (tris-p-biphenylcarbinol) [Beil. VI-738, V₁-(369)], colorless cryst. from AcOH, m.p. 207–208° (36), 207° (38), 206–207° (37). — Č with Na + benzophenone (1:5150) in C_6H_6 gives (67% yield (34)) diphenyl-p-xenyl-carbinol [Beil. VI-732], colorless cryst. from lgr., stable form, m.p. 135–136° (34), metastable form, m.p. 112–113° (34).]

[For reactn. of \bar{C} with Na + AsCl₃ giving (39) tri-(p-xenyl)arsine, with Na + SbCl₃ giving (40) tri-(p-xenyl)stibine, with Na + PCl₃ giving (41) tri-(p-xenyl)phosphine, or with Na + SiCl₄ giving (42) tetra-(p-xenyl)silane see indic. refs.]

[\bar{C} + stearoyl chloride (3:9960) + AlCl₃ in CS₂ gives (43) heptadecyl *p*-chloroxenyl ketone, m.p. 96-97° (43). — \bar{C} + cyclohexene (1:8070) + AlCl₃ gives (44) a mixt. of cyclohexyl-*p*-chlorobiphenyls.]

 $[\tilde{C} + \text{phthalic anhydride } (1:0725) + \text{AlCl}_3 \text{ as directed } (45) (46) \text{ gives } (93\% \text{ yield } (45))$ $o-[4-(p-\text{chlorophenyl})\text{benzoic acid, colorless rods from AcOH or toluene, m.p. } 251^{\circ}$ cor. (45), $249.6-250.6^{\circ}$ (46).]

The nitration of \bar{C} does not appear to have been reported.

 $\tilde{\mathbf{C}}$ on oxidn. with CrO₃ in AcOH yields (10) (25) p-chlorobenzoic acid (3:4940), m.p. 237° (10) (25).

3:1912 (1) Gomberg, Bachmann, J. Am. Chem. Soc. 46, 2339-2343 (1924). (2) Weissberger, Sängewald, Z. physik. Chem. B-20, 155 (1933). (3) Fichter, Adler, Helv. Chim. Acta 9, 284-286 (1926). (4) Gelissen, Hermans, Ber. 58, 292 (1925). (5) Jenkins, McCullough, Booth, Ind. Eng. Chem. 22, 31-34 (1930). (6) Elbs, Haworth, Hey, J. Chem. Soc. 1940, 1285. (7) L. Klemm, W. Klemm, Schiemann, Z. physik. Chem. A-165, 383-384, 388 (1933). (8) Fuoss, J. Am. Chem. Soc. 63, 371 (1941). (9) Brull, Gazz. chim. ital. 65, 24 (1935). (10) Schultz, Ann. 174, 209-210 (1874).

(11) Adam, Russell, J. Chem. Soc. 1930, 205. (12) Kramers, Ann. 189, 142-145 (1877), (13) Bamberger, Ber. 53, 2315-2316, 2320 (1920). (14) Britton, Stoesser (to Dow Chem. Co.). U.S. 1.835,754, Dec. 8, 1931; Cent. 1932, I 1440. (15) Hale, J. Am. Chem. Soc. 54, 4458-4459 (1932). (16) Prahl, Mathes (to F. Raschig), Ger. 575,765, May 3, 1933; Cent. 1933, II 134; Ger. 580,512, July 13, 1933; Cent. 1933, II 1763. (17) Malowan (to Swann Research, Inc.), U.S. 1,951,577, March 20, 1934; Cent. 1934, II 3183. (18) Federal Phosphorus Co., French 702,497, April 9, 1931; Cent. 1931, II 2096. (19) Britton, Stoesser (to Dow Chem. Co.), U.S. 1,890,427, Dec. 6, 1932; Cent. 1933, II 2894. (20) Hodgson, Marsden, J. Chem. Soc. 1949, 211.

(21) Bamberger, Ber. 29, 465-466 (1896). (22) Hey, J. Chem. Soc. 1934, 1967. (23) Wieland, Rasuwajeu, Ann. 486, 168-169 (1930). (24) Böeseken, Gelissen, Rec. trav. chim. 43, 871 (1924). (25) Behaghel, Hofmann, Ber. 72, 592 (1939). (26) du Pont Co., Brit. 406,319, March 22, 1934. Cent. 1934, I 3801. (27) Britton (to Dow Chem. Co.), U.S. 1,996,744, April 9, 1935; Cent. 1935, II 1962. (28) Britton (to Dow Chem. Co.), U.S. 1,959,283, May 15, 1934; Cent. 1934, II 1688. (29) Booth (to Swann Research, Inc.), U.S. 1,925,367, Sept. 5, 1933; Cent. 1934, I 128. (30) Groggins, Sţirton, Ind. Eng. Chem. 28, 1051-1063 (1926).

(31) Booth (to Swann Research, Inc.), U.S. 1,954,469, April 10, 1934; Cent. 1934, II 1846.
(32) Müller, Töpel, Ber. 72, 285 (1939).
(33) Morton, LeFevre, Hechenbleikner, J. Am. Chem. Soc. 58, 754-755 (1936).
(34) Clapp, Morton, J. Am. Chem. Soc. 59, 2074-2075 (1937).
(35) Bachmann, Wiselogle, J. Org. Chem. 1, 371-372 (1936).
(36) Morton, Myles, Emerson, Org. Syntheses 23, 95-97 (1943).
(37) Morton, Emerson, J. Am. Chem. Soc. 59, 1948 (1937).
(38) Morton, Stevens, J. Am. Chem. Soc. 53, 4029-4030 (1931).
(39) Worrall, J. Am. Chem. Soc. 53, 666 (1930).
(40) Worrall, J. Am. Chem. Soc. 52, 2048 (1930).

(41) Worrall, J. Am. Chem. Soc. 52, 2934-2935 (1930). (42) Schumb, Ackerman, Saffer, J. Am. Chem. Soc. 60, 2487 (1938). (43) Ralston, Christensen, Ind. Eng. Chem. 29, 194-196 (1937). (44) Martin, Coleman (to Dow Chem. Co.), U.S. 1,969,984, Aug. 14, 1934; Cent. 1935, I 2258. (45) Groggins, Ind. Eng. Chem. 22, 622 (1930). (46) Groggins, U.S. 1,786,526, 1,786,528, Dec. 30, 1930; Cent. 1931, II 3157-3158 (1931).

Colorless ndls. from alc., 80% alc., or ether + alc. — Eas. sol. hot alc. but spar. sol. cold alc., eas. sol. ether, spar. sol. cold lgr. [For search for possible polymorphic forms see (4) (9) (10).]

72-73°

(8)

[For prepn. of $\bar{\mathbb{C}}$ from benzoic acid (1:0715) + chlorobenzene (3:7903) with AlCl₃ (82.4% yield $\bar{\mathbb{C}}$ + 11.9% 2-chlorobenzophenone (3:0715) (1)), or with P_2O_5 at 180–200° (5), see indic. refs.; from benzoyl chloride (3:6240) + chlorobenzene (3:7903) with AlCl₃ (yields: 97% (37), 86% (8), 80–90% (7) (11), 45% (4), 40% (2)) (3) (some 2-chloro isomer also being formed (12)) see indic. refs.; from p-chlorobenzoyl chloride (3:6550) + benzene with AlCl₃ (84.6% yield) see (6); from tetra-(4-chlorophenyl)ethylene glycol bis-(magnesium iodide) in quant. yield with I₂ or O₂ see (13); from p-chlorobenzohydrylidene- α -phenylethylamine by hydrol. with warm dil. H₂SO₄ see (8).]

[\bar{C} on reduction with Al/Hg in 80% alc. (3) (14) or with 3% Na/Hg (7) or on boilg. with alc. KOH for 2 days (15), or exposure to sunlight for 7 days of its soln. in isopropyl alc. contg. Na isopropylate, gives (85% yield (3) (14), 80% yield (16)) 4-chlorophenyl-phenyl-carbinol. (4-chlorobenzohydrol) [Beil. VI-680, VI₁-(327)], m p. 67.5° (3) (14), 62° (7), accompanied by a little (14% (3) (14)) α,α' -diphenyl- α,α' -hs-(4-chlorophenyl)ethylene glycol (sym.-4,4'-dichlorobenzopinacol) [Beil. VI₁-(523)], m.p. 179° (3) (14). — \bar{C} with Zn + AcOH yields 4-chlorobenzohydryl acetate (12) or a mixt. (7) of 4-chlorobenzohydrol (above) + the corresp. pinacol (see below).]

[\bar{C} with Mg + MgI₂ in ether + C₆H₆ or \bar{C} in very dil. alc. soln. in sunlight (7) gives (94% yield (13)) sym.-4,4'-dichlorobenzopinacol, m.p. 172-178° (see above). — \bar{C} with Zn dust + H₂SO₄ in aq. AcOH yields (12) sym.-4,4'-dichloro- α -benzopinacoline (sym.-4,4'-dichlorotetraphenylethylene oxide) [Beil. XVII₁-(45)], ndls. from AcOH, m.p. 220° dec. (12). — For oxidn.-reductn. potential of \bar{C} see (35).]

[\bar{C} with conc. HI + red P in AcOH refluxed 14 hrs. gives (7) 4-chlorodiphenylmethane [Beil. V-590, V₁-(278), V₂-(500)], b.p. 298° at 742.5 mm. (7).]

[C with diphenylmethyl sodium (benzohydryl-sodium) followed by aq. gives (18) corresp. tertiary alc., viz., benzohydryl-p-chlorophenyl-phenyl-carbinol, m.p. 176-178° (18), which with acetyl chloride loses H₂O to give 4-chlorotetraphenylethylene [Beil. V₁-(376), V₂-(679)], m.p. 166-167° (18). — C with MeMgI in dry ether yields (19) p-chlorophenyl-phenyl-methyl-carbinol which on loss of aq. by htg. as directed gives (66% overall yield) a-(4-chlorophenyl)-a-phenylethylene, b.p. 164° at 16 mm. (19); note that this prod. with

Br₂ does not add halogen but rather evolves HBr yielding (20) both solid (m.p. 94–95°) and liq. stereoisomers of β -(4-chlorophenyl)- β -phenylvinyl bromide. — \bar{C} with β -(4-chlorophenyl)- β -phenylvinyl MgBr as directed (23) gives 1,4-di-(p-chlorophenyl)-1,4-diphenyl-butadiene-1,3, yellowish green ndls. from amyl alc., m.p. 230° (23). — \bar{C} with triphenyl-methyl MgBr in ether + C_6H_6 , followed by dil. Λ cOH, gives (21) 78% yield sym.-4,4-dichlorobenzopinacol (see above) + 80% yield triphenylmethyl peroxide.]

[Č with ethyl bromoacctate + Zn in dry C_6H_6 gives (yields: 79% (22), 67% (24)) ethyl β -(4-chlorophenyl)- β -hydroxy- β -phenyl-propionate, m.p. 79-80.5° (22), 69° (24); this prod. on htg with 85% formic acid gives (66% yield (24)) ethyl β -(4-chlorophenyl)cinnamate, b.p. 210-212° at 13 mm. (24), or on hydrolysis gives (22) β -(4-chlorophenyl)- β -hydroxy- β -phenylpropionic acid, m.p. 188.5-189.° dec. (22).]

 \bar{C} with PCl₅ at 150° gives (yields: 90% (25) (27), 88% (26) (8)) α , α , 4-trichlorodiphenylmethane (4-chlorobenzophenone dichloride) [Beil. V-592, V₁-(279)], b.p. 191-193° at 13 mm. (8), 189-194° at 12 mm. (25). $D_1^{20} = 1.302$ (25), $n_D^{20} = 1.6110$ (25); this prod. with Zn dust refluxed in dry ether for 1 hr gives (12% yield (25)) α , β -di-(p-chlorophenyl)- α , β -di (phenyl)ethylene, ndls. from alc., m p. 202-203° (25).

 \bar{C} fused with KOH/NaOH gives (28) benzoic and (66%) + p-chlorobenzoic acid (3:4940) (18%) + a little p-hydroxybenzoic acid (1:0840). — \bar{C} with 10% aq. NaOH in pres. of Cu under press. at 190° yields (29) 4-hydroxybenzophenone (1:1560).

[C with NH₃ in pres. of Cu cpds. at 170–300° under press. gives (30) 4-aminobenzophenone [Beil. XIV-81, XIV₁-(388)], lfts. from dil. alc., mp. 123–124°. — C condensed with NaNH.C₆H₅ as directed (31) yields 4-anilinobenzophenoneanil, m.p. 56° (for other amines and use of products as antioxidants see (31)); note, however, that by a closely similar method (36) p-chlorobenzophenoneanil, m.p. 64–64.5°, can also be obtd]

C on dinitration with abs. HNO₃ gives (32) a mixt. contg. 4-chloro-3,3'-dinitrobenzophenone, cryst. from toluene, m p. 166°, 4-chloro-3,2'-dinitrobenzophenone, cryst. from alc., m.p. 123.5°, and 4-chloro-3,4'-dinitrobenzophenone, m p. 136-136.5°.

- ① 4-Chlorobenzophenone oxime: This prod. is known in two stereoisomeric forms: the higher-melting isomer, m.p. 155-156° (6) (corresp. acetate, m.p. 147-148° (6), corresp. benzyl ether, m.p. 74-75° (6)), which on Beckmann rearr. (6) (34) with PCl₅, with conc. H₂SO₄ at 100°, or with AcOH/Ac₂O/HCl yields 4-chlorobenzanilide, is in the light of modern views on trans interchange regarded as the syn-(p-chlorophenyl) stereomer; the lower-melting isomer, m.p. 95° (6) (corresp. acetate, m.p. 105-106° (6), corresp. benzyl ether, m.p. 98-99° (6)), which on Beckmann rearr. with PCl₅ yields benz-p-chloroanilide, is now regarded as the trans-(p-chlorophenyl) stereomer. [A mixt. of these two stereoisomeric oximes contg. 56% high-melting form + 44% low-melting form (33) is obtd. from C with NH₂OH.HCl + pyridine in abs. alc. (33) or from C + NH₂OH.HCl + dil. alc. KOH (6); the two isomers are separated by means of their different solubilities in alc. (6) (34). Note that the lower-melting isomer is itself converted to the higher-melting form by htg. 3 hrs. at 100° (6) and also (in part) during Beckmann rearr.]
- **D** 4-Chlorobenzophenone phenylhydrazone: cryst. from ether /AcOH, m.p. 106° (34). [From $\bar{\mathbf{C}}$ with phenylhydrazine or phenylhydrazine acetate in alc. as directed (34).]
- 4-Chlorobenzophenone p-nitrophenylhydrazone: unreported.
- **10** 4-Chlorobenzophenone, 2,4-dinitrophenylhydrazone: m.p. 184-185° (Heilbron).
- 3:1914 (1) Newton, Groggins, Ind. Eng. Chem. 27, 1398 (1935). (2) Wegerhoff, Ann. 252, 5-11 (1889). (3) Cohen, Rec. trav. chim. 38, 115, 123 (1919). (4) Schaum, Unger, Z. anorg, allgem. Chem. 132, 91-93 (1923-24). (5) Kollarits, Merz, Ber. 6, 547 (1873). (6) Demuth, Dittrich, Ber. 23, 3609-3614 (1890). (7) Montagne, Rec. trav. chim. 26, 262-267 (1907). (8)

Ingold, Wilson, J. Chem. Soc. 1933, 1502. (9) Schaum, Ann. 462, 203 (1928). (10) Schaum, Naumann, Z. anorg. allgem. Chem. 148, 222 (1925).

- (11) Gomberg, Cone, Ber. 39, 3278 (1906). (12) Montagne, Kirpal, Rec. trav. chim. 29, 138, 143, 145-147 (1910). (13) Gomberg, Bachmann, J. Am. Chem. Soc. 49, 239, 250 (1927). (14) Böeseken, Cohen, Cent. 1915, I 1376. (15) Montagne, Rec. trav. chim. 27, 334-335 (1908). (16) Bachmann, J. Am. Chem. Soc. 55, 394 (1933). (17) Cohen, Rec. trav. chim. 39, 258 (1920). (18) Bergmann, J. Chem. Soc. 1936, 412-413. (19) Bergmann, Bondi, Ber. 64, 1468 (1931). (20) Bergmann, Engel, Meyer, Ber. 65, 456 (1932).
- (21) Bachmann, J. Am. Chem Soc 53, 2762 (1931). (22) Alexander, Jacoby, Fuson, J. Am. Chem. Soc. 57, 2209 (1935). (23) Ref 24, p. 256. (24) Bergmann, Hoffmann, Meyer, J. prakt. Chem. (2) 135, 261 (1932). (25) Price, Fanta, J. Am. Chem. Soc. Soc. 64, 2726-2727 (1942). (26) Peterson, Am. Chem. J. 46, 332 (1911). (27) Morgan, J. Am. Chem. Soc. 38, 2100 (1916). (28) Lock, Rödiger, Ber. 72, 868 (1939). (29) Britton (to Dow Chem. Co.), U.S. 1,961,630, June 5, 1934; Cent. 1934, I 1846. (30) Britton (to Dow Chem. Co.), U.S. 1,946,058, Feb. 6, 1934; Cent. 1934, I 3396.
- (31) Britton, Heindel, Bryner (to Dow Chem. Co), U.S. 2,063,868, Dec 8, 1936; Cent. 1937, I 4559; C.A. 31, 705 (1937) (32) Montagne, Ber. 49, 2274-2276 (1916). (33) Bachmann, Barton, J. Org. Chem. 3, 303 305 (1938). (34) Overton, Ber. 26, 27-28 (1893). (35) Adkins, Cox, J. Am. Chem. Soc 60, 1153 (1938). (36) Britton, Bryner (to Dow Chem. Co), U.S. 1,938,890, Dec. 12, 1933; Cent. 1934, I 3801. (37) Borcherdt, Adkins, J. Am. Chem. Soc. 60, 5 (1938).

3:1915 DI-(TRICHLOROMETHYL) OCCl₃ (°₃O₃Cl₆ Beil. III - 17 CARBONATE III₁-(8) Carbonate, hexachlorodimethyl carbonate)

M.P.	78-79°	(1)	B.P. 203° at 760 mm., sl. dec.	(3)
	79°	(2) (3) (4)	124° at 50 mm.	(3)
			117° at 36 mm.	(2)
			105° at 22 mm.	(2)

Cryst. from anhydrous ether (1) (2) or pet. eth. (4). — Disagreeable penetrating odor; attacks mucous membrane.

 \bar{C} on distriction dissociates slightly into phosgene (3:5000) and diphosgene (trichloromethyl chloroformate) (3:5515) (4) (5); solid \bar{C} when mixed with powdered charcoal and heated to just above m.p. rapidly decomposes to phosgene (3:5000) (5).

[For prepn. of \bar{C} from dimethyl carbonate (1:3046) by chlorination in sunlight see (1); from methyl chloroformate (3:5075) by chlorination see (2)

 \bar{C} on treatment at 20° for 1 hr. with NaI in acetone evolves CO and separates iodine to 84% of amt. expressed by the reactn. Cl₃C.O CO.O.CCl₃ + 6NaI \rightarrow 3CO + 3I₂ + 6NaCl (6).

 \bar{C} with most reagents behaves like phospene; e.g., \bar{C} with alcohols gives ultimately dialkyl carbonates (7); \bar{C} with aniline in ether (7) or aq. (2) gives N,N-diphenylurea, m.p. 233° (7); \bar{C} with phenol + aq. NaOH gives (90% yield (7)) diphenyl carbonate (1:2335) cryst. from alc., m.p. 77.5-78° (7).

[For use of \bar{C} in prepn. of acid chlorides of carboxylic or sulfonic acids see (8); similarly \bar{C} htd. with anhydrous NaOAc yields Ac₂O (9).]

3:1915 (1) Councier, Ber. 13, 1697-1699 (1880). (2) Grignard, Rivat, Urbain, Ann. chim. (9) 13, 263-265 (1920). (3) Kling, Florentin, Jacob, Ann. chim. (9) 14, 208-210 (1920). (4) Marotta, Gazz. chim. ital. 59, 959 (1929). (5) Hood, Murdock, J. Phys. Chem. 23, 508-512 (1919). (6) Perret, Biechler, Compt. rend. 203, 84-87 (1936); C.A. 30, 7423 (1936). (7) Nekrassow, Melnikov, J. prakt. Chem. (2) 126, 95-96 (1930). (8) Brit 401,643, Dec. 14, 1933; Cent. 1934, II 2133. (9) Melnikov, Sidorova, J. Gen. Chem. (U.S.S.R.) 1, 740-742 (1931); C.A. 26, 3234 (1932); Cent. 1932, II 2313.

3:1925 1,1-DICHLORO-2-(o-CHLOROPHENYL)-2-(p-CHLOROPHENYL)

C14H8Cl4 Beil. S.N. 480

M.P. 78.4-79.5° cor. (1)

Rectangular pl. from MeOH or EtOH.

[For prepn. of \bar{C} from 1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)-thane ("o,p'-DDT") (3:1820) by elimination of 1 HCl with alc. KOH on refluxing 3 hrs. (97% yield) see (1).]

C on oxidn. with CrO₃/AcOH gives (1) 2,4-dichlorobenzophenone (3:1565), m.p. 64.2-65.2° cor.

3:1925 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., J. Am. Chem. Soc. 67, 1599, 1602 (1945).

3:1930 1,2,5-TRICHLORONAPHTHALENE

M.P. 79° (1) 78-78.5° (2) (4) 77° (3) (See text.)

Cryst. volatile with steam. — \bar{C} if fused at 79° in cap. m.p. tube, and then allowed to cool slowly in the bath or rapidly in air, solidifies at 69° to a translucent cryst. mass which (if the temperature is immediately raised) melts at 74° but if allowed to remain at or below 69° for a few minutes becomes opaque and then melts at 79° (1).

[For prepn. of Č from 1-chloro-5-sulfonaphthylamine-2 [Beil. XIV-750] via diazotization and use of Cu₂Cl₂ reactn. see (1) (4); from 1-chloro-2-nitronaphthalenesulfonic acid-5 [Beil. XI-170] (3), 2-chloro-1-nitronaphthalenesulfonyl chloride-5 [Beil. XI-169] (3), 2-chloronaphthalene-1,5-bis-(sulfonyl chloride) [Beil. XI-213] (5), or 1,2-dichloronaphthalenesulfonic acid-5 [Beil. XI-163] (2) with PCl₅ see indic. refs.]

[Č treated with ClSO₃H in CS₂ and conv. to K salt as directed (1) gives a mixt. contg. 70% (less sol.) K 1,2,5-trichloronaphthalenesulfonate-X (corresp. sulfonyl chloride, m.p. 146°) and 30% (more sol.) K 1,2,5-trichloronaphthalenesulfonate-Y (corresp. sulfonyl chloride, m.p. 179°).]

3:1936 (1) Turner, Wynne, J. Chem. Soc. 1941, 247, 251-252. (2) Armstrong, Wynne, Chem. News 59, 188 (1889). (3) Cleve, Chem. Ztg. 17, 398 (1893). (4) Armstrong, Wynne, Proc. Chem. Soc. 1839, 36, 49. (5) Armstrong, Wynne, Chem. News 62, 164 (1890).

Colorless cryst. from alc.; 100 pts. 90% alc. dis. in cold 11.91 pts. \bar{C} , on boilg. 19.87 pts. \bar{C} (8). — \bar{C} is eas. sol. ether, CHCl₃, or CS₂; less so in alc. or C₆H₆.

PREPARATION OF C

[For prepn. of Č from 1,1,1-trichloro-2,2-diphenylethane (3:1420) by splitting out 1 HCl on distn. (9) cf. (10) (6), or with alc. KOH (2) (1) (for study of rate see (11)), or alc. NaOEt (1) see indic. refs.; from unsym.-diphenylethane [Beil. V-605, V₁-(285), V₂-(509)] with Cl₂ at 100-150° in quartz flask in light for 10 hrs. followed by distn. at ord. press. (16% yield) see (3); from unsym.-diphenylethylene [Beil. V-639, V₁-(308), V₂-(543)] with Cl₂ followed by distn. see (12).]

[For form. of $\tilde{\mathbb{C}}$ from α, α -dichloro- β, β -diphenylethylene sulfide ($\mathbb{C}l_2\mathbb{C}$ — $\mathbb{C}(\mathbb{C}_6\mathbb{H}_6)_2$) by

htg. at 100° for 2 hrs. (or for shorter time at 160°), or by boilg. with MeOH, or htg. with Zn see (13); from α,α -dichloro- β,β -diphenylethyl p-tolyl sulfone with PCl₅ at 200° for 2 hrs. see (4); for formn. of \tilde{C} during condensation of chloral (3:5210) with C_6H_6 + AlCl₅ in CS₂ see (10) (6).]

CHEMICAL BEHAVIOR OF C

Reduction. [\bar{C} on reduction with conc. HI + P at 170-210° gives (7) unsym.-diphenylethane [Beil. V-605, V₁-(285), V₂-(509)] and bibenzyl (1:7149).]

Addition of halogens. \tilde{C} with Cl_2 in dry CHCl₃ adds 1 mole halogen giving (6) (5) 1,1,1,2-tetrachloro-2,2-diphenylethane, m.p. $S5^{\circ}$ (6). — \tilde{C} with excess Br_2 htd. on aq. bath until excess reagt. evaporates gives (6) 1,2-dibromo-1,1-dichloro-2,2-diphenylethane, cryst. from alc., m.p. $120.0-120.5^{\circ}$ (6).

Behavior with alkalies. [\bar{C} with aq. NaOH at 150°, or with alc. NaOH in s.t. at 100°, is substantially unaffected within 24 hrs. (3); however, \bar{C} with alc. KOH in stainless-steel bomb at 150° for 24 hrs. gives (73% yield (3)) diphenylacetic acid (1:0765), m.p. 147-148° cor. (3) cf. (1). — Note also that, although \bar{C} with dry NaOMe in C_6H_6 does not react even in s.t. at 180° for 36 hrs. yet \bar{C} with dry NaOMe (2 moles) on direct distn. gives diphenylacetylene (tolane) and other products (15).]

[Note also that \tilde{C} with Na phenolate at 225° for 24 hrs. gives (3) α -hydroxy- α , α -diphenylacetaldehyde diphenylacetal (benzilaldehyde diphenylacetal), m.p. 111.5°-112° (3).]

Behavior with H_2SO_4 or HNO_3 . With H_2SO_4 . \bar{C} with conc. H_2SO_4 on warming first becomes yellow, then dark green, later violet, and ultimately brownish red. (5) (6).

With HNO₃. Č on addition to 12 pts. ice-cold fumg. HNO₃ and subsequently pouring onto ice gives (14) 1,1-dichloro-2,2-bis-(p-nitrophenyl)ethylene, yellowish ndls. from hot alc., m.p. 172° (14); note also that from the mother liquors of recrystn. there can also be obtd. some 4,4'-dinitrobenzophenone, m.p. 188-189°, resulting from some simultaneous oxidn. (14).

3:1938-3:1945 DIVISION A 250

Behavior with active metals. [C with Li in dry ether followed by treatment with alc. gives according to conditions (16) (17) (18) either or both 1,2,3-triphenylnaphthalene, m.p. 151-152° (16) (17) (18) (mononitro deriv., m.p. 200-201° (18)), and 1,2,3,4-tetraphenyl-butadiene-1,3, m.p. 183° (18) (17) (16); for explanation see (18).]

3:1938 (1) Harris, Frankfurter, J. Am. Chem. Soc. 48, 3147-3148 (1926). (2) Bayer, Ber. 6, 223 (1873). (3) Sheibley, Prutton, J. Am. Chem. Soc. 62, 840-841 (1940). (4) Kohler, Potter, J. Am. Chem. Soc. 57, 1321 (1935). (5) Biltz, Ann. 296, 240-241 (1887). (6) Biltz, Ber. 26, 1955-1956 (1893). (7) Redsko, J. Russ. Phys.-Chem. Soc. 21, 424 (1889). (8) Elbs, J. prakt. Chem. (2) 47, 78 (1893). (9) Goldschmiedt, Ber. 6, 987 (1873). (10) Biltz, Ann. 296, 221 (1897). (11) Brand, Busse-Sundermann, Ber. 75, 1822, 1828 (1942). (12) Hepp. Ber. 7, 1411 (1874).

(11) Brand, Busse-Sundermann, Ber. 75, 1822, 1828 (1942). (12) Hepp, Ber. 7, 1411 (1874). (13) Staudinger, Siegwart, Helv. Chim. Acta 3, 846 (1920). (14) Lange, Zufall, Ann. 272, 2-3 (1892). (15) Staudinger, Rathsam, Hclv. Chim. Acta 5, 648, 654 (1922). (16) Schlenk, Bergmann, Ann. 463, 72-75, 80-81 (1928). (17) Bergmann, Schreiber, Ann. 500, 118-120 (1933). (18) Smith, Hoehn, J. Am. Chem. Soc. 63, 1184-1187 (1941).

Colorless cryst. from alc. — \bar{C} is eas. sol. alc., ether, acetone, AcOH, lgr., or CHCl₃. — \bar{C} with conc H₂SO₄ or with AlCl₃ gives a red color.

[For prepn. of \bar{C} from dichloroacetaldehyde diethylacetal (3:6110) with C_6H_6 + conc. H_2SO_4 (1) (5) (3) (yields not reported) see indic. refs.; for formn. of \bar{C} from dichloroacetaldehyde (3:5180) with C_6H_6 + AlCl₃ (6), or from 1,1,1-trichloro-2,2-diphenylethane (3:1420) during reduction in alc./pyridine with H_2 + Ni (7) or during electrolytic reduction as specified (8) (9) (2), see indic. refs.]

 \bar{C} on distn. at ord. press. (1) or with boilg. alc. KOH (1) or NaOH (2) loses HCl giving 1-chloro-1,2-diphenylethylene [Beil. V-639], m.p. 42°. — Note, however, that \bar{C} with KNH₂ in liq. NH₃ (3) (5) not only loses HCl but the resulting intermediate reacts further with rearrangement giving (91% yield) diphenylacetylene (tolane) [Beil. V-656, V₁-(319), V₂-(568)].

Č on boilg. with aq. is not hydrolyzed and no trace of the expected diphenylacetaldehyde results (1).

C on addition to fumg. HNO₃ at 0°, stdg. 24 hrs., and pouring into aq. gives (1) a dinitrobenzophenone of unknown structure (corresp. phenylhydrazone, m.p. 234° (1)).

3:1940 (1) Buttenberg, Ann. 279, 324-327 (1894). (2) Brand, Ber. 46, 2937-2941 (1913).
 (3) Coleman, Holst, Maxwell, J. Am. Chem. Soc. 58, 2312 (1936). (4) Combes, Ann. chim. (6) 12, 271 (1887). (5) Coleman, Maxwell, J. Am. Chem. Soc. 56, 132-134 (1934). (6) Delacre, Bull. soc. chim. (3) 13, 858, Note 4 (1895). (7) Brand, Horn, J. prakt. Chem. (2) 115, 353, 361 (1927). (8) Brand, Z. Elektrochem. 16, 669 (1910). (9) Brand, Ber. 54, 1987 (1921).

3:1945 1,1,2,3,4,4-HEXACHLORO-BUTENE-2

(solid stereoisomer)

Cl Cl Cl Cl
$$C_4H_2Cl_6$$
 Beil. S.N. 11
$$HC-C=C-CH$$

M.P. 80° (1)

[See also liquid stereoisomer (3:9046).]

Colorless shining lfts. (from alc.) with camphoraceous odor. Eas. sol. ether, C_6H_6 , CHCl₃, or CCl₄.

[For prepn. of \bar{C} (100% yield (1)) from the solid stereoisomer (3:0870) of 1,2,3,4-tetra-chlorobutadiene-1,3 see (1); for formn. of \bar{C} from 1,1,2,2-tetra-chloroethane (acetylene tetra-chloride) (3:5750) by actn. of u.v. light see (1).] [Note that octa-chlorobutane (3:2000) has also been reported in same reactn.] [For formn. of \bar{C} together with its liquid stereo-isomer (3:9046) by actn. of Cl_2 upon the high-boilg, fraction obtd in the prepn. of tri-chloroethylene (3:5170) from 1,1,2,2-tetra-chloroethane (acetylene tetra-chloride) (3:5750) see (1).]

Č in alc refluxed with Zn/Cu couple for 1 hr. yields (1) the solid stereoisomer of 1,2,3,4-tetrachlorobutadiene-1,3 (3:0870), m.p. 50° (1).

3:1945 (1) Müller, Huther, Ber. 64, 589-600 (1931); C.A. 25, 3956-3957 (1931).

[For prepn. of \bar{C} from piperonylic acid (1:0865) with excess SOCl₂ at 100° (1) or in C_6H_6 (90–95% yield (4)), or with PCl₅ (2), see indic. refs. — Note, however, that at higher temps. the dioxymethylene group is also attacked: e g, piperonylic acid htd. in a s.t. with SOCl₂ at 180–200° for 8 hrs. (1) or refluxed 3 hrs. with 3 moles PCl₅ (1) yields μ,μ -dichloropiperonoyl chloride [Beil. XIX-272, XIX₁-(743)], b.p. 149–150° at 12 mm. (1).]

[C with diazomethane yields (3) piperonyl diazomethyl ketone which with ammonia yields (3) homopiperonylamide, m.p. 173°; C with ethyl sodio-acetoacetate in dry ether, followed by hydrolysis (as specified (4)) of the acetyl group, yields ethyl piperonoylacetate, m.p. 42.5° (4)]

C on hydrolysis with aq. yields piperonylic acid (1:0865), m.p. 228°.

- Deperonvlamide [Beil. XIX-270]: tbls. from alc., m p. 169°.
- ① Piperonylanilide [N-phenyl-piperonylamide]: cryst. from dil. alc., m.p. 146-147° cor. (5) [From $\tilde{C}+2$ moles aniline in C_6H_6 (5).]
- D Piperonylo-p-toluidide: cryst. from dil. alc., m.p. 149-149.5° cor. (5). [Similarly using p-toluidine (5).]
- D Piperonylo-α-naphthalide: cryst. from dil. alc., m.p. 192-193° cor. (5). [Similarly using α-naphthylamine (5).]
- Dependence Piperonylo-β-naphthalide: cryst. from dil. alc., m.p. 156.5–157° cor. (5). [Similarly using β-naphthylamine (5).]

3:1960 (1) Barger, J. Chem. Soc. 93, 567-568 (1908). (2) Perkin, Robinson, Chem. News 92, 293 (1905). (3) Arndt, Eistert, Ger. 650,706, Sept. 30, 1937; Cent. 1937, II 4390; C.A. 32, 595 (1938). (4) Bruchhausen, Gerhard, Ber. 72, 835-836 (1939). (5) Gertler, Haller, J. Am. Chem. Soc. 64, 1741 (1942).

M.P. 80-81°

See 3:2662 under anhydrous product.

3:1975 1,8,6-TRICHLORO-NAPHTHALENE

M.P. 80.5°-81° (1) (2)

[For prepn. of Č from 3,6-dichloronaphthalenesulfonyl chloride-1 (1), from 6-chloronaphthalene-1,3-bis-(sulfonyl chloride) [Beil. XI-212] (2), from 3-chloronaphthalene-1,6-bis-(sulfonyl chloride) [Beil. XI-214] (2), from 1-chloronaphthalene-3,6-bis-(sulfonyl chloride) [Beil. XI-217] (3), or from 1-nitronaphthalene-3,6-bis-(sulfonyl chloride) [Beil. XI-218] (1) (3) (4), each with PCl₅ as directed, see indic. refs.]

[C treated with CISO₃H in CS₂ and prod. converted to sodium salt yields (1) sodium 1,3,6-trichloronaphthalenesulfonate-7 (corresp. sulfonyl chloride, m.p. 156° (1)).]

3:1975 (1) Turner, Wynne, J. Chem. Soc. 1941, 247, 253, 256. (2) Armstrong, Wynne, Chem. News 62, 164-165 (1890). (3) Armstrong, Wynne, Chem. News 71, 254 (1895). (4) Armstrong, Wynne, Proc. Chem. Soc. 1895, 81.

3:1990 1,3-DICHLORONAPHTHOL-2

CI OH CI C₁₀H₆OCl₂ Beil. VI - 649

VI₁---VI₂-(604)

M.P. 80-81° (1) 78° (2)

Ndls. from lgr.; eas. sol. alc., ether, AcOH, or C6H6 (1).

[For prepn. see Beil. VI-649 and (2).]

 \bar{C} in AcOH oxidized with conc. HNO₃ (D=1.42) yields mainly 3-chloronaphthoquinone-1,2 [Beil. VII-720], red ndls. from CHCl₃, m.p. 172° (1).

 \bar{C} in alc. boiled 15 hrs. with coppered Zn dust yields 3-chloronaphthol-2 (3:2545), m.p. 93° (4); but \bar{C} is not reduced by Na/Hg (3).

[For study of reaction of C with alkali sulfites see (5).]

① 1,3-Dichloro-2-naphthyl acetate: from $\ddot{C} + AcCl$; m.p. 79-80° (1). [Note that this m.p. is close to that of original \ddot{C} .]

3:1990 (1) Zincke, Ber. 21, 3385-3387 (1888). (2) Fries, Schimmelschmidt, Ann. 484, 297 (1930). (3) Marschalk, Bull. soc. chim. (4) 43, 1361 (1928). (4) Herzberg, Spengler, Schmid (to I.G.), Ger. 431,165, June 30, 1926; Cent. 1926, 1196 (1926). (5) Marschalk, Bull. soc. chim. (4) 45, 651-662 (1929).

CHAPTER VI

DIVISION A. SOLIDS

(3:2000-3:2499)

3:2000 1,1,2,2,3,3,4,4-OCTA-CHLOROBUTANE

C₄H₂Cl₈ Beil. S.N. 10

M.P. 81° (1)

Colorless cryst. from alc. with odor resembling honey.

[For formn. of \bar{C} from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) by protracted action of ultra-violet light see (1); considerable amts. of dichloroacetic acid (3:6208), m.p. 10.85°, and small amts. of oxalic acid (1:0445) are also formed (1), and the solid stereoisomer (3:1945) of 1,1,2,3,4,4-hexachlorobutene-2, m.p. 81° has also been reported (3) from the same reaction.]

[An octachlorobutane of m.p. 75.0-76.0° obtd. (2) from trichloroethylene (3:5170) by actn. of F_2 is not regarded (2) as having the structure of \tilde{C} .]

3:2000 (1) Müller, Luber, Ber. 65, 985-987 (1932). (2) Miller, J. Am. Chem. Soc. 62, 343 (1940). (3) Müller, Hüther, Ber. 64, 599 (1931).

3:2100 2,4,5-TRICHLOROTOLUENE

$$\begin{array}{cccc} CH_3 & C_7H_5Cl_3 & \textbf{Beil. V - 299} \\ & & & & & & & & \\ Cl & & & & & & & \\ Cl & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & \\ & & \\ & & & \\ & & \\ & & & \\ & &$$

White ndls. or lfts. from alc. [For sepn. of \bar{C} from 2,3,4-trichlorotoluene (3:0425) by sulfonation of latter under conditions not affecting \bar{C} see (2) (7).]

[For prepn. of \bar{C} from 4,5-dichloro-2-aminotoluene [Beil. XII-837] (8), or from 4,6-dichloro-3-aminotoluene [Beil. XII-872] (8) (5), or from 2,5-dichloro-4-aminotoluene [Beil. XII-990] (3), via dizactization and use of Cu_2Cl_2 reactn. see indic. refs.; from toluene + AlCl₃ with SO_2Cl_2 at 70° (40% \bar{C} + 34% 2,3,4-trichlorotoluene (3:0425) (1)) see (1).]

[For formn. of \bar{C} (together with other products) from toluene with Cl₂ (9) in pres. of I₂ (10) or MoCl₅ (11) or FeCl₃ (11) on silica gel (4), or by electrolysis in HCl/AcOH soln. (12), see indic. refs.; from o-chlorotoluene (3:8245) or p-chlorotoluene (3:8287) with Cl₂ in pres. of MoCl₅ or FeCl₃ see (2); from 2,4-dichlorotoluene (3:6290) in pres. of Al/Hg

(13) or Fe (6) or from 3,4-dichlorotoluene (3:6355) in pres. of Al/Hg (13) see indic. refs.; from sodium p-toluenesulfonate with Cl_2 see (14).]

[\bar{C} with Cl_2 yields (15) 2,4,5-trichlorobenzal dichloride (3:6910) (together with other products).]

 \bar{C} on mononitration, e.g., by soln. inHNO₃ (D=1.52) yields (16) (2) (8) 2,4,5-trichloro-3-nitrotoluene [Beil. V-333], ndls. from alc., m.p. 92° (2), 91-92° (8), 88.5-90.5° (17), 88.5° (16) (note that the isomeric 2,4,5-trichloro-6-nitrotoluene (prepd. indirectly (18)) has m.p. 93-94° (18)); \bar{C} on dinitration, e.g., on warming with a mixt. of HNO₃ (D=1.5) + conc. H₂SO₄, yields (16) (2) (8) 2,4,5-trichloro-3,6-dinitrotoluene [Beil. V-346], ndls. from alc., m.p. 227° (1) (2), 226-227° (8), 226° u.c. (18), 225° (16).

 \ddot{C} on oxidn. with $K_2Cr_2O_7 + H_2SO_4$ (19) or with dil. HNO₃ in s.t. at 150° (8) (6) yields 2,4,5-trichlorobenzoic acid (3:4630) q.v.

3:2100 (1) Silberrad, J. Chem. Soc. 127, 2681 (1925).
(2) Seelig, Ann. 237, 131, 140, 156 (1887).
(3) Morgan, Drew, J. Chem. Soc. 117, 789 (1920).
(4) Firth, Smith, J. Chem. Soc. 1936, 339.
(5) Musante, Fusco, Gazz chim. ital. 66, 645 (1936).
(6) Feldman, Kopeliowitsch, Arch. Pharm.
273, 493-495 (1935).
(7) Prentzell, Ann. 296, 181-182 (1897).
(8) Cohen, Dakin, J. Chem.
Soc. 81, 1332-1335 (1902).
(9) Limpricht, Ann. 139, 326 (1866).
(10) Beilstein, Kuhlberg, Ann. 146, 326 (1868).

(11) Aronheim, Dietrich, Ber. 8, 1405 (1875). (12) Fichter, Glantzstein, Ber. 49, 2481-2487 (1916). (13) Ref. 8, pp. 1340-1343. (14) British Dyestuffs Lds., Green, Chibben, Brit. 169,025, Oct. 13, 1921, Cent. 1922, IV 376. (15) Leopold Cassella Co., Ger. 363,290, Nov. 6, 1922; Cent. 1923, II 482-483. (16) Schultz, Ann. 187, 277, 280 (1877). (17) Qvist, Holmberg, Acta Acad. Aboensis Math. et Phys. 6, No. 14, 3-28 (1932), Cent. 1932, II 2815 2816, C A. 27, 5726-5727 (1933). (18) Levy, Stephen, J. Chem. Soc. 1931, 78. (19) Jannasch, Ann. 142, 301 (1867).

3:2115 5-CHLORO-2,3-DIMETHYL- OII
$$C_8H_9OCl$$
 Beil. VI — PHENOL (5-Chloro-o-3-xylenol) CI CH_3 VI $_2$ -(454)

Ndls. from hot lt. pet. in which it is readily sol. hot but spar. sol. cold. — Volatile with steam.

[For prepn. of \bar{C} from 5-amino-2,3-dimethylphenol (5-amino o-3-xylenol) [Beil. XIII₁-(244)] (3) via diazotization and use of Cu₂Cl₂ reaction (yield not stated) see (2), for formn. of \bar{C} from 4,5-dichloro-1,1-dimethylcyclohexen-5-one-3 on htg. see (1).]

C with Cl₂ in lt. pet. gives (2) 4,5,6-trichloro-2,3-dimethylphenol (3:4742), m.p. 180-181°.

The nitration of $\tilde{\mathbf{C}}$ has not been reported, and none of the products to be expected is known.

- --- 5-Chloro-2,3-dimethylphenyl acetate: unreported.
- D 5-Chloro-2,3-dimethylphenyl benzoate: pr. from alc., m p. 88° (2).

3:2115 (1) Hinkel, J. Chem. Soc. 125, 1852 (1924). (2) Hinkel, Collins, Ayling, J. Chem. Soc. 123, 2970-2971 (1923). (3) Crossley, J. Chem. Soc. 103, 2181 (1913).

3:2125 1.2.3-TRICHLORONAPHTHALENE

$$\begin{array}{c|c} Cl & C_{10}H_{\delta}Cl_{3} & \text{Beil. V - 544} \\ \hline & & V_{1}- \\ \hline & & V_{2}- \\ \end{array}$$

Pr. from ether + alc. — The behavior of \tilde{C} on fusion is characteristic: if the fused \tilde{C} in a m.p. tube is allowed to cool to 68° and then withdrawn, it immediately solidifies to a translucent mass which on swift reimmersion into the bath shows m.p. 66-67° but if left for a few seconds in the air suddenly becomes opaque forming a cylinder of m.p. 82-83°, retracted from the wall of the capillary m.p. tube. This change (although slower) also occurs in the translucent form if cooled below 66° (1).

[For prepn. of \bar{C} from 1-chloronaphthalene tetrachloride [Beil. V-493] with alc. NaOEt (61.6% yield (1)) (2) (3) see indic. refs.; from 1,3-dichloronaphthol-2 (3:1990) by distn. with PCl₅ see (2); from sodium 1,2,3-trichloronaphthalenesulfonate-7 (1) by hydrolysis with superhtd. steam see (1).]

- [C treated with ClSO₃H in CS₂ and reactn. prod. conv. to sodium salt as directed (1) gives mixt. of sodium 1,2,3-trichloronaphthalenesulfonate-5 (corresp. sulfonyl chloride, m.p. 131°, corresp. sulfonamide, m.p. 249°) and sodium 1,2,3-trichloronaphthalenesulfonate-7 (corresp. sulfonyl chloride, m.p. 157°, corresp. sulfonamide, m.p. 245°) (1).]
- [Č with 7 pts. fumg. H₂SO₄ (10% SO₃) shaken 15 min. at 100° yields (1) 1,2,3-trichloro-naphthalene-5,7-disulfonic acid (corresp. bis-(sulfonyl chloride), m.p. 184° (1)).]
- 3:2125 (1) Turner, Wynne, J. Chem. Soc. 1941, 248-251. (2) Faust, Saame, Ann. 160, 71 (1871). (3) Armstrong, Wynne, Chem. News 61, 285 (1890).

3:2145
$$\beta_1\beta_2$$
-DICHLORO- α -HYDROXYISO- CH₃ C₄H₆O₃Cl₂ Beil. III - 317 BUTYRIC_ACID Cl₂CH—C—COOH III₁— III₂-(224)

M.P. 82-83° (1) (2) Neut. Eq. 173

Pr. from EtOH/ether (1). - Cannot be distd. without decompn. but sublimes.

[For prepn. from β,β -dichloro- α -hydroxyisobutyronitrile (addn. prod. from α,α -dichloroacetone (3:5430) + HCN) [Beil. I-317] by digestion with strong HCl at 100° see (1).]

The corresp. anilide has been prepd. indirectly by interaction of phenyl isocyanide with α,α -dichloroacetone (3:5430) in aq. (2); pr. from CHCl₃, m.p. 132-133° (2).

3:2145 (1) Bischoff, Ber. 8, 1334 (1875). (2) Passerini, Gazz. chim. ital. 54, 540 (1924).

Microscopic ndls. from alc. (1) (6) or n-PrOH (2); spar. sol. alc. (1), pet. ether (6), eas. sol. C_6H_6 (6).

[For prepn. from m-chlorobenzoyl chloride (3:6590) + C_6H_6 + AlCl₃ (64.7% yield (2)) see (2) (1) (6) (5).]

 \bar{C} on reduction with Na/Hg + alc. (100% yield (7)) or Al/Hg + 80% alc. (4) or boilg. alc. KOH (8) yields exclusively 3-chlorodiphenylcarbinol [Beil. VI₁-(327)], m.p. 40° (7), 39-40° (5), 38° (4). — \bar{C} with Zn + AcOH (7) or \bar{C} in alc. on long exposure to sunlight (7) gives sym.-3,3'-dichlorobenzpinacol [Beil. VI₁-(523)], cryst. from pet. eth., m.p. 137-138° (7), 135° (4).

C fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (3) BzOH (1:0715) (80% yield (3)) and a little (5% (3)) m-chlorobenzoic acid (3:4392), m.p. 158° (3), together with chlorobenzone (3:7903) from cleavage of most of the m-chlorobenzoic acid

Č with CH₃MgI yields (2) 1-(m-chlorophenyl)-1-phenylethylene, oil, b.p. 152-153° at 14 mm. (2).

- **3-Chlorobenzophenone oxime:** from \bar{C} + NH₂OH.HCl + alk.; the two stereoisomers are sepd. by fractnl. pptn. of their AcOH soln. with aq. (1).
- a-form (less-sol. isomer); cryst. pdr., m p. 132-133° (1). [With PCl₅ in dry ether, followed by aq., this form yields m-chlorobenzanilide [Beil. XII-267], cryst. from alc., m.p. 122-125° (1).]
- β-form (more-sol. isomer); cryst. pdr., m.p. 105-106° (1). [With PCl₅ in dry ether, followed by aq., this forms benz-m-chloroanilide [Beil. XII-605], ndls from alc., m.p. 118° (1), accompanied by some m-chlorobenzanilide (see above) (1).]
- 3:2160 (1) Hantzsch, Ber. 24, 57-58 (1891). (2) Bergmann, Bondi, Ber 64, 1477 (1931). (3) Lock, Rödiger, Ber. 72, 867 (1939). (4) Cohen, Böeseken, Rec. trav. chim. 38, 115, 123 (1919). (5) Norris, Blake, J. Am. Chem. Soc. 50, 1812 (1928). (6) Koopal, Rec. trav. chim. 34, 153 (1915). (7) Ref. 6, pp. 160-161. (8) Montagne, van Charante, Rec. trav. chim. 31, 312 (1912)

M.P. 83° (1) B.P. 117-118° at 13 mm. (5 82° (2) 81-82° (3) (4)

White cryst., eas. sol. ether or AcOH, can be recrystallized from pet. ether (1) or from hot aq. (5). — \bar{C} distils under reduced press. without decomposition (5). — Note that m.p. 76.7-77.5° first reported (5) was later (2) found to be erroneous and same sample had actually m.p. 81-82° (2).

Note that, although $\bar{\mathbf{C}}$ is capable of existing in two geometrically isomeric forms, only this one is known; collateral evidence (but not actual proof) indicates that $\bar{\mathbf{C}}$ probably represents the *trans* stereoisomer.

[For prepn. of \tilde{C} from ethyl γ -chlorocrotonate (3:8657) by hydrolysis with Ba(OH)₂ below 0° (60% yield (1) (6)) (4), or less advantageously with 30% aq. KOH in alc. soln. at -15° (40% yield (1)) (5) (note that γ -chlorovinylacetic acid, m.p. 10° (1), is often obtd. (1) (4) as by-prod.); for formn. of \tilde{C} from β - γ -dichloro-n-butyric acid [Beil. II-280] with KOH (poor yield (5)), from trans- γ -hydroxycrotonic acid [Beil. III-376] with SOCl₂ in pyridine (2), or from methyl α -chloro- α -vinylacetate by hydrolysis (3) (7) (presumably as a result of allylic transposition of α -chloro- α -vinylacetic acid under the influence of alkali) see indic. refs.]

Č dissolved in excess aq. 1 N NaOH and shaken with H₂ in pres. of Pd/activated carbon is readily dehalogenated giving (95% yield (1)) crotonic acid (1:0425); with sufficient H₂ this prod. ultimately reduces to n-butyric acid (1:1035).

[\bar{C} by cat. hydroxylation with BaClO₃/osmic acid gives (yields: 75% (6), 78% (9)) threo- γ -chloro- α,β -dihydroxy-n-butyric acid, m.p. 100° (9); this prod. with silver oxide as directed replaces Cl by OH giving (59% yield (6)) d_i -threonic acid, m.p. 98° (6).]

 \tilde{C} adds $\tilde{B}r_2$ (1 mole) yielding (3) γ -chloro- α,β -dibromo-n-butyric acid, cryst. from cyclohexane, m.p. 119–120° (3).

 \bar{C} with NaI in dry acetone ppts. NaCl and gives (86% yield (1)) γ -iodocrotonic acid, yel. ndls. from lgr., m.p. 108-108.5° (1).

[C̄ on neutralization with NH₄OH and htg. with (NH₄)₂SO₃ at 50° for 12 hrs. gives (4) γ-sulfocrotonic acid, very hygroscopic cryst., m.p. 94–96°.]

The acid chloride corresponding to $\bar{\mathbf{C}}$ is unreported.

- Methyl γ -chlorocrotonate: unreported.
- Ethyl γ -chlorocrotonate: b.p. 191–193° at 760 mm. (5) (see 3:8657).
- γ-Chlorocrotonamide: cryst. from hot aq., m.p. 135.5-136° (8), 130-132° (5). [Reported only by partial hydrolysis of γ-chlorocrotononitrile (5) (8).]
- —— γ-Chlorocrotonanilide: unreported.

3:2170 (1) Braun, J. Am. Chem. Soc. 52, 3167-3176 (1930). (2) Rambaud, Bull. soc. chim. (5) 1, 1340 (1934). (3) Rambaud, Bull. soc. chim. (5) 1, 1348 (1934). (4) Backer, Benninga, Rec. trav. chim. 55, 610 (1936). (5) Lespieau, Bull. soc. chim. (3) 33, 466-467 (1905). (6) Glattfeld, Rietz, J. Am. Chem. Soc. 62, 976 (1940). (7) Rambaud, Compt. rend. 197, 769 (1933). (8) Berthet, Bull. acad. roy. Belg., Classe sci. 27, 212-228 (1941); Cent. 1942, I 2115-2116; C.A. 37, 3400 (1943). (9) Braun, J. Am. Chem. Soc. 52, 3176-3185 (1930).

3:2174 2,4,6-TRICHLORORESORCINOL OH C₆H₃O₂Cl₃

M.P. 83° (1) (2) (3) (4)

Colorless cryst. from hot aq. (2). — \bar{C} is spar. sol. cold aq.; eas. sol. alc., ether. \bar{C} sublimes but with appreciable decompn.

[For prepn. of C from resorcinol (1,3-dihydroxybenzene) (1:1530) with Cl₂ in aq. (4), AcOH (3) (2), or CHCl₃ (2), or with SO₂Cl₂ (excess) (4) or with dichlorourea (1), see indic. refs.]

[For formn. of C from 2,4,4,6,6-pentachlorocyclohexen-1-dione-3,5 ("pentachlorore-sorcinol") [Beil. VII-572, VII₁-(323)] by reduction with sulfite (2) (5) or SnCl₂ (2) see

indic. refs.; from 2,2,4,4,5,6,6-heptachlorocyclohexanedione-1,3 ("heptachlorodihydroresorcinol") [Beil. VII-555] by similar reduction see (6).]

[C on oxidn. with alk. K₃Fe(CN)₆ gives (7) a yel. prod., m.p. 60°.]

C in not too dilute aq. soln. with FeCl3 gives on warming a wine-red color (4).

- --- 2,4,6-Trichlororesorcinol diethyl ether: unreported.
- 2.4.6-Trichlororesorcinol diacetate: cryst. from alc., m.p. 116° (2).
- © 2,4,6-Trichlororesorcinol dibenzoate: pr. from alc, m.p. 133° (4). [From C with BzCl on htg. (4).]

3:2174 (1) Likhosher stov, J. Gen. Chem. (U.S.S.R.) 3, 164-171 (1933); Cent. 1934, I 1876; C.A. 28, 1675 (1934). (2) Zincke, Rabinowitsch, Ber. 23, 3776-3777 (1890). (3) Benedikt, Monatsh. 4, 224-226 (1883). (4) Reinhard, J. prakt. Chem. (2) 17, 336-341 (1878). (5) Claasen, Ber. 11, 1441 (1878). (6) Zincke, Rabinowitsch, Ber. 24, 913 (1891). (7) Stenhouse, Groves, Ber. 13, 1307 (1880). (8) Ciamician, Silber, Ber. 24, 2979-2980 (1891).

3:2178 2,3,6-TRICHLOROBENZAL (DI)- Cl $C_7H_3Cl_5$ Beil. S.N. 466 CHLORIDE (2,3,6-Trichlorobenzylidene (di)- Cl C_1 Chloride)

M.P. 83° (1) B.P. 145-150° at 12 mm. (1)

Colorless ndls. from MeOH.

[For prepn. of \tilde{C} (81% yield) from 2,3,6-trichlorobenzaldehyde (3·2287) with PCl₅ see (1),]

Note that C depresses the m.p. (86-87°) of the corresp. aldehyde (3:2287).

[For study of rate of hydrolysis of C see (1)]
3:2178 (1) Asinger, Lock, Monatsh. 62, 338 (1933)

3:2180 4-CHLORO-2,6-DIMETHYL-PHENOL

(5-Chloro-m-2-xylenol)

$$\begin{array}{cccc} & \text{OH} & \text{C}_8\text{H}_9\text{OCl} & \text{Beil. S.N. 529} \\ & & \text{CH}_3 & & & \\ & & & \text{Cl} & & & \\ \end{array}$$

M.P. 83° (1)

[For prepn. of C from 4-chloro-2,6-dimethylphenol (vic-m-xylenol) (1:1425) by chlorination with SO₂Cl₂ in AcOH (100% yield) see (1)]

[For study of bactericidal action of C see (1)]

- ---- 4-Chloro-2,6-dimethylphenyl acetate: unreported.
- --- 4-Chloro-2,6-dimethylphenyl benzoate: unreported.

3:2180 (1) Heicken, Angew. Chem. 52, 264-265 (1939).

3:2182 2,4-DICHLORO-3,5-DIMETHYL- OH C₈H₈OCl₂ Beil. VI— PHENOL Cl VI₁— (2,4-Dichloro-m-5-xylenol) CH₃ CH₄

M.P. 83° (1)

Cryst. from lgr.

[For prepn. of \bar{C} from 4-chloro-3,5-dimethylphenol (2-chloro-m-5-xylenol) (3:3505) by chlorination with N-chloroacetamide see {1}.]

The nitration of C has not been reported, and the expected 6-nitro-2,4-dichloro-3,5-dimethylphenol is unknown.

[For conversion of C to various ethers see (1)]

- D 2,4-Dichloro-3,5-dimethylphenol methyl ether: m.p. 82° (1).
- 2,4-Dichloro-3,5-dimethylphenol ethyl ether: m.p. 53° (1).
- 2,4-Dichloro-3,5-dimethylphenyl p-nitrobenzyl ether: m.p. 157° (1).

3:2182 (1) Jones, J. Chem. Soc. 1941, 275.

3:2185 2,3,4-TRICHLOROPHENOL

$$\begin{array}{c|c} \mathrm{OH} & \mathrm{C_6H_3OCl_3} & \quad \textbf{Beil. VI} \hfill & \quad \textbf{VI_1-} \\ \mathrm{Cl} & \quad \textbf{VI_{2-}(179)} \\ \end{array}$$

Ndls. from pet. eth. (1) (3). — Volatile with steam (1). — Ionization const. at 25° is 2.5×10^{-8} (6); \bar{C} is too weakly acidic to be titrated (1) although sol. in alk.

[For prepn. from 1,2,3-truchlorobenzene (3:0990) via nitration, reduction, and use of diazo reaction see (1) (4); from barium 3-chlorophenol-6-sulfonate by htg with 80% H_2SO_4 see (3); by chlorination of 3,4-dichlorophenol see (2)]

C treated with Br₂/aq. in excess yields on pptn. with more aq. 6-bromo-2,3,4-trichloro-phenol, pl. from lt. pet., m.p. 84-85° (5).

 \bar{C} treated with $(CH_3)_2SO_4$ + aq. NaOH yields the methyl ether, 2,3,4-trichloroanisole, pr. from alc., m.p. 69.5° (3).

① 2,3,4-Trichlorophenyl benzoate: m p. 143° (2); 141° (4).

3:2185 (1) Tiessens, Rec. trav. chim. 50, 112-113 (1931). (2) Groves, Turner, Sharp, J. Chem. Soc. 1929, 523. (3) Hodgson, Kershaw, J. Chem. Soc. 1930, 1421. (4) Holleman, Rec. trav. chim. 39, 743 (1920). (5) Fox, Turner, J. Chem. Soc. 1930, 1863. (6) Tiessens, Rec. trav. chim. 48, 1068-1068 (1929).

3:2192 3,5-DICHLOROCATECHOL

(3,5-Dichloropyrocatechol)

$$\begin{array}{c|c} \mathrm{OH} & \mathrm{C_6H_4O_2Cl_2} & \mathbf{Beil.} \ \mathbf{VI} - \mathbf{783} \\ \mathrm{OH} & \mathbf{VI_1} - \\ \mathrm{Cl} & \mathbf{VI_2} - \end{array}$$

M.P. 83-84° (1)

Colorless cryst. — Very eas. sol. hot, spar. sol. cold, aq.

[For prepn. of \bar{C} from 3,5-dichloro-2-hydroxybenzaldehyde (3,5-dichlorosalicylaldehyde) (3:2637) with H_2O_2 in alk. soln. see (1).]

Č reduces NH₄OH/AgNO₃ (1).

C with FeCl₃ gives green color turning violet on addn. of NaHCO₃ (1).

- ---- 3.5-Dichloropyrocatechol diacetate: unreported.
- --- 3.5-Dichloropyrocatechol dibenzoate: unreported.

3:2192 (1) Dakin, Am. Chem. J. 42, 488-489 (1909).

Ndls. or lfts. from lgr. (1). — Vapors of C are lachrymatory and attack mucous membranes (5).

[For prepn. of \bar{C} from terephthalic acid (1:0910) with PCl₅ (96% yield (29)) (9) (10) (15), with PCl₅ + POCl₃ (yield: 90% (2), 85–90% (7), 83% (5)) (4) (18), with SOCl₂ + pyridine (alm. quant. yield (11)) or SOCl₂ + AlCl₃, SnCl₄, or SbCl₅ (3) (SOCl₂ alone fails), with acetyl chloride in s.t. at 130° (1), or with benzotrichloride + ZnCl₂ (12) (13) see indic. refs.; for prepn. of \bar{C} from 1,4-bis-(trichloromethyl)benzene [Beil. V-385] by partial catalytic hydrolysis see (14) cf. (30). — Note that the half acid chloride, p-carboxybenzoyl chloride, m.p. above 300°, ndls. from C₆H₆, is known (1); its presence may account for the numerous recorded low m.p.'s.]

C with excess MeOH yields (9) (15) (cf. also 1:0910) dimethyl terephthalate (1:2550), m.p. 140-141°; C with excess EtOH yields (15) (16) (cf. also 1:0910) diethyl terephthalate (1:2106), m.p. 44°; C with excess phenol (1:1420) yields (6) diphenyl terephthalate, ndls. from alc., m.p. 191° (6).

[C on cat. hydrogenation in xylene with Pd cat. as specified (17) (18) gives (81% yield (17)) terephthaldialdehyde [Beil. VII-675, VII₁-(364)], m.p. 115-116° (dioxime, m.p. 200°; bis-(phenylhydrazone), m.p. 278° dec. (17), bis-(p-nitrophenylhydrazone), m.p. 281° dec. (17)).]

[\bar{C} with AlCl₃ + benzene yields (19) (20) 1,4-dibenzoylbenzene (terephthalophenone) [Beil. VII-829, VII₁-(444)], m.p. 159-160° (20) (dioxime, m.p. 235° (20), monoxime, m.p. 212-213° (19)); for corresp. reactn. of \bar{C} with AlCl₃ + toluene see (21) (29).]

[Č treated with dry HBr at 150-160° for 30 hrs. gives alm. quant. (22) terephthalyl dibromide, pr. from pet. eth., m.p. 84-85° (22).]

[For reactions of C with various cpds. (mainly aminoanthraquinone derivs.) giving vat dves or intermediates for the prepn. of vat dyes, see (23) (24) (25) (26) (27) (28).]

C on hydrolysis yields terephthalic acid (1:0910) q.v.

3:2265 (1) Liebermann, Kardos, Ber. 46, 211-212 (1913). (2) Bogert, Nisson, Proc. Natl. Acad. Sci. 10, 423 (1924). (3) I.G., French 810,595, March 24, 1937; Cent. 1937, I 5047; C.A. 32, 592 (1938). (4) Kohlrausch, Pongratz, Stockmair, Monatsh. 67, 110 (1935). (5) Berend, Herms, J. prakt. Chem. (2) 74, 123-124 (1906). (6) Schreder, Ber. 7, 707 (1874). (7) Locher, Bull. soc. chim. (3) 11, 927 (1894). (8) Berger, Ber. 10, 1743 (1877). (9) de la Rue, Muller, Ann. 121, 90 (1862). (10) Cohen, de Pennington, J. Chem. Soc. 113, 61-62 (1918).

(11) Carré, Libermann, Compt. rend. 199, 1423 (1934). (12) Hopff (to I.G.), Ger. 680,182, Aug. 24, 1939; Cent. 1939, II 3488; C.A. 36, 1951 (1942). (13) I.G., Brit. 455,668, Nov. 19, 1936; Cent. 1937, I 2025; C.A. 31, 1824 (1937). (14) I.G., French 820,697, Nov. 16, 1937; Cent. 1938, I 1661; C.A. 32, 3422 (1938). (15) Schwanert, Ann. 133, 268-269 (1864). (16) Perkin, J. Chem. Soc. 69, 1178 (1896). (17) Rosenmund, Zetsche, Ber. 54, 2890-2892 (1921). (18) Fröschl, Maier, Monatsh. 59, 274 (1932). (19) Noelting, Kohn, Ber. 19, 147 (1886). (20) Munchmeyer, Ber. 19, 1847-1848 (1886).

(21) Connerade, Bull. soc. chim. Belg. 40, 144-157 (1931). (22) Davies, Hambly, Semmens, J. Chem. Soc. 1933, 1313. (23) Soc. Chem. Ind. Basel, Swiss 203,953, July 1, 1939; C.A. 35, 2731 (1941). (24) I.G., French 819,778, Oct. 26, 1937; Cent. 1938, I 1226; C.A. 32, 3162 (1938), (25) Gubelmann, Murphy (to du Pont Co.), U.S. 1,913,383, June 13, 1933; Cent. 1933, II 1257; Brit. 418,455, Nov. 22, 1934; Cent. 1935, I 1775. (26) Kacer (to Badische Anilin- und Sods-Fabrik), Ger. 424,030, Jan. 21, 1926; Cent. 1926, I 2849. (27) Kacer (to I.G.), Ger. 439,614, Feb. 1, 1927; Cent. 1927, I 2366. (28) B. A. & S. F., U.S. 1,459,536, June 19, 1923; Brit. 204,249, Oct. 18, 1923; Ger. 384,674, Nov. 8, 1923; Swiss 101,169, Sept. 1, 1923; Cent. 1924, I 1449. (29) Koelsch, Bryan, J. Am. Chem. Soc. 67, 2041-2042 (1945). (30) I.G., Ger. 708,149, June 5, 1941; C.A. 37, 2746 (1943).

3:2212 2,3,4-TRICHLOROBENZAL Cl CHCl2 C7H3Cl5 Beil. V - 303 V1-(153) (2,3,4-Trichlorobenzylidene (di)chloride)

M.P. 84° (1) B.P. 275–285° (1)

Cryst. from lgr.

[For prepn. of \tilde{C} from 2,3,4-trichlorotoluene (3:0425) at its b.p. with Cl_2 see (1); for formn. in small amt. from trichloroethylene (3:5170) at 700° see (2).]

C with fumg. H₂SO₄ as directed (1) (2) hydrolyzes to 2,3,4-trichlorobenzaldehyde (3:2445), m.p. 90-91°.

3:2212 (1) Seelig, Ann. 237, 146-147, 149-150 (1887). (2) Nicodemus, J. prakt. Chem. (2) 83, 319 (1911).

3:2216 2,5-DICHLORO-3,4DIMETHYLPHENOL
(3,6-Dichloro-o-4-xylenol)
Cl
CH₂
OH
C₈H₈OCl₂
Beil. VI —
VI₁—
VI₂-(456)

M.P. 84° (1)

Ndls. for lt. pet. - Volatile with steam.

[For prepn. of C from 2,5-dichloro-3,4-dimethylaniline (3,6-dichloro-o-4-xylidine) (2) via diazotization and hydrolysis (yield not stated) see (1).]

The nitration of \bar{C} has not been reported, and the expected 6-nitro-2,5-dichloro-3,4-dimethylphenol is unknown.

2,5-Dichloro-3,4-dimethylphenyl acetate: unreported.
 2,5-Dichloro-3,4-dimethylphenyl benzoate: m.p. 124° (1).

3:2216 (1) Hinkel, Ayling, Bevan, J. Chem. Soc. 1928, 2533. (2) Hinkel, Ayling, Bevan, J. Chem. Soc. 1928, 1878.

3:2218 4-CHLORO-2,3-DIMETHYLPHENOL OH C_8H_9OCl Beil. VI — (6-Chloro-o-3-xylenol) CH₃ VI₁— VI₂-(454)

M.P. 84.5° (1) (2)

Ndls. from lt. pet. — Sol. in most org. solvents except lt. pet. — Volatile with steam. [For prepn. of C from 4-amino-2,3-dimethylphenol (6-amino-0-3-xylenol) (1) via diasotisa-

262

tion and use of Cu₂Cl₂ reaction (1), or from 4-chloro-2,3-dimethylanline (6-chloro-o-3-xylidine) (1) via diazotization and hydrolysis (70% yield (1)), see indic. refs.]

[For studies of bactericidal action of C see (2) (3) (4).

C with Cl2 in lt. pet. does not (1) give a trichloro derivative but is decomposed.

The nitration of C has not been reported and neither of the corresp. mononitro derivs. nor the dinitro deriv. is known.

---- 4-Chloro-2,3-dimethylphenyl acetate: unreported.

4-Chloro-2,3-dimethylphenyl benzoate: m.p. 102° (1).

3:2218 (1) Hinkel, Collins, Ayling, J. Chem. Soc. 123, 2971-2972 (1923). (2) Heicken, Angew. Chem. 52, 263-265 (1939). (3) Lockemann, Kunzmann, Angew. Chem. 46, 296-301 (1933). (4) Lockemann, Heicken, Zentr. Bakt., Parasitenk. I Abt., Orig. 145, 61-71 (1939), C.A. 34, 2534 (1940).

M.P. 84° (1) 83° (2)

Ndls. from alc.

[For prepn. of C from 8-chloro-1-nitronaphthalenesulfonic acid-2 [Beil XI-187] (3), from 7,8-dichloronaphthol-1 (3:2635) (2), or from 1,2-dichloronaphthalenesulfonyl chloride-8 [Beil. XI-164] (1), each with PCl₅, see indic. refs.]

[C treated with ClSO₃H in CS₂ and prod. conv. to potassium salt yields (1) potassium 1,2,8-trichloronaphthalenesulfonate-X (corresp. sulfonyl chloride, m.p. 105° (1)).]

3:2220 (1) Turner, Wynne, J. Chem. Soc. 1941, 247, 252. (2) Armstrong, Wynne, Chem. News 71, 253 (1895). (3) Cleve, Chem. Ztg. 17, 398 (1893).

3:2240
$$\beta$$
-CHLOROACRYLIC ACID $C_3H_3O_2Cl$ Beil. II - 400 H.C.Cl Cl.C.H II₁-(186) H.C.COOH H.C.COOH

M.P. trans 85-86° (1) 84-85° (2) M.P. cis 63-64° (1)

[For prepn. of mixt. of cis and trans forms of $\bar{\mathbf{C}}$ from propiolic acid (acetylenecarboxylic acid) [Beil. II-477, II₁-(208), II₂-(449)] by htg with cone HCl (yield: cis 34%, trans 18% (1)) (3) (the cis is sepd. from trans by means of the lesser soly. in alc. of its potassium salt (1)), see indic. refs.; for prepn. of trans $\bar{\mathbf{C}}$ from β -chloropropionic acid (3:0460) by loss of HCl on passing its vapor over BaCl₂ at 280–300° see (4); from ethyl β , β -dichloropropionate with 3 moles alc. KOH see (5); from chloralide (3:3510) in alc. by protracted treatment with Zn + HCl see (2) (5).]

The cis isomer of \bar{C} on htg. in a s.t. at 125° for 15 hrs. is partially conv. (1) to the trans isomer.

C (both forms) readily reduces KMnO₄ in the cold (1).

[\overline{C} on htg. with 5 pts. 40% HCl in s.t. at 80-85° for 35-40 hrs. yields (5) α,β -dichloropropionic acid (3:0855), m.p. 56° (5).]

 $[\bar{C} \text{ on esterification with EtOH yields ethyl } \beta\text{-chloroacrylate, b.p. } 143-145^{\circ}$ (2), 146° (6).]

3:2240 (1) Backer, Beute, Rec. trav. chim. 54, 167-170 (1935). (2) Wallach, Ann. 193, 28-34 (1878). (3) Bandrowski, Ber. 15, 2702 (1882). (4) I.G., French 697,311, Jan. 15, 1931; Cent. 1931, I 2934. (5) Otto, Ann. 239, 261-272 (1887). (6) Pinner, Bischoff, Ann. 179, 88 (1875).

3:2265
$$\alpha,\beta$$
-DICHLOROACRYLIC ACID $C_3H_2O_2Cl_2$ Beil. II - 401 CH =-C-COOH II_1 -(186) II_2 —

Monoclinic (5) pr. (from CHCl₃ (5)); cryst. from pet. eth. (4) or CS₂ (7). — Eas. sol. aq., alc., ether (2) (4), CHCl₃ (2); spar. sol. in cold (1) but eas. sol. in hot C_6H_6 , CS₂ or pet. eth. (2). — Rapidly volatilizes in air (2) or on warming (4) — May be purified by melting with a little aq. (2).

Although two geom. isomers are possible only one is known.

[For prepn. from various sources see Beil. II-401, Beil. II₁-(186), and (3).]

Salts: AgĀ, pptd. in fine ndls. from even dil. aq. solns. of Č on addn. of AgNO₃; can be recrystd. from hot aq. (1) (2) (4) (6); Ag content = 43.54%; BaĀ₂.H₂O, sol. in 16 pts. cold aq. (1) (2) (4) (6); CaĀ₂.3H₂O, extremely sol. aq., loses cryst. aq. at 80° (1) (2); KĀ, quite sol. even in cold aq. but may be obtained in long slender anhyd. ndls. from conc. solns. (1) (2).

 \bar{C} in CHCl₃ does not add Br₂ (2), but \bar{C} on htg. (in s.t.) with 1 mole Br₂ at 100° gives (9) α,β -dibromo- α,β -dichloropropionic ac. [Beil. II-259], pr. from CS₂ or CHCl₃, m.p. 94–95° (9).

C is not decomposed by excess boil. Ba(OII)₂ (7).

 \bar{C} with thionyl chloride yields (7) α,β -dichloroacrylyl chloride, b.p. 145–146°, $n_D^{T}=1.5288$, which is only slowly hydrolyzed by aq. but which on cautious addn. to conc. NH₄OH yields α,β -dichloroacrylamide, cryst. from dil. alc, m.p. 134° (7), 132° (10).

3:2265 (1) Bennett, Hill, Ber. 12, 655-657 (1879). (2) Hill, Am. Chem J. 3, 167-172 (1881/2). (3) Klebansky, Wolkenstein, Orlowa, J. prakt Chem. 145, 12-13 (1936). (4) Zincke, Ber. 24, 918 (1891). (5) Melville, Am Chem. J. 4, 174-176 (1882/3). (6) Ciamician, Silber, Ber. 16, 2392 (1883). (7) Prins, J. prakt. Chem. (2) 89, 420 (1914). (8) Prins, Rec. trav. chim. 56, 780-781 (1937). (9) Hill, Maberry, Ber. 14, 1679-1680 (1881); Am. Chem. J. 4, 267-270 (1882/3). (10) Prins, Ger. 261,689, July 2, 1913, Cent. 1913, II 394.

3:2280 3-CHLORO-2-METHYLPHENOL OH
$$C_7H_7OCl$$
 Beil. VI - 359 VI_1 — VI_2 —

M.P. 86° (1) (2) (3) B.P. 225° (2)

Long white ndls. (from aq.) (1). — Volatile with steam (2).

[For prepn. (75-86% yield) from 3-chloro-2-methylaniline [Beil. XII-836] see (1) (2); from 3-hydroxy-2-methylaniline [Beil. XIII-579] (45-50% yield) see (1).]

C on nitration (1) in AcOH with 100% HNO₃ at +10° yields mixt. of equal amts. of two mononitration products: 6-nitro-3-chloro-2-methylphenol [Beil. VI-366], volatile with steam, yel. cryst. from alc., m.p. 64.5° (1), and 4-nitro-3-chloro-2-methylphenol [Beil. VI-367], not volatile with steam, cryst. from aq., m.p. 135° (1).

 \cdot \bar{C} on nitration (4) with 3 pts. HNO₃ (D=1.48) at 0° gives a dinitro compd., 4,6-dinitro-3-chloro-2-methylphenol, long yel. ndls. from dil. alc., m.p. 82-83° (4); acetyl deriv., m.p. 95° (4).

Č in alk. soln. coupled with diazotized p-nitroaniline yields (1) 3-chloro-2-methyl-6-(p-nitrobenzene-azo-)phenol [Beil. XVI-132], cryst. from 50% alc., m.p. 230°.

Č in 3 pts. 20% NaOH shaken with 1 pt. (CH₃)₂SO₄, distilled with steam, gives 3-chloro-2-methylanisole [Beil. VI-359], b.p. 213.5° (2).

3:2280 (1) Noelting, Ber. 37, 1019-1021 (1904). (2) Ullmann, Panchaud, Ann. 350, 112-113 (1906). (3) Zincke, Ann. 417, 207 (1918). (4) Zincke, Ann. 417, 234-235 (1918).

3:2285 2,6-DICHLOROBENZOPHENONE
(2,6-Dichlorophenyl phenyl ketone)

M.P. 86° (1)

Colorless cryst. (from alc. (1)).

C does not react with the usual ketone reagents (1).

 $\overset{\circ}{\text{C}}$ fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (1) BzOH (1:0715)(96% yield) and m-dichlorobenzene (3:5960).

3:2285 (1) Lock, Rödiger, Ber. 72, 869 (1939).

3:2287 2,3,6-TRICHLOROBENZALDEHYDE

TDE C₇H₃OCl₃ Beil. VII - 238
Cl CHO
Cl Cl

M.P. 86-87° (1) 86° (2) (3)

Colorless ndls. from lgr.

[For prepn. of \vec{C} from 3-amino-2,6-dichlorobenzaldehyde by diazotization and use of Cu_2Cl_2 reaction see (1) (2).]

 \bar{C} with PCl₅ gives (81% yield (4)) 2,3,6-trichlorobenzal (di)chloride (3:2178), m.p. 83°; note that this prod. depresses m.p. of \bar{C} .

 \tilde{C} with 50% aq. KOH at 100° for 5 hrs. under N₂ undergoes cleavage of the aldehyde group giving (88% yield (3)) 1,2,4-trichlorobenzene (3:6420) and the corresp. potassium formate.

Č with anhydrous NaOAc + Ac₂O on htg. (Perkin synthesis) gives (64-68% yield (5)) 2,3,6-trichlorocinnamic acid, cryst. from AcOH, m.p. 189°.

[C with MeMgI in dry ether, followed by usual hydrolysis, gives (85% yield (2)) methyl-2,3,6-trichlorophenyl-carbinol, m.p. 87-88°, b.p. 149-155° at 11 mm. (corresp. benzoate, m.p. 106.5°).]

- ---- 2,3,6-Trichlorobenzaldoxime: unreported.
- ---- 2,3,6-Trichlorobenzaldehyde phenylhydrazone: unreported.
- ---- 2,3,6-Trichlorobenzaldehyde p-nitrophenylhydrazone: unreported.
- ----- 2.3.6-Trichlorobenzaldehyde 2.4-dinitrophenylhydrazone: unreported.

3:2287 (1) Geigy and Co., Ger. 199,943, July 4, 1908; Cent. 1908, II 363-364; C.A. 2, 3000 (1908); (2) Lock, Böck, Ber. 70, 924 (1937). (3) Lock, Ber. 66, 1531 (1933). (4) Asinger, Lock, Monatch. 62, 338 (1933). (5) Böck, Lock, Schmidt, Monatch. 64, 408 (1934).

3:2290 PENTACHLOROBENZENE

Long colorless ndls. from alc.; volatile with steam; sublimes readily. — Almost insol. cold alc., apprec. sol. boilg. alc.; eas. sol. ether, C₆H₆, CHCl₃, CCl₄, or CS₂; spar. sol. conc. HNO₃.

[For prepn. of \bar{C} from nonachlorobenzophenone-o-carboxylic acid [o-(pentachlorobenzoyl)-tetrachlorobenzoic acid] [Beil. X₁-(358)] by htg. with 10 pts. conc. H₂SO₄ at 200-250° for ½ hr. (simplest prepn. of pure \bar{C}) see (12); for formn. of \bar{C} from 2,3,4,5,6-pentachloroacetophenone (6) or 2,3,4,5,6-pentachlorobenzophenone (11) by KOH/NaOH fusion see indic. refs.; from 2,3,4,5,6-pentachlorobenzaldehyde (3:4892) (2) by htg. with 50% aq. KOH 5 hrs. at 100° (88% yield) see (2).]

[For prepn. of C from 2,3,5,6-tetrachloroaniline (7) via diazotization and use of Cu₂Cl₂ reactn. see (7); from 2,3,5-trichloro-p-phenylenediamine via tetrazotization in AcOH with nitrosylsulfuric acid and use of Cu₂Cl₂ reactn. (80% yield) see (3).]

[For formn. of \bar{C} from benzene with Cl_2 (7), or $Cl_2 + cat$. (20), or Cl_2 in pres. of I_2 (18), or $AlCl_3$ (19) see indic. refs.; from chlorobenzene with $Cl_2 + Cu$ at 200° see (21); from 1,3,5-trichlorobenzene (3:1400) with $Cl_2 + Al/Hg$ see (17); from all three tetrachlorobenzenes with $Cl_2 + Al/Hg$ see (17); from 1,2,4,5-tetrachlorobenzene (3:4115) in $SOCl_2$ or CCl_4 with $SO_2Cl_2 + AlCl_3 + S_2Cl_2$ see (8) (note that under these circumstances p-dichlorobenzene (3:0980) gives a mixt. of tetra and hexachlorobenzenes (8) (22)); from lower chlorinated derivs. of benzene by htg. with $FeCl_3$ see (5); from diphenyl sulfone with Cl_2 in sunlight followed by treat. with alc. KOH see (13) (23); from tetrachlorobenzyl chloride with Cl_2 see (16); from acet-N-nitro-2,3,5,6-tetrachloroaniline on htg. in toluene or from parent base on attempted acetylation see (15); from trichloroethylene (3:5170) at 700° see (9); from iodopentachlorobenzene with MeOH/NaOH see (1).

[For form. of \bar{C} from various chlorine addition products derived from o-dichlorobenzene (3:6055) (4), m-dichlorobenzene (3:5960) (4), p-dichlorobenzene (3:0980) (4), 1,2,4,5-tetrachlorobenzene (3:4115) (24), and even \bar{C} itself (25) see indic. refs.]

[C with liq. Cl₂ in s.t. in sunlight adds 2 Cl₂ with considerable sluggishness yielding (26) (25) a mixt. of two stereoisomeric nonachlorocyclohexenes.]

[C with fumg. H₂SO₄ gives on protracted htg. (27) a red dyestuff, sol. in alk. with deep red color.]

[C with N/2 NaOMe in MeOH in s.t. at 180° for 7½ hrs. gives (7) 2,3,5,6-tetrachlorophenol, m.p. 115° (7) (benzoate, m.p. 136° (28)), accompanied by a small amt. 2,3,4,5-tetrachlorophenol, itself not obtd. pure but yielding (28) a benzoate of m.p. 110° (28). — [For further study of actn. of MeOH/NaOH on C see (29) (30).]

 \bar{C} on nitration, e.g., with 7-8 wt. pts. HNO₃ (D=1.52) at 100° for 1 hr. (7), gives (7) (9) (18) (31) pentachloronitrobenzene [Beil. V-247], ndls. from alc., tbls. from CS₂, m.p. 146° (9) (18) (31), 143° (7); note that since \bar{C} is spar. sol. in conc. HNO₃ any unchanged material may separate with the crude prod. (31). — [This pentachloronitrobenzene with

N/10 NaOMe in MeOH boiled for 8 hrs. loses NO₂ instead of Cl yielding (31) methyl pentachlorophenyl ether (pentachloroanisole), m.p. $104-105^{\circ}$ (31); cf. also under pentachlorophenol (3:4850).]

3:2290 (1) van der Linden, Rec. trav. chim. 55, 285 (1936). (2) Lock, Ber. 66, 1533 (1933). (3) Schoutissen, J. Am. Chem. Soc. 55, 4539-4540 (1933). (4) van der Linden, Ber. 45, 411-418 (1912). (5) Thomas, Compt. rend 126, 1212 (1898). (6) Lock, Bock, Ber. 76, 925 (1937). (7) Holleman, van der Hoeven, Rec. trav. chim. 39, 745-746, 749 (1920). (8) Silberrad, J. Chem. Soc. 121, 1020-1021 (1922). (9) Nicodemus, J. prakt. Chem. (2) 83, 319 (1911). (10) Ladenburg, Ann. 172, 344 (1874).

(11) Lock, Rödiger, Ber. 72, 870 (1939). (12) Eckert, Steiner, Monatsh. 36, 183 (1915); Ber. 47, 2629 (1914). (13) Otto, Ann. 154, 185 (1870). (14) Dadieu, Pongratz, Kohlrausch, Monatsh. 61, 434 (1932). (15) Peters, Rowe, Stead, J. Chem. Soc. 1943, 372. (16) Beilstein, Kuhlberg, Ann. 152, 247-248 (1869). (17) Cohen, Hartley, J. Chem. Soc. 87, 1366 (1905), (18) Jungfleisch, Ann. chim. (4) 15, 283-287 (1868). (19) Mouneyrat, Pouret, Compt. rend. 127, 1028 (1898). (20) Moose, Malowan (to Swann Research, Inc.), U.S. 2,010,495, Aug. 6, 1935; Cent. 1936, 2984; C.A. 29, 6330 (1935).

(21) Tei, Komatsu, Mem. Coll. Sci., Kyoto Imp. Univ. A-10, 325-330 (1927); Cent. 1928, I 2370. (22) Roberts and Co., & Silberrad, Brit. 193,200, March 15, 1923, Cent. 1925, I 904. (23) Otto, Ostrop, Ann. 141, 107-108 (1867). (24) van der Linden, Rec. trav. chim. 55, 425-427 (1936). (25) van der Linden, Rec. trav chim. 55, 569-570 (1936). (26) van der Linden, Rec. trav. chim. 55, 322 (1936). (27) Istrati, Bull. soc. chim. (2) 48, 36-41 (1887). (28) Holleman, Rec. trav. chim. 40, 318 319 (1921). (29) de Crauw, Rec. trav. chim. 50, 787 (1931). (30) van der Linden, Rec. trav. chim. 57, 787 (1938).

(31) Berckmans, Holleman, Rec. trav. chim. 44, 857-858 (1925).

3:2295 PENTACHLOROBENZOYL CHLORIDE

M.P. 87° (1)

Colorless tbls. from hot alc.

[For prepn. of C from *unsym.*-tetrachlorophthalyl (di)chloride (3,3,4,5,6,7-hexachlorophthalide) [Beil. XVIII₁-(484)] on htg. at 300° in pres. of Cl₂ see (1)]

C during protracted htg loses CO yielding (1) hexachlorobenzene (3:4939) (this type of decompn. is generally facilitated by AlCl₃ although in this case this aspect has not been reported).

Č with MeOH on refluxing for 30 hrs. gives (1) methyl pentachlorobenzoate m.p. 97° (1); note that esterification is slow and that Č can be recrystallized from EtOH without change.

Č on hydrolysis with alc. KOH, followed by acidification, yields (1) pentachlorobenzoic acid (3:4910).

3:2295 (1) Kirpal, Kunze, Ber. 62, 2104-2105 (1929).

3:2300 TRICHLOROPARALDEHYDE

(Chloroacetaldehyde trimer; 2,4,6-tris-(chloromethyl)trioxane-1,3,5)

C₆H₉O₃Cl₃

Beil. XIX - 386

XIX1-(807)

M.P. 87-87.5° cor. (1) B.P. 142-144° at 10 mm. (2) 140° at 10 mm. (1)

Colorless ndls. from ether; insol. aq., spar. sol. cold alc., eas. sol. hot alc. or in ether.

[For prepn. of \bar{C} from chloroacetaldehyde (3:7212) (or its hydrate) with $\frac{1}{2}$ vol. cold conc. H_2SO_4 see (1) (3) (4).]

C on distn. at ord. press. (1) (2) (3) (4) depolymerizes to monomeric chloroacetaldehyde (3:7212), b.p. 85°.

3:2300 (1) Natterer, Monatsh. 3, 459-464 (1882). (2) Späth, Monatsh. 36, 6-7 (1915). (3) Helferich, Speidel, Ber. 54, 2634-2635 (1921). (4) Lespieau, Bull. soc. chim. (4) 43, 200-201 (1928).

3:2325 1,2,7-TRICHLORONAPHTHALENE

M.P. 88° also 84° (1) (2) (See Text)

C shows the double m.p. behavior indicated also for several of its isomers, e.g., 1,2,3-isomer (3:2125), 1,2,5-isomer (3:1930), 1,3,8-isomer (3:2420), 1,4,6-isomer (3:1625).

[For prepn. of C from 1-chloro-7-sulfonaphthylamine-2 [Beil. XIV-765] via diazotization and use of Cu₂Cl₂ reactn. see (1) (2); from 1,2-dichloronaphthalenesulfonyl chloride-2 [Beil. XI-184] (2) (3), from 1-chloro-7-nitronaphthalenesulfonyl chloride-2 [Beil. XI-188] (4), from 2-chloro-1-nitronaphthalenesulfonyl chloride-2 [Beil. XI-189] (5) (2), or from 1-chloronaphthalene-2,7-bis-(sulfonyl chloride) [Beil. XI-217] (2), each with PCl₅ as directed, see indic. refs.]

[C treated with CISO₃H in CS₂ and reactn. prod. conv. to sodium salt as directed (1) yields sodium 1,2,7-trichloronaphthalenesulfonate-X (corresp. sulfonyl chloride, m.p. 176° (1)).]

3:2325 (1) Turner, Wynne, J. Chem. Soc. 1941, 247, 252. (2) Armstrong, Wynne, Chem. News 71, 253-254 (1895). (3) Armstrong, Wynne, Chem. News 59, 189 (1889). (4) Cleve, Chem. Ztg. 17, 398 (1893). (5) Cleve, Ber. 25, 2486-2487 (1892).

3:2340 2,5-DICHLOROBENZOPHENONE

(2,5-Dichlorophenyl phenyl ketone)

M.P. 88° (1) (3) 85-86° (2)

Cryst. (from alc. (1)). — C does not form a NaHSO3 cpd. (1).

[For prepn. (20% yield (1)) from p-dichlorobenzene (3:0980) + BzCl (3:6240) + AlCl₃ see (1) (2).]

 \bar{C} fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (3) p-dichlorobenzene (3:0980) (65% yield (3)) and BzOH (1:0715) (91% yield (3)).

C on oxidn. with KMnO4 soln. yields (1) 2,5-dichlorobenzoic ac. (3:4340), m.p. 150° (1).

D 2,5-Dichlorobenzophenone oxime: from C in alc. on htg. with NH₂OH.HCl + BaCO₃ for 3 days (10% yield (1)); m.p. 135° (on rapid htg.), 207° (on slow htg.) (1). [This

oxime upon Beckmann rearr. with 10 pts. conc. H₂SO₄ at 100° for 1 hr. gives benz-2,4-dichloroanilide, m.p. 122° (1).]

3:3340 (1) de Crauw, Rec. trav. chim. 50, 767-768 (1931). (2) Ganzmüller, J. prakt. Chem. 138, 311-312 (1933). (3) Lock, Rödiger, Ber. 72, 869 (1939).

3:2360 2,3,5,5,6,6-HEXACHLORO-CYCLOHEXENE-2-DIONE-1,4

M.P. 89° (1) B.P. 275-285° dec. (1) 86-87° (2) 182-185° at 45-50 mm. (1)

Cryst. (from ether/pet. ether). — Lachrymatory odor. — Eas. volatile with steam; on distn. at atm. press. dec. into chloranil (3:4978) and Cl₂. — Eas. sol. ether, CHCl₃; fairly eas. sol. alc., C₆H₆, lgr.; insol. aq.

[For prepn. from chloranil (3:4978) by treatment with $MnO_2 + conc.$ HCl in s.t. for 10 hrs. at 180° see (1); from p-aminophenol hydrochloride in AcOH on treatment with Cl_2 see (1).]

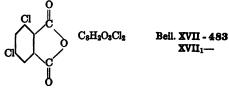
[For use of C as fungicide see (3).]

Č with KI in AcOH yields (1) chloranil (3:4978). — Č on reduction with SnCl₂ yields (1) tetrachlorohydroquinone (3:4941).

Č on shaking with 10% aq. NaOH slowly dissolves with decompn. into dichloromaleic acid, trichloroethylene, and HCl (1).

3:2360 (1) Zincke, Fuchs, Ann. 267, 15-24 (1892). (2) Theilacker, Ber. 71, 2069 (1938). (3) Ladd (to U.S. Rubber Co.), U.S. 2,362,565, Nov. 14, 1944; C.A. 39, 2832 (1945).

3:2375 3,5-DICHLOROPHTHALIC ANHYDRIDE



M.P. 89° (1) (2)

[See also 3,5-dichlorophthalic acid (3:4580).]

Ndls. from lgr.; eas. sol. ether, C6H6, CHCl3.

[For prepn. from 3,5-dichlorophthalic acid (3:4580) by htg. alone (2), or with AcCl (1), see indic. refs.; from 3,5-disulfophthalic anhydride (2) with SOCl₂ in s.t. 11 hrs. at 180° see (2).]

 \tilde{C} htd. with resorcinol + a drop of conc. H₂SO₄, then dislvd. in alk. and diluted, gives brilliant greenish fluorescence (1).

[C with hydroquinone (1:1590) + AlCl₃ + NaCl htd. at 200-220° for 40 min. gives (3) 5,7-dichloro-1,4-dihydroxyanthraquinone (5,7-dichloroquinizarin), red ndls. from xylene, m.p. 231-232° (3).]

[Č with steam passed over cat. at 380-420° loses CO₂ presumably yielding (4) 2,4-dichlorobenzoic acid (3:4560) and /or 3,5-dichlorobenzoic acid (3:4840).

Č on melting and treatment with dry NH₃ gas yields (1) 3,5-dichlorophthalimide [Beil. XXI-504], yel. ndls. from hot alc., m.p. 208° (1); Č on htg. with 1 mole aniline until evoln. of gas stops gives (1) 3,5-dichlorophthalanil [Beil. XXI-504], yel. ndls. from alc., m.p. 150.0-150.5° (1).

 \tilde{C} is insol. in cold aq. but hydrolyzes on boilg.; \tilde{C} on sapon. with standard alk. (Sap. Eq. = 108.5) followed by acidifn. yields 3,5-dichlorophthalic acid (3:4840) q.v.

3:2375 (1) Crossley, LeSueur, J. Chem. Soc. **81**, 1536-1537 (1902). (2) Waldmann, Schwenk, Ann. **487**, 293-294 (1931). (3) Waldmann, J. prakt. Chem. (2) **130**, 99-100 (1931). (4) Jaeger (to Selden Co.), U.S. 1,964,516, June 26, 1934; Cent. **1934**, II 3047.

3:2395 unsym.-o-PHTHALYL DICHLORIDE (unsym.-o-Phthaloyl dichloride; 3,3-dichlorophthalide) C C₈H₄O₂Cl₂ Beil. IX - 805 XVII₁-(162)

[See also sym.-o-phthalyl dichloride (3:6900).]

M.P. 89° (1)
$$D_4^{99.6} = 1.3320$$
 (6) $D_4^{50} = 1.351$ (5) $D_4^{50} = 1.351$ (5) $D_4^{50} = 1.351$ (6) $D_4^{50} = 1.351$ (7) $D_4^{50} = 1.351$ (8) $D_4^{50} = 1.351$ (9) $D_4^{50} = 1.351$ (10) $D_4^{50} = 1.351$

Prisms from C_6H_6 (2), cryst. from pet eth. (b.p. $20-50^\circ$) (4). — \bar{C} is much less reactive but far more lachrymatory (7) than sym.-o-phthalyl dichloride (3:6900). — The m.p. of \bar{C} is not sharp because of beginning of conversion to sym. isomer (4) (5), and \bar{C} shows progressive change of density when kept at 90° for 1 hr. (5). — \bar{C} on distillation is converted to the sym. isomer and therefore shows b.p. of the latter; this change is accelerated by presence of AlCl₃ or SnCl₄ (1) (2) or by HCl. — \bar{C} should therefore be preserved in a desiccator over soda-lime (2). — For f.p./compn. diagram of \bar{C} with its sym. isomer see (3); the eutectic has m.p. +8° and conts 23% \bar{C} .

[For prepn. of \bar{C} from sym.-o-phthalyl dichloride by htg. with AlCl₃ at 100° for 8-10 hrs. (72% yield) see (4).]

 \bar{C} in anhydrous formic acid reacts below 40° evolving HCl + CO (7) (the sym. isomer reacts much more readily, even below 25° (7)).

Č on shaking at 0° with 10 vols. 7% aq. NH₄OH followed by acidification yields (1) (7) o-cyanobenzoic acid [Beil. IX-814, IX₁-(365)], m.p. 190° dec., converted by htg. to phthalimide, m.p. 228.5° u.c. [Exactly this same result is obtd. with the sym. isomer.]

[For studies of rate of reactn. of C with MeOH or with aniline see (2) (8).]

[For differentiation of \bar{C} from its sym. isomer by use of piperidinium N-piperidyldithio-carbamate (from piperidine + aq. + CS_2) see (6) (7).]

270

Ndls. from alc. in which it is eas. sol — Note that \bar{C} (like certain of its isomers) shows a peculiar characteristic; if the fused \bar{C} in a m.p. tube is allowed to cool and withdrawn it solidifies to a translucent form which on immediate reheating shows m.p. 84-85° but if left for a time is conv to an opaque mass which on htg. shows m.p. 89°.

[For prepn. of \bar{C} from 1-chloronaphthalene-3,8-brs-(sulfonyl chloride) [Beil. XI-214] with PCl₅ see (1) (3); from 1-nitronaphthalene [Beil. V-553, V₁-(264)] with Cl₂ see (4) (2)]

[C treated with ClSO₃H in CS₂ and prod. conv. to sodium salt yields (1) sodium 1,3,8-trichloronaphthalenesulfonate-5 (corresp. sulfonyl chloride, m.p. 127° (1)).]

3:2420 (1) Turner, Wynne, J. Chem. Soc. 1941, 247, 254. (2) Armstrong, Wynne, Chem. News 71, 255 (1895). (3) Armstrong, Wynne, Chem. News 61, 94 (1890). (4) Atterberg, Ber. 9, 926 (1876).

Cryst. from alc. or hexane. — Volatile with steam.

[For prepn. of Č from 1,8-diaminonaphthalene [Beil. XIII-205, XIII₁-(54)] via tetrazotization and htg. with Cu₂Cl₂ (59% yield) see (1); from 8-chloronaphthylamine-1 [Beil. XII-1256] via diazotization and use of Cu₂Cl₂ reactn. (52% yield (7)) (2) (6) see indic. refs.; from 1,8-dinitronaphthalene [Beil. V-559, V₁-(265)] with PCl₅ see (5) (11); from 8-chloronaphthalenesulfonyl chloride-1 [Beil. XI-162] by htg. at 200–230° as long as SO₂ is evolved see (4); from 4,5-dichloronaphthalenesulfonic acid-1 [Beil. XI-162] by hydrolytic cleavage of —SO₃H group at 230° see (9) (3); from K salt of 4,5-dichloronaphthalenesulfonic acid-2 [Beil. XI-182] by htg. with 1% H₂SO₄ or 50% H₃PO₄ in s.t. at 290° see (9).]

Č htd. with HCl in s.t. at 250-290° rearranges (9) to 1,5-dichloronaphthalene (3:3200), m.p. 107°.

[C in CS₂ treated with ClSO₃H yields (10) 1,8-dichloronaphthalenesulfonic acid-4 [Beil. XI-162] (corresp. sulfonyl chloride, m.p. 114° (10), corresp. sulfonamide, m.p. 228° (10)).]

3:2435 (1) Hampson, Weissberger, J. Chem. Soc. 1936, 394. (2) Weissberger, Sangewald, Hampson, Trans. Faraday Soc. 36, 890 (1934). (3) Cleve, Chem. Zig. 17, 398 (1893). (4) Armstrong, Wynne, Chem. News 71, 255 (1895). (5) Atterberg, Ber. 9, 1732 (1876). (6) Atterberg, Ber. 10, 548 (1877). (7) Bergmann, Hirshberg, J. Chem. Soc. 1936, 334. (8) Krollpfeiffer, Ann. 430, 198 (1923). (9) Armstrong, Wynne, Chem. News 76, 69-70 (1897). (10) Armstrong, Wynne, Chem. News 61, 273-274 (1890).

(11) Woroshtzow, Koslow, Ber. 69, 413 (1936).

3:2438 1,1-DICHLORO-2,2-bis-(p-CHLOROPHENYL)-ETHYLENE

C₁₄H₈Cl₄ Beil. S.N. 480

M.P. 89° (1)

88-89° (2)

86-87° (3)

Colorless cryst. from alc.

[For prepn of C from 1,1,1-trichloro-2,2-bis-(p-chlorophenyl)ethane ("DDT") (3:3298) by elimination of 1 HCl with alc KOH under reflux (1) for 10 hrs. (3) or 15-20 min. (4) (yields: almost 100% (4), 81% (3)) (for study of rate see (5)), or by htg. at 110-120° with a trace of FeCl₃ or AlCl₃ (2), see indic. refs.; for prepn. of C from 1,1,1,2-tetrachloro-2,2-bis-(p-chlorophenyl)ethane (3.2477) by elimination of two adjacent chlorine atoms with Zn dust in boilg. abs. alc refluxed 8 hrs. (66% yield) see (3)

Č on oxidn. with CrO₃/AeOH refluxed 4 hrs. gives (100% yield (3)) 4,4'-dichlorobenzo-phenone (3:4270), m.p. 144° (3).

 \bar{C} in boilg. CHCl₃ contg. a little PCl₃ with Cl₂ for 3 hrs. (but without special radiation) adds 1 mole halogen giving (70% yield (3)) 1,1,1,2-tetrachloro-2,2-bis-(p-chlorophenyl)-ethane (3:2477), m.p. 91-92° (3).

 \bar{C} with KOH in ethylene glycol refluxed 10–12 hrs. gives (almost 100% yield (4)) 4,4'-dichlorodiphenylmethane (3·1057) m.p. 55°; but note that \bar{C} with excess Ba(OH)₂.8H₂O in ethylene glycol refluxed 10–12 hrs. (4) or \bar{C} with alc KOH in st at 150–160° for 24 hrs. (7) gives (yields 57% (7), 33% (4)) di-(p-chlorophenyl)acetic acid (3:4612), m.p. 166.0–166 5° u.c. (4), 163–164° (7), this acid undoubtedly being the precursor which by loss of CO₂ with the above KOH gives the indicated prod.

 \bar{C} with anhydrous AlCl₃ in large excess C_6H_6 does not (6) give 1,1,2,2-tetraphenylethane (dif. from "DDT" (3:3298) q v)

3:2438 (1) Zeidler, Ber. 7, 1181 (1874).
 (2) Fleck, Haller, J. Am. Chem. Soc. 66, 2095 (1944).
 (3) Grummitt, Buck, Jenkins, J. Am. Chem. Soc. 67, 155-156 (1945).
 (4) White, Sweeney, U.S. Pub. Health Repts. 60, 66-71 (1945).
 (5) Brand, Busse-Sundermann, Ber. 75, 1828 (1942).
 (6) Fleck, Haller, J. Am. Chem. Soc. 67, 1420 (1945).
 (7) Grummitt, Buck, Stearns, J. Am. Chem. Soc. 67, 156 (1945).

3:2440 3,4,5-TRICHLOROBENZALDE-HYDE

C₇H₃OCl₃ Beil. S.N. 635

Colorless ndls. from alc. — Somewhat sol. boilg. aq.; volatile with steam. — Eas. sol. in hot alc.; also in ether, acetone, C6H6, or CHCl3; fairly sol. pet ether.

[For prepn. of C from 4-amino-3,5-dichlorobenzaldehyde (1) by diazotization and use of Cu₂Cl₂ reaction (yield of crude C 80%) see (1).]

Č on oxidn. with alk. KMnO₄ gives (1) 3,4,5-trichlorobenzoic acid (3:4920), m.p. 210°.

C on mononitration, with abs. HNO3 in cold, gives (86% yield crude (1)) 2-nitro-3,4,5trichlorobenzaldehyde, m.p. 118.5–119° (corresp. phenylhydrazone, m.p. 229° dec.; corresp. p-nitrophenylhydrazone, m.p. 293-294° dec.; corresp. semicarbazone, m.p. 278-279° dec.).

- 3,4,5-Trichlorobenzaldoxime: unreported.
- ② 3.4.5-Trichlorobenzaldehyde phenylhydrazone: m.p. 147° (1).
- 3,4,5-Trichlorobenzaldehyde p-nitrophenylhydrazone; orange ndls. from nitrobenzene, m.p. 342° dec. (1).
- 3.4.5-Trichlorobenzaldehyde semicarbazone: cryst. from alc., m.p. 252-254° (rap. htg.), but after fusion resolidifies and remelts at 284-285° (1).
- 3:2440 (1) Van de Bunt, Rec. trav. chim. 48, 131-137 (1929).

M.P. 90° (1) [95° (2)]

Cryst. from lt. pet. — Volatile with steam.

[For prepn. of C from 5,6-dichloro-2,3-dimethylaniline (4,5-dichloro-o-3-xylidine) (3) via diazotization and hydrolysis (yield not stated) see (1); for formn. of C from 4,5,6-trichloro-1,1-dimethylcyclohexen-4-one-3 with quinoline at 170° for 30 min. (yield not stated) see (2).1

C with Cl₂ in CHCl₃ does not give the expected 4,5,6-trichloro-2,3-dimethylphenol (3:4742) but instead (2) a tetrachloro deriv. (apparently containing a chlorinated methyl group), m.p. 127.5° (2).

The nitration of C has not been reported, and the expected 4-nitro-5,6-dichloro-2,3dimethylphenol is unknown.

- 5,6-Dichloro-2,3-dimethylphenyl acetate: unreported.
- 6 5.6-Dichloro-2.3-dimethylphenyl benzoate: m.p. 133° (1), 128° (2).

3:2442 (1) Hinkel, Ayling, Bevan, J. Chem. Soc. 1928, 2533. (2) Hinkel, J. Chem. Soc. 125, 1850-1851 (1924). (3) Hinkel, Ayling, Bevan, J. Chem. Soc. 1928, 1876-1877.

M.P. 91° (1) 90° (2)

Ndls. from alc.

[For prepn. of C from 2,3,4-trichlorobenzal (di)chloride (3:2212) in 58% yield by hydrolysis with fumg. H₂SO₄ as directed see (2).]

C on oxidn. with KMnO4 gives (1) 2,3,4-trichlorobenzoic acid (3:4810), m.p. 186-187°.

 \bar{C} with anhydr. NaOAc + Ac₂O on htg. (Perkin synthesis) gives (2) 2,3,4-trichloro-cinnamic acid [Beil. IX-597], m.p. 185°.

- 2,3,4-Trichlorobenzaldoxime: unreported.
- ---- 2,3,4-Trichlorobenzaldehyde phenylhydrazone: unreported.
- ---- 2,3,4-Trichlorobenzaldehyde p-nitrophenylhydrazone: unreported.
- ---- 2,3,4-Trichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.
- 3:2445 (1) Nicodemus, J. prakt. Chem. (2) 83, 319 (1911). (2) Seelig, Ann. 237, 149-151 (1887).

M.P. 91° (1) 90.5–91° (2) '

[For prepn. of Č from 3,6-dichloronaphthalenesulfonyl chloride-2 [Beil. XI-182] (1) (2), from 3-chloronaphthalene-2,7-bis-(sulfonyl chloride) [Beil. XI-217] (1) (3), or from 3-chloronaphthalene-2,6-bis-(sulfonyl chloride) [Beil. XI-216] (4), all with PCl₅, see indic. refs. cf. (6).]

[For study of oxidn. of C with CrO₃/AcOH see (5).]

[Č with ClSO₃H in CS₂ followed by conv. to salts yields a mixt. (1) derived from 2,3,6-trichloronaphthalenesulfonic acid-8 (corresp. sulfonyl chloride, m.p. 118° (1)), and from 2,3,6-trichloronaphthalenesulfonic acid-X (corresp. sulfonyl chloride, m.p. 94° (1)).]

3:2455 (1) Turner, Wynne, J. Chem. Soc. 1941, 247, 256-257. (2) Armstrong, Wynne, Chem. News 61, 275 (1890). (3) Armstrong, Wynne, Chem. News 61, 92 (1890). (4) Armstrong, Wynne, Chem. News 62, 163 (1890). (5) Claus, Schmidt, Ber. 19, 3177-3179 (1886). (6) Franzen, Stauble, J. prakt. Chem. (2) 103, 356, 377 (1921/22).

M.P. 90-91° (1) (2)

Ndls. from lgr. or aq. — Sol. hot aq. and most organic solvents. — Volatile with steam. [For prepn. of \bar{C} from 5-chloro-2,4-dimethylaniline [Beil. XII₁-(486)] via diazotization and hydrolysis see (1); for formn. of \bar{C} from 2,4-dimethylquinol (*m*-xyloquinol) [Beil. VIII-22, VIII₁-(514)] by action of HCl (1) (2) in AcOH at 0° (1) (note that some of the isomeric 6-chloro-2,4-dimethylphenol (3:8784) is also formed) see indic. refs.]

The nitration of \bar{C} has not been reported, and none of its mononitro- or dmitro-derivatives is known.

Č in alc. soln. with FeCl₃ gives a deep olive-green color becoming blue on dilution with aq. or reddish brown on htg. (1).

- ---- 5-Chloro-2,4-dimethylphenyl acetate: unreported.
- © 5-Chloro-2,4-dimethylphenyl benzoate: m.p. 84.5-85.5° (1). [From Č with benzoyl chloride + aq. NaOH (1).]
- 5-Chloro-2.4-dimethylphenyl p-nitrobenzoate: unreported.
- --- 5-Chloro-2.4-dimethylphenyl N-phenylcarbamate: unreported.
- 3:2460 (1) Bamberger, Reber, Ber. 46, 793-803 (1913). (2) Bamberger, Reber, Ber. 46, 2268 (1907).

3:2470 4-CHLOROCATECHOL (4-Chloropyrocatechol)

$$\begin{array}{ccc} C_6H_5O_2Cl & & Beil.\ VI\ -\ 783 \\ & & VI_1\ -\ (389) \\ & & VI_2\ -\ (787) \end{array}$$

Anhydrous \tilde{C} exists in two forms melting at 90-91° and 59-61° (1); after fusion of the higher-melting form the resolidified \tilde{C} melts 59-61° (1).

 \bar{C} can be recrystd. from C_6H_6 , CHCl₃ from which it separates in scaly lfts., or from CS₂ from which it separates in prisms. — \bar{C} cryst. from ord. ether as hemihydrate, \bar{C} . ½H₂O, which loses its aq. upon distn. in vac. (1). — \bar{C} is cas. sol. aq., alc, ether, Λ cOH, or acetone; spar. sol. lgr. (1).

[For prepn. of \bar{C} from catechol (1:1520) by action of SOCl₂ see (3) (5) (1) (4); for prepn. from 5-chloro-2-hydroxybenzaldehyde (3:2800) + alk H₂O₂ see (6); for prepn. from obenzoquinone [Beil. VII-600] by actn. of dry HCl in CHCl₃ see (7)]

C with FeCl₃ gives scarab-green color, which on addn. of Na₂CO₃ becomes dark red, or with NaOAc turns blue (1).

 \tilde{C} in AcOH treated with xanthydrol (1:5205) soon ppts. 4-chloro-5-xanthydryleatechol, cryst. from C_6H_6 , mp. 224° (block) (8).

[For reaction with boric ac. see (2); for use in prepn. of dyestuffs see (9); for oxidn. with Ag₂O in abs. ether to 4-chlorobenzoquinone-1,2 see (1).]

D 4-Chlorocatechol dibenzoate: from \tilde{C} + BzCl in pyridine; ndls. (from ether), m.p. 96-97° (1).

3:2470 (1) Willstätter, Müller, Ber. 44, 2182-2184 (1911) (2) Bocscken, Mijs, Rec. 44, 758-760 (1925). (3) Frejka, Safranek, Zik, Collection Czechoslov Chem Commun 9, 245 (1937).
(4) Peratoner, Gazz. chim. ital. 28, I 222 (1898). (5) Urede, Muhlroth, Ber. 63, 1932-1933 (1930).
(6) Dakin, Am. Chem. J. 42, 488 (1909). (7) Jackson, Koch, Am. Chem. J. 26, 28-30 (1901).
(8) Fabre, Ann. chim. (9) 18, 114-115 (1922). (9) Lehmann (to I.G.), Ger. 648,713, Aug. 6, 1937; Cent. 1938, I 187.

3:2475 1,1-DI-(
$$p$$
-CHLOROPHENYL)- $C_{14}H_{10}Cl_2$ Beil. S.N. 480 ETHYLENE Cl
 $C=CH_2$

M.P. 91° (1) 85-87° (2)

Colorless cryst. from MeOH contg. some C6H6 (1).

[For prepn. of \bar{C} from di-(p-chlorophenyl)-methyl-carbinol (itself prepared from 4,4'-dichlorobenzophenone (3:4270) with MeMgI) by dehydration see (1) (2)

C on cat. hydrogenation gives (62% yield (4)) 1,1-di-(p-chlorophenyl)ethane (3:0995), m.p. 54-55°.

Č with PCl₅ in C₆H₆ stood 24 hrs. then poured into aq. gives (61% yield {1}) β,β -bis-(p-chlorophenyl)vinyl-phosphinic acid, (Cl.C₆H₄.)₂C = CH.PO.(OH)₂, cryst. from AcOH, m.p. 158-159° (1).

 \bar{C} with O_3 in CCl₄ soln. in acetone/solid CO₂ cooling bath, subsequently decomposed with H_2O_2 , gives (2) p-chlorobenzoic acid (3:4940), oxalic acid (1:0445), 4,4'-dichlorobenzophenone (3:4270), and a little 4,4'-dichlorobenzophenone peroxide, cryst. from acetone, m.p. 217.5-218.5° (2).

[For behavior of \bar{C} with $C_6H_6 + AlCl_3$ (3 moles) in reverse Friedel-Crafts reaction see (3).]

3:2475 (1) Bergmann, Bondi, Ber. 64, 1470 (1931). (2) Marvel, Nichols, J. Org. Chem. 6, 301 (1941) (3) Alexander, Chem. Age 36, 50 (1937); Cent. 1937, I 4085; not in C.A. (4) Grummitt, Buck, Becker, J. Am. Chem. Soc. 67, 2265-2266 (1945).

3:2477 1,1,1,2-TETRACHLORO-2,2-bis-(p-CHLOROPHENYL)ETHANE

Beil. S.N. 479

M.P. 91-92° (1)

Colorless cryst. from abs. alc.

[For prepn. of C from 1,1,1-trichloro-2,2-bis-(p-chlorophenyl)ethane ("DDT") (3:3298) with Cl₂ in CCl₄ contg a little PCl₃ (73% yield (1)), or from 1,1-dichloro-2,2-(p-chlorophenyl)ethylene (3:2438) with Cl₂ in CHCl₃ contg. a little PCl₃ (70% yield (1)), see indicrefs.

Č with Zn dust in abs. alc. refluxed 8 hrs loses 2 chlorine atoms giving (66% yield (1)) 1,1-dichloro-2,2-bis-(p-chlorophenyl)cthylene (3:2438).

Despite the presence in C of one tertiary chlorine atom, C does not (1) react with 5% alc. AgNO₃ at room temp

 \bar{C} with 5% aq. N₂OH refluxed for 15 min. is appreciably hydrolyzed, but with aq. alone similar treatment gives no appreciable reaction (1).

3:2477 (1) Grummitt, Buck, Jenkins. J. Am. Chem. Soc. 67, 155-156 (1945).

3:2480 2,3,4,6-TETRACHLOROTOLUENE

$$\begin{array}{cccc} CH_3 & C_7H_4Cl_4 & \text{Beil. V - } 302 \\ Cl & & & V_{1^-}(153) \\ Cl & & & V_{2^-}(234) \\ \end{array}$$

Ndls. from alc., ether, or alc. + ether.

[For prepn of \tilde{C} from 2,4,6-trichloro-3-aminotoluene [Beil. XII-873] (1) via diazotization and use of Cu_2Cl_2 reactn. (yield 92% (2)) (1) see indic. refs; from toluene (1:7405) with Cl_2 in pres. of anhydrous $FeCl_3$ at 15-50° (90% yield) see (3) cf. (5); for formn. of \tilde{C} (together with other isomers) from 2,3,4-trichlorotoluene (3:0425) or 2,4,6-trichlorotoluene (3:0380) with Cl_2 in CCl_4 in pres. of Al/Hg (2), or from 2,4,5-trichlorotoluene (3:2100) with $SO_2Cl_2 + AlCl_3 + S_2Cl_2$ as directed (4), see indic. refs.]

 \bar{C} (1 wt. pt.) on nitration with a mixt. of 3 wt. pts. HNO₃ (D=1.48) + 7.4 wt. pts. conc. H₂SO₄ (D=1.84) at 105° for ½ hr gives (4) 2,3,4,6-tetrachloro-5-nitrotoluene, cryst. from alc., m.p. 154° (4). — Note that the value of 131-134° reported previously (2) was undoubtedly (4) incorrect. — Note also that the m.p. of this nitration prod. is only

slightly lower than that (159°) for the corresp. prod. from 2,3,4,5-tetrachlorotoluene (3:2710).

3:2480 (1) Bures, Trpisovska, Časopis Českoslov. Lékárnictva 15, 179–186 (1935); Cent. 1936, I 1209; C.A. 30, 1753 (1936). (2) Cohen, Dakin, J. Chem. Soc. 85, 1280, 1282–1285 (1904). (3) Casella and Co., Ger. 282,567, April 7, 1915; Cent. 1915, I 862. (4) Silberrad, J. Chem. Soc. 127, 2682–2683 (1925). (5) Beilstein, Kuhlberg, Ann. 150, 287–290 (1869).

3:2490 1.2.4-TRICHLORONAPHTHALENE

M.P. 92° (1) (2)

Ndls. somewhat spar. sol. in alc. or AcOH.

[For prepn. of \tilde{C} from 2,4-dichloronaphthylamine-1 [Beil. XII-1256] via diazotization and use of Cu₂Cl₂ reactn. see (1) (3); from 2,4-dichloronaphthol-1 (3:3250) by htg. with PCl₅ see (2); from 1,3-dichloronaphthalene (3:1310) with Cl₂ in CHCl₃ see (4).]

[C treated with ClSO₂H in CS₂ and reactn. prod. conv. to Na salt as directed (1) yields sodium 1,2,4-trichloronaphthalenesulfonate-6 (corresp. sulfonyl chloride, m.p. 158° (1)).]

3:2490 (1) Turner, Wynne, J. Chem. Soc. 1941, 247, 251. (2) Cleve, Ber. 21, 893 (1888). (3) Armstrong, Wynne, Chem. News 61, 273 (1890). (4) Cleve, Ber. 23, 954 (1890).

CHAPTER VII

DIVISION A. SOLIDS

(3:2500-3:2999)

3:2515 1,2,6-TRICHLORO-NAPHTHALENE

$$\begin{array}{c|cccc} Cl & C_{10}H_{b}Cl_{3} & \textbf{Beil. V - 544} \\ & V_{1}-- & V_{2}-- & \end{array}$$

M.P. 92.5° (1)

92° (2) (8)

91° (3)

90° (4)

Ndls. from alc.; very eas. sol. CHCl₃.

[For prepn. of Č from 1-chloro-6-sulfonaphthylamine-2 [Beil. XIV-763] via diazotization and use of Cu₂Cl₂ reactn. see (2) (5); from 1,2-dichloronaphthalenesulfonyl chloride-6 [Beil. XI-183] (6), 2-chloro-1-nitronaphthalenesulfonyl chloride-6 [Beil. XI-188] (4), 2-chloronaphthalene-1,6-bis-(sulfonyl chloride) [Beil. XI-214] (3), or 1-chloro-6-bromonaphthol-2 [Beil. VI-651] (7) by htg. with PCl₅ as directed see indic. refs.: for formn. of Č from 2,6-dichloronaphthalene (3:4040) with Cl₂ in CHCl₃ (9% yield) see (8).]

[C treated with ClSO₃H in CS₂ and prod. conv. to sodium salt yields (2) sodium 1,2,6-trichloronaphthalenesulfonate-4 (corresp. sulfonyl chloride, m.p. 184° (2)).]

3:2515 (1) Armstrong, Wynne, Chem. News 71, 255 (1895). (2) Turner, Wynne, J. Chem. Soc. 1941, 247, 252. (3) Forsling, Ber. 21, 3498 (1888). (4) Cleve, Chem. Ztg. 17, 398 (1893). (5) Armstrong, Wynne, Proc. Chem. Soc. 1869, 36, 49. (6) Armstrong, Wynne, Chem. News 59, 189 (1889); 61, 274 (1890). (7) Armstrong, Rossitter, Chem. News 63, 137 (1891). (8) Wynne, J. Chem. Soc. 1946, 61.

3:2545 3-CHLORONAPHTHOL-2

OH C₁₀H₇OCl Beil, VI — VI₁— VI₂-(603)

M.P. 93° (1)

92° (2)

90° (2)

Colorless ndls. from pet. ether. — Spar. sol. cold aq.; sol. boilg. aq., and readily sol. org. solvents. — Volatile with steam; can also be distilled without decompn. but b.p. is not stated (2). [The identity of the product of m.p. 63-64.5° obtd. from supposed 3-chloronaphthyl-2 methyl ether by HI splitting (3) and regarded by its sponsors as \bar{C} is in doubt.] — Note that \bar{C} does not depress m.p. of β -naphthol (2).

[For prepn. of Č from 1,3-dichloronaphthol-2 (3:1990) with Fe(OH)₂ htd. under press. 8 hrs. at 120° (2) or htd. in alc. with Zn/Cu couple (1) see indic. refs.; from 3-chloronaphthalene-1,2-diazooxide with alk. SnCl₂ see (2); from 3-chloro-2-hydroxynaphthalenesulfonic acid-1 by htg. with 50% H₂SO₄ see (4).]

 $\ddot{\mathbf{C}}$ is eas. sol. in aq. alk. and also in aq. Na₂CO₃ soln. on warming (1); the alk. soln. of $\ddot{\mathbf{C}}$ couples with diazonium salts to give azo dyestuffs; e.g., $\ddot{\mathbf{C}}$ with benzenediazonium chloride. soln. yields a prod., m.p. 139° (4), presumably 1-(benzeneazo)-3-chloro-2-hydroxynaphthalene.

C in dil. aq. NaOH, treated with NaNO₂, chilled, and acidified dropwise with H₂SO₄ gives (4) 3-chloro-1-nitrosonaphthol-2 (3-chloronaphthoquinone-1,2-oxime-1) [Beil. VII-721], which on hydrolysis with AcOII/HCl for 3 hrs. yields 3-chloronaphthoquinone-1,2 (3:4704), m.p. 214-215° (4).

3:2545 (1) Herzberg, Spengler, Schmid, Ger. 431,165, June 30, 1926; Cent. 1926, II 1196. (2) Marschalk, Bull. soc. chim. (4) 43, 1365–1367 (1928). (3) Jambuserwala, Holt, Mason, J. Chem. Soc. 1931, 375. (4) Marschalk, Bull. soc. chim. (4) 45, 658, 661 (1929).

3:2565
$$\beta_1\beta'$$
-DICHLORO- α -HYDROXYISO- $C_4H_6O_3Cl_2$ Beil. III - 318 BUTYRIC ACID CH_2Cl III₁— III_2 -(224) $ClCH_2$ — C -COOII

M.P. 93° (1) Neut. Eq. 173 (1) 91–92° (2) (3)

Deliquescent tbls, eas. sol. alc., ether; cryst from CHCl₃ (1); spar. sol. pet. ether. [For prepn. from α,α' -dichloroacetone (3:0563) + HCN, followed by hydrolysis of the resultant nitrile with HCl (overall yield alm. quant. (4)), see (3) (4)]

3:2565 (1) Smith, Z. physik Chem. A-177, 137-138 (1936). (2) Favrel, Bull. soc. chim. (5) 1, 985 (1934). (3) Grimaux, Adam, Bull. soc. chim. (2) 36, 20 (1881), Ann. chim (5) 23, 361-362 (1881). (4) Glattfeld, Schneider, J. Am. Chem. Soc. 60, 417 (1938).

3:2570 d,l-1,2-DICHLORO-1,2-DIPHENYLETHANE (d,l- α,α_l -Dichlorobibenzyl; " β " stilbene dichloride)

$$\begin{array}{c|c} & C_{14}H_{12}Cl_2 & \text{Beil. V - 601} \\ & V_{1}\text{-(282)} \\ & V_{2}\text{--} \\ \\ Cl\text{--}C\text{--}H & \\ & \\ \end{array}$$

[See also the isomeric meso or " α " stilbene dichloride (3:4854).]

Colorless tbls. or lfts. — Eas. sol. most org solvents but least in lgr. — Readily separable from the much less soluble isomeric " α " stilbene dichloride (3:4854) by recrystn. from alc. — Sublimes without decompn.

[For preparation of \bar{C} see text of the isomeric " α " stilbene dichloride (3:4854) cf. also (8), noting that many (but not all) of its methods of prepn. give more or less \bar{C} .— Note also that by reaction of the optically active forms of α -amino- α' -hydroxybibenzyl in HCl with NOCl both of the corresp. optical antipodes of \bar{C} have been prepd. (5).]

 \bar{C} on htg. above its m.p. is partially isomerized to the isomeric " α " stilbene dichloride (3:4854) so that m.p. gradually rises to about 160° (1).

[C with AgOAc (2 moles + 25% excess) in AcOH at 100° for 9 hrs. gives (8) mixts. of hydrobenzoin diacetate, m.p. 133-134°, and isohydrobenzoin diacetate, m.p. 114-116° (for m.p./compn. diagram of this pair see (8) (9))

 \bar{C} with pyridine in s.t. at 200° for 8 hrs. loses 1 HCl giving (2) one of the two stereoisomeric α -chlorostilbene's, viz., the solid stereoisomer [Beil V-633, V₁-(304)], m.p. 52-54° (2); note that the isomeric " α " stilbene dichloride (3:4854) is inert to pyridine and does *not* show this behavior.

3:2570 (1) Zincke, Ann. 198, 129-141 (1879); Ber. 10, 999-1004 (1877). (2) Pfeiffer, Ber. 45, 1816-1817 (1912). (3) Kayser, Ann. chim. (11) 6, 220-222 (1936). (4) Weissberger, Bach, Z. physik. Chem. B-9, 140 (1930). (5) Weissberger, Bach, Ber. 64, 1095-1108 (1931). (6) Newman, Joshel, Wise, J. Am. Chem. Soc. 62, 1862 (1940). (7) Kharasch, Brown, J. Am. Chem. Soc. 61, 3434 (1939). (8) Winstein, Seymour, J. Am. Chem. Soc. 68, 119-122 (1946). (9) Böeseken, Elsen, Rec. trav. chim. 47, 696 (1928).

3:2575 2,3,5,6-TETRACHLOROTOLUENE

M.P. 93-94° (1) 93° (2)

Ndls. from MeOH.

[For prepn. of \bar{C} from 2,5,6-trichloro-3-aminotoluene [Beil. XII-873] via diazotization and use of Cu_2Cl_2 reactn. (80% yield) see (1); for formn. of \bar{C} (together with other isomers) from 2,3,5-trichlorotoluene (3:0610) or from 2,3,6-trichlorotoluene (3:0625) in CCl_4 with Cl_2 in pres. of Al/Hg see (1); for formn. of \bar{C} as by-prod. of oxidn. of tetrachloro-p-cymene see (2).

C on nitration with 10 pts. fumg. HNO₃ at 100° for 1½ hrs. gives (1) 2,3,5,6-tetrachloro-4-nitrotoluene, pl. from MeOH, m.p. 150-152° (1).

3:2575 (1) Cohen, Dakin, J. Chem. Soc. 85, 1280-1284 (1904). (2) Qvist, Holmberg, Acta Acad. Aboensis Math. et Phys. 6, No. 14, 3-28 (1932); Cent. 1932, II 2815-2816, C.A. 27, 5726-5727 (1933).

3:2615 6-CHLORONAPHTHOL-1

$$\begin{array}{cccc} OH & C_{10}H_7OCl & \textbf{Beil.\,VI-612} \\ & & & & & & & & & \\ CI & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & \\ & & \\ & \\ & & \\ & \\ & \\ & & \\ &$$

M.P. 94° (1)

Long white pr. from CS2; C rapidly turns gray-violet in air.

[For prepn. of \tilde{C} from γ -(3-chlorophenyl)paraconic acid [Beil. XVIII-421] on distillation see (1).]

C dis. in aq. alk. and this soln. couples (1) with diazonium salts.

Č with aq. FeCl₃ gives a yellowish-white ppt. unchanged on stdg.; Č with Ca(OCl)₂ solns. gives (1) a pale violet ppt.

Č (1 mole) with PkOH (1 mole) in CHCl₃ yields an addn. cpd., Č.PkOH, yel.-red ndls., m.p. 165° (1).

6-Chloro-1-naphthyl acetate: tbls. from alc. + ether, m.p. 47° (1). [From C on boilg. with excess Ac₂O (1).]

3:2615 (1) Erdmann, Kirchhoff, Ann. 247, 376-378 (1888).

[See also β -chloroisocrotonic acid (3:1300).]

Cryst. from lgr. or CS₂. — \bar{C} is sol. in 35.2 pts. aq. at 19° (2), in 44.4 pts. aq. at 12° (3).— \bar{C} is only slightly volatile with steam (2) (dif. from isomeric β -chloroisocrotonic acid (3:1300)).— \bar{C} in either cis- α,β -dichloroethylene (3:5042) or $trans-\alpha,\beta$ -dichloroethylene (3:5028) at 0° is very much less soluble than the isomeric β -chloroisocrotonic acid (3:1300) (11). — \bar{C} can be sublimed at 120° (1).

For f.p./compn. data and diagram of system $\ddot{\mathbf{C}}$ + the isomeric β -chloroisocrotonic acid (3:1300) (eutectic, m.p. 38.9°) contg. 33.2 mole % $\ddot{\mathbf{C}}$) see (12).

Preparation. [The most frequently used method of preparation of \tilde{C} is that from ethyl acetoacetate (1:1710) with PCl₅; this treatment leads to the formation of a mixt. of the acid chlorides of \tilde{C} and of the isomeric β -chloroisocrotonic acid (3:1300) which upon hydrolysis with aq. gives a mixt. of the two acids; from this mixture the β -chloroisocrotonic acid is removed (together with any unreacted ethyl acetoacetate) by distillation with steam; the residual \tilde{C} is then further purified by recrystallization. — The yield of the mixt. of \tilde{C} with its stereoisomer is variously reported, e.g., 43.7% (4), 36.5% (10); the yield of pure \tilde{C} is relatively small; e.g., 16.9% (4), 11% (13). — The PCl₅ reactn. has often been carried out in dry C_6H_6 (14) (15) (10) (4), but its use is regarded (1) as disadvantageous. — For many important details of procedure see indic. refs.]

[For formn. of \bar{C} from α, β, β -trichloro-n-butyric acid (3:0925) by removal of the α and one β chlorine atoms with Zn see (16); from tetrolic acid, CH₃—C \equiv C.COOH [Beil. II-479, II₁-(208), II₂-(451)] by addn. of 1 HCl from conc. aq. HCl on stdg. some weeks in s.t. at room temp. see (17); from the stereoisomeric β -chloroisocrotonic acid (3:1300) with conc. aq. HCl in s.t. at 100° for 6 hrs. see (18).]

Chemical behavior. \vec{C} on htg. at 150–160° for 20 hrs. (17) or at 130° in s.t. (22) is largely isomerized to β -chloroisocrotonic acid (3:1300).

[\bar{C} in alc. (5) or aq. (5) (19) NaOH with $H_2 + Pd/BaSO_4$ or \bar{C} with Na/Hg (20) (2) yields crotonic acid (1:0425), m.p. 72°; note that \bar{C} is thus dehalogenated more slowly (5) than the isomeric β -chloroisocrotonic acid (3:1300), and that with excess H_2 the crotonic acid is further reduced to n-butyric acid (1:1035).]

C on oxidn. with aq. KMnO₄ yields (21) only AcOH (1:1010) and oxalic acid (1:0445).

 $\bar{\mathbb{C}}$ with $\mathrm{Cl_2}$ in $\mathrm{CS_2}$ soln. adds 1 mole halogen yielding (16) α,β,β -trichloro-n-butyric acid (3:0925), m.p. 52°; $\bar{\mathbb{C}}$ undoubtedly also adds 1 Br₂ to yield β -chloro- α,β -dibromo-n-butyric acid, but the latter has never been reported.

 \tilde{C} behaves as a monobasic acid, dissociation const. at $25^{\circ} = 1.44 \times 10^{-4}$ (23). — \tilde{C} on neutralization with cold dilute alk. gives Neut. Eq. = 120.5, forms stable salts. — Note, however, that \tilde{C} with 6.7% aq. KOH at 70-80° (24) cf. (25) (26) splits off HCl yielding tetrolic acid, CH₃.C=C—COOH; \tilde{C} with excess conc. aq. KOH (e.g., abt. 7 N) begins to decompose even below 100° yielding (24) acetone (1:5400) + K_2CO_3 + KCl.

Salts. [NH₄ \bar{A} , (27); Na \bar{A} . $\frac{1}{2}$ H₂O, very sol. aq., and does not isomerize on htg. (2); Ag \bar{A} on htg. with aq. in s.t. at 170° dec. yielding CO₂ + propadiene (allylene) but does so more slowly than the silver salt of the isomeric β -chloroisocrotonic acid (3:1300) (18); Ba \bar{A}_2 , very sol. aq. (2); Cu \bar{A}_2 .H₂O (2).]

 $[\bar{C}]$ with PCl₅ yields (28) (29) β -chlorocrotonoyl chloride; note, however, that, although this product is presumably involved in the prepn. of \bar{C} from ethyl acetoacetate with PCl₅ (see above under preparation of \bar{C}) cf. (29), yet it has never been isolated in pure form nor its properties specifically characterized (the m.p. 94° reported in various places is an error, the value referring in fact (28) to \bar{C}); this lack of data is presumably due to its easy isomerization to the stereoisomeric β -chloroisocrotonoyl chloride, b.p. 135–136° at 760 mm. (30).]

[\bar{C} (as K salt) with alc. NaOEt on htg. gives after acidification (24) β -ethoxycrotonic acid [Beil. III-371, III₁-(135)], m.p. 137-138° (24), 141° (31). — \bar{C} (as Na salt) with Na benzylate on htg. gives after acidification (32) β -benzyloxycrotonic acid, m.p. 121-122° (32). — \bar{C} (as Na salt) with Na salt of benzyl mercaptan in the cold gives after acidification (32) a β -benzylmercaptocrotonic acid, m.p. 192-194°; at 100°, however, there is also obtained (32) a stereoisomer, m.p. 130°.]

[For behavior of \bar{C} (as NH₄ salt) with (NH₄)₂SO₃ yielding β -sulfocrotonic acid (33) or of \bar{C} (as K salt) with K₃AsO₃ yielding β -arsonocrotonic acid (9) see indic. refs.]

- [\bar{C} with C_6H_6 + AlCl₃ not only undergoes Friedel-Crafts reactn. but also addition of C_6H_6 to unsatd. linkage giving (35–38% yield (34)) β,β -diphenyl-n-butyric acid, m.p. 102–103° (35).]
 - Methyl β-chlorocrotonate: b.p. 64-67° at 14 mm. (see 3:9244). [For study of rate of esterification of C with MeOH see (36) (37).]
 - Ethyl β -chlorocrotonate: b.p. 179–180° (see 3:8538).
 - \bigcirc β -Chlorocrotonamide: ndls. from ether, pr. from aq., m.p. 99-101° (28). [From β -chlorocrotonoyl chloride (see above) with conc. aq. NH₄OH (28).]
 - β-Chlorocrotonanilide: pr. from alc., m.p. 123-124° (28). [From β-chlorocrotonoyl chloride (see above) with aniline + excess cold dil. aq. NaOH (28).]
 - ⑤ β-Chlorocroton-α-naphthalide: pr. from alc., m.p. 169-170° (28). [From β-chlorocrotonoyl chloride (see above) with α-naphthylamine + excess cold dil. aq. NaOH (100% yield (28)).]

3:2625 (1) Dadieu, Pongratz, Kohlrausch, Monatsh. 60, 211-212 (1932); Sitzber. Akad. Wiss. Wien, Math. naturw. Klasse, Abt. II-a, 140, 359-360 (1931). (2) Geuther, Zeit. Chemie 1871, 240. (3) Kahlbaum, Ber. 12, 2337-2338 (1879). (4) Backer, Beute, Rec. trav. chim. 54, 552-553 (1935). (5) Paal, Schiedewitz, Rauscher, Ber. 64, 1521-1530 (1931). (6) Bruylants, Castille, Bull. soc. chim. Belg. 34, 277 (1925). (7) von Auwers, Wissebach, Ber. 56, 724 (1923). (8) Stelling, Z. physik. Chem. B-24, 423 (1934). (9) Backer, van Oosten, Rec. trav. chim. 59, 49-50 (1940). (10) Skau, Saxton, J. Am. Chem. Soc. 50, 2693-2701 (1928).

Lebrun, Bull. soc. chim. 39, 429-430 (1930).
 Skau, Saxton, J. Phys. Chem. 37, 183-196 (1933).
 Autenrieth, Ann. 259, 358-362 (1890).
 Michael, Schulthess, J. prakt.
 Chem. (2) 46, 236-238 (1892).
 Scheibler, Voss, Ber. 53, 381-382 (1920).
 Szenic, Taggesell, Ber. 28, 2665-2667 (1895).
 Friedrich, Ann. 219, 363, 370-371 (1883).
 (18)

Michael, Clark, J. prakt. Chem. (2) 52, 326-329 (1895). (19) Rosenmund, Zetsche, Ber. 51,

583 (1918). (20) Michael, Schulthess, J. prakt. Chem. (2) 46, 248-249 (1892).

(21) Kondakow, J. Russ. Phys.-Chem. Soc. 24, 508 (1892). (22) Michael, Schulthess, J. prakt. Chem. (2) 46, 264-266 (1892). (23) Ostwald, Z. physik. Chem. 3, 245 (1889). (24) Friedrich, Ann. 219, 346-349 (1883). (25) Michael, J. prakt. Chem. (2) 38, 9-10 (1888). (26) Michael, Schulthess, J. prakt. Chem. (2) 46, 254-255 (1892). (27) McMaster, Magill, J. Am. Chem. Soc. 38, 1796-1797 (1916). (28) Autenrieth, Ber. 29, 1665-1669 (1896). (29) Shriner, Keyser, J. Am. Chem. Soc. 60, 287 (1938). (30) Scheibler, Topouzada, Schulze, J. prakt. Chem. (2) 124, 16 (1930).

(31) Nef, Ann. 276, 234 (1893). (32) Autenrieth, Ber. 29, 1646-1652 (1896). (33) Backer, Beute, Rec. trav. chim. 54, 559-560; 622-624 (1935). (34) Koelsch, Hochmann, LeClaire, J. Am. Chem. Soc. 65, 59 (1943). (35) Bergmann, Taubadel, Weiss, Ber. 64, 1501 (1931). (36) Sudborough, Roberts, J. Chem. Soc. 87, 1846 (1905). (37) Michael, Oechslin, Ber. 42, 322 (1909).

M.P. 95° (1) (2)

Ndls. from alc. (1) (2); much more sol. in lgr than isomeric 6,7-dichloronaphthol-1 (3:4315) (3).

[For prepn. from β -(3,4-dichlorobenzal)propnonic ac. [Beil. IX-614] by distn. see (1) (2) (3); \bar{C} is separated from the larger proportion of 6,7-dichloronaphthol-1 (3:4315) by its greater soly. in lgr (3)]

C in alk. soln. coupled with diazotized naphthionic acid (1-aminonaphthalenesulfonic acid-4) gives a dark violet color which upon acidification turns bluish cherry-red (3). [Dif. from 6,7-dichloronaphthol-1 (3:4315) q.v.]

1) 7,8-Dichloro-1-naphthyl acetate: cryst. from dil. alc., m.p. 87-88° (1) (2).

3:2635 (1) Armstrong, Wynne, Chem. News 71, 253 (1895). (2) Armstrong, Wynne, Proc. Chem. Soc. 11, 78-79 (1893); Bcr. 29, Referate 223-224 (1896). (3) Erdmann, Schwechten, Ann. 275, 286 (1893).

3: 2637 3,5-DICHLORO-2-HYDROXYBENZALDEHYDE (3,5-Dichlorosalicylaldehyde) CI CHO C₇H₄O₂Cl₂ Beil. VIII - 54 VIII₁—

M.P. 95-96° (1) 95° (2) (3) 94-95° (4)

Pale yel. scales from AcOH; insol. aq., sol. in usual org. solvents.

[For prepn. of \bar{C} from o-hydroxybenzaldehyde (salicylaldehyde) (1:0205) in AcOH or CHCl₃ with Cl₂ (2moles) (yields: 90% (3), 70% (4)) (1) see indic. refs.; for formn. from 2,4-dichlorophenol (3:0560) with hexamethylenetetramine in glycerol + H_3BO_3 with H_2SO_4 as directed (7% yield) see (1).]

[For study of bactericidal props. of C see (9)]

C is sol. in dil. aq. alk. or NH₄OH yielding yel. solns.; C is stable toward dil. aq. acids or even hot conc. HCl but with conc. H₂SO₄ or HNO₃ dec. on warming (2).

[\bar{C} in dil. aq. NaOH oxidized with dil. (3%) H_2O_2 as directed yields (1) 3,5-dichloro-1,2-dihydroxybenzene (3,5-dichlorocatechol) (3:3525), pr. from cold aq., m.p. 83-84° (1).]

[C with Ac2O + NaOAc (Perkin condensation) yields (5) (6) 6,8-dichlorocoumarin.

cryst. from C_6H_6 , m.p. 160° (5), 157° (6) (this prod. on reduction with Na/Hg gives (6) γ -(3,5-dichloro-2-hydroxyphenyl)propionic acid (3,5-dichloromelilotic acid), m.p. 122° (6), on soln. in aq. alk. and boilg. with HgO or Hg(OAc)₂ yields (7) 3,5-dichloro-2-hydroxycinnamic acid (3,5-dichloro-o-coumaric acid), cryst. from dil. alc., dec. 242° (7), or on oxidn. with KMnO₄ gives alm. quant. yield (5) of 3,5-dichlorosalcylic acid (3:4935), m.p. 214° (5)).] — [\bar{C} with ω -(phenylacetyl)acetophenone (1,4-diphenylbutanedione-1,3) in abs. alc. with a little piperidine 7-11 hrs. at 100° condenses giving (16% yield (8)) 6,8-dichloro-3-phenylcoumarin, colorless ndls. from AcOH, m.p. $193-195^\circ$ (8).]

[Č with EtMgBr yields corresp. ter. alc., viz., 3,5-dichloro-2-hydroxyphenyl-ethyl-carbinol, which at 16 mm. press. loses aq. at 140° giving (80% yield (4)) 2,4-dichloro-6-propenylphenol, m.p. 46-47° (4).]

- (3,5-dichloro-2-hydroxybenzaldoxime): colorless ndls. from alc./aq. (4:1) (3), m.p. 195-196° (4), 195° (2). [From $\bar{C} + NH_2OH.HCl$ in alc. on htg. 1 hr. and pouring into aq. (alm. quant. yield) (4) [This oxime with Ac₂O on boilg. 3 hrs. gives alm. quant. yield (4) of 3,5-dichloro-2-acetoxybenzonitrile, colorless ndls from alc., m.p. 78° (4).]
- D 3,5-Dichloro-2-hydroxybenzaldehyde phenylhydrazone: pale yel. tbls. from alc., m.p. 153° (4). [From C in alc. with phenylhydrazine on shaking 10 min. (4).]
- 3,5-Dichloro-2-hydroxybenzaldehyde semicarbazone: alm. colorless ndls. from AcOH, m.p. 227° dec. (4) [From C in AcOH with semicarbazide HCl in alm. quant. yield after ½ hr. boilg. (4)]

3:2637 (1) Dakin, Am. Chem. J. 42, 488-489 (1909). (2) Duff, J. Chem. Soc. 1941, 547-549. (3) Biltz, Stepf, Ber. 37, 4027-4031 (1904). (4) Claisen, Tietze, Ann. 449, 100 (1926). (5) Dey, Row, J. Chem. Soc. 125, 560 (1924). (6) Chem. Werke Grenzach A.G., Ger. 386,619, Dec. 13, 1923; Cent. 1924, I 2633 (7) Sen, Chakravarti, J. Indian Chem. Soc. 7, 249-250 (1930). (8) Lovett, Roberts, J. Chem. Soc. 1928, 1977-1978. (9) Delauney, J. pharm. chim. (8) 25, 254-266, 545-560 (1937), (8) 26, 177-216 (1937), Cent. 1938, I 2019.

3:2638 2,6-DICHLORO-3,5-DIMETHYL-PHENOL

(2,6-Dichloro-m-5-xylenol)

Beil. S.N. 529

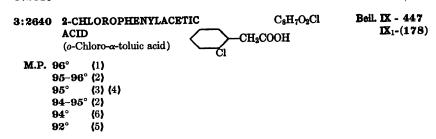
M.P. 95-96° (1) (See also text.)

Cryst. from pet. ether. — Eas. sol. CHCl3, CCl4.

[For prepn. of \bar{C} from 3,5-dimethylphenol (m-5-xylenol) (1:1455) with SO₂Cl₂ (2 moles) in CHCl₃ see (1); note, however, that structure there assigned is 2,4-dichloro-3,5-dimethylphenol (3:2182) q.v.]

The nitration of C has not been reported, and the expected 4-nitro-2,6-dichloro-3,5-dimethylphenol is unknown.

- ---- 2,6-Dichloro-3,5-dimethylphenyl acetate: unreported.
- ---- 2,6-Dichloro-3,5-dimethylphenyl benzoate: unreported.
- 3:2638 (1) Lesser, Gad, Ber. 56, 975 (1923).



284

Colorless ndls. from aq. [For study of ioniz, const. of \bar{C} see (1) (6) (9) (10) (13); for fate in animal body see (3); for studies of bacteriostatic props. see (11) (12).]

[For prepn. of \tilde{C} from o-chlorobenzyl chloride (3:6400) via conversion to o-Cl.C₆H₄.-CH₂MgCl and subsequent carbonation with CO₂ see (2); from o-chlorophenylacetamide (see below) with nitrous acid see (3) (4) (6); from 2-phenyl-4-(2-chlorobenzal)oxazolone-5 (the azlactone from o-chlorobenzaldehyde + N-benzoylglycine + Ac₂O (5)) [Beil. XXVII₁-(298)] on boilg. with aq. NaOH and afterward treated with H₂O₂ see (5).]

[For reactns. of closely related o-Cl.C₆H₄ CH₂.COOMgCl with large excess of isopropyl MgCl or C₆H₅MgBr yielding o-chlorophenylmalonic acid, cryst. from alc., m.p. 139° (7), see (7) (8).]

[For condens. of \ddot{C} with pyrene-3-aldehyde (14) or with N-ethylcarbazole-3-aldehyde (15) in prepn. of intermediates for dyes or pharmaceuticals see indic. refs.]

[Č with PCl₅ yields (3) 2-chlorophenylacetyl chloride, b.p. 119-121° at 12 mm., 118-120° at 10 mm.; this prod. with aminoacetic acid (glycine) in dil. aq. alk. gives (35% yield (3)) o-chlorophenylacetaminoacetic acid (o-chlorophenylaceturic acid), cryst. from hot aq., m.p. 134-135° (3).]

[C converted to Pb salt, latter dried at 110° and distilled, yields (16) 2,2'-dichlorodibenzyl ketone, ndls. from alc., m.p. 102° (16) (oxime, m.p. 112° (16), semicarbazone, m.p. 149° (16)).] [For soly. of many other salts see (4).]

- Methyl 2-chlorophenylacetate: oil, b.p. 125-128° at 23 mm. (4). [From C in MeOH with HCl gas (4); also from o-Cl.C₆H₄.CH₂.MgCl with methyl chloroformate in ether (2); alkaline hydrolysis gives (2) C.]
- Ethyl 2-chlorophenylacetate: oil, b.p. 134° at 23 mm. (4). [From C in EtOH with HCl gas (4).]
- ② 2-Chlorophenylacetamide: lfts. from aq., m.p. 175° (4), 172-175° (3). [From 2-chlorophenylacetonitrile (o-chlorobenzyl cyanide) by partial hydrol. with H₂SO₄ (4) (3); actn. of HNO₂ yields C (see above).]
- ② (2-Chlorophenylacet)anilide: white ndls. from alc., m.p. 138.5° (4). [From C + 1 mole aniline on htg. at 180-190° for ½ hr. (4).]
- ② (2-Chlorophenylacet)-m-chloroanilide: white ndls. from dil. alc., m.p. 154° cor. (17). [From $\ddot{\mathbf{C}} + m$ -chloraniline (1 mole) on htg. at 180–190° for 2 hrs. (17); also from o-chlorobenzyl m-chlorophenyl ketoxime by Beckmann rearr. with PCl₅ in ether (17).]
- ① (2-Chlorophenylacet)-p-toluidide: white ndls. from dil. alc., m.p. 169.5° (4). [From Č on htg. with 1 mole p-toluidine as for the anilide (above) (4).]
- (2-Chlorophenylacet)phenylhydrazide: white lfts. from C₆H₆, m.p. 175° (4). [From C on htg. with 1 mole phenylhydrazine (as above) (4).]

3:2640 (1) Dippy, Williams, J. Chem. Soc. **1934**, 1888–1892. (2) Austin, Johnson, J. Am. Chem. Soc. **54**, 657 (1932). (3) Cerecedo, Sherwin, J. Biol. Chem. **58**, 220–222 (1923/24). (4) Mehner, J. prakt. Chem. (2) **62**, 554–560 (1900). (5) Mauthner, J. prakt. Chem. (2) **95**, 61 (1917). (6)

Betti, Manzoni, Atti accad. Lincei 22, 284-287 (1935); Cent. 1936, I 3665; C.A. 36, 6349 (1936). (7) Ivanov, Spassov, Bull. soc. chim. (4) 49, 22 (1931). (8) Ivanov, Bull. soc. chim. (5) 4, 682-686 (1937). (9) Betti, Lucchi, Atti acad. Lincei 22, 367-370 (1935); Cent. 1936, I 3665; C.A. 36, 6349 (1936). (10) Lucchi, Zymologica 15, 130-134 (1938); Cent. 1939, I 4030; C.A. 34, 7703 (1940). (11) Gross, Degering, Tetrault, Proc. Indiana Acad. Sci. 49, 42-44 (1939); C.A. 35, 5337 (1941). (12) Feasley, Gwynn, Degering, Tetrault, J. Am. Pharm. Assoc. 30, 41-44 (1941); C.A. 35, 3034 (1941). (13) Betti, Lucchi, Mem. accad. sci. ist. Bologna, Classe sci. fis. 6, 37-42 (1939); Cent. 1940, II 2597; C.A. 36, 5470 (1942). (14) I.G., Brit. 469,633, Aug. 26, 1937; Cent. 1938, I 181. (15) I.G., French 807,704, Jan. 20, 1937; Cent. 1937, I 5053. (16) Kenner, Morton, J. Chem. Soc. 1934, 680. (17) Jenkins, J. Am. Chem. Soc. 55, 2898 (1933).

M.P. 96-97° (1)

Ndls. from dil. alc.; insol. aq., sol. hot alc.

[\bar{C} is readily obtd. by spontaneous polymerization of β -chloro-n-butyraldehyde (3:9110).] \bar{C} on htg. with conc. H₂SO₄ not only depolymerizes but also loses HCl yielding (1) crotonaldehyde (1.0150).

 \bar{C} on oxidn. with CrO₃ yields (1) acetic acid (1:1010); with conc. HNO₃ yields β -chloro-n-butyric acid (3:0035).

 \bar{C} on boiling with an aq. suspension of Ag₂O yields (1) silver salt of β -hydroxy-n-butyric acid.

3:2650 (1) Kekulé, Ann. 162, 100-102 (1872).

3:2662 1,1,1-TRICHLORO-2-METHYL-
$$CH_3$$
 $C_4H_7OCl_3$ Beil. I - 382 PROPANOL-2 CH_3 — C — CCl_3 I_{1-} (192) I_{2-} (415) alcohol; acetone chloroform; CH_3 — C — CCl_3 CH_4 — C — CCl_3 CH_5 — C — CCl_3 C — CCl_3 C — CCl_3 C — CCl_3 C — C — CCl_3 C — C — CCl_3

Colorless cryst. with camphoraceous odor; like camphor the cryst. rotate vigorously when placed on clean aq.

 \bar{C} is spar. sol. cold aq. (1 g. \bar{C} dis. in 200 ml. aq. at 15.5°, in 125 ml. aq. at 25° (6), cf. (7) (9)). — \bar{C} is easily sol. hot aq., eas. sol. alc., ether, acetone, AcOH, or CHCl₃.

 \bar{C} is very easily volatile with steam (use in detection of small amts. \bar{C} in aq. soln. (8) (19)). — From hot aq. \bar{C} seps. in ndls. contg. water of hydration: this prod., m.p. 80-82° (5), 80° (6), 80-81° (9) (18) (2), 77° (11), 77.8° (6), 78.8° (6), is often regarded as (5) (18) a hemihydrate; note, however, that its aq. content may vary and the prod. may comprise a solid soln. of aq. in \bar{C} (for extensive study see (1)); in any case distillation of the hydrate

removes the aq. and yields (5) anhydrous $\bar{\mathbb{C}}$ (for conv. of the "hemihydrate" to anhydrous $\bar{\mathbb{C}}$ by use of CaO, CaCl₂, MgCl₂ see (12)); note, however, that anhydrous $\bar{\mathbb{C}}$ on stdg. in air is converted to the "hemihydrate" in less than 30 min. (11). — $\bar{\mathbb{C}}$ readily sublimes even at room temp. and by repeated sublimation yields (18) anhydrous form.

Č has hypnotic, sedative, local anesthetic, and antiseptic characteristics and finds extensive use in medicine and in preservation of biological solns.; it has been used in treatment of nausea and seasickness, e.g., German "Nautissan" or (together with caffeine) as the British "Motherhill's Seasick Remedy" (10).

Č is also employed as a modifier for cellulose acetate (13) (14) (15) (16) or cellulose ethers (17).

[For detn. of C by complete hydrolysis with hot MeOH/KOH and subsequent detn. of chlorine by either volumetric or gravimetric methods see (3) (19).]

[For prepn. of \bar{C} from a setone (1:5400) + CHCl₃ (3:5050) by addn. of dry powdered KOH (0.5 mole) below 0° (5) or 2-3° (4) or KOH in alc. as directed (11) (yields: 25% (11), 23% (5)) (2) (4) see indic. refs.; note that use of NaOH lowers the yield (5) and that Ca(OH)₂ (11), Zn(OH)₂ (5), or Al(OH)₃ (5) yields no \bar{C} ; note also that the crude prod. contains some diacetone alcohol (1:6423) which is best removed by treatment with aq. (11) since otherwise it appears to form with \bar{C} a const.-boilg. mixt.

[For prepn. of C from trichloroacetyl chloride (3:5420) with MeMgI in ether (4) or from ethyl trichloroacetate (3:5950) with MeMgBr in ether (20) see indic. refs]

[\bar{C} with granulated Zn + conc. HCl (in pres. of a little ether) is reduced (21) to terbutyl alc. (1:6140), m.p. 25°, but \bar{C} in 70% alc. warmed with Zn dust for 5 hrs. gives (4% yield (22)) 1,1-dichloro-2-methylpropene-1 (3:5300) + 1-chloro-2-methylpropene-1 (3:7120) + isobutylene (23). — \bar{C} with granulated Zn in boilg. AcOH yields (21) terbutyl acetate (1:3057).]

[\bar{C} with Na/Hg in moist ether (21), or with aq. in s.t. at 180° for 3 hrs. (24), or \bar{C} with aq. alc. KOH (25) undergoes hydrol. of its —CCl₃ group yielding α -hydroxy-isobutyric acid (1:0431), m.p. 79°.]

Anhydrous \ddot{C} in dry ether poured onto a lower layer of colorless fuchsin-aldehyde reagt. (Schiff's soln.) gives a purple color (26), but this behavior is not shown by the "hemi-hydrate." — \ddot{C} also reduces NH₄OH/AgNO₃ soln. slowly in the cold (2).

[C with cold 10% aq. KOH is claimed (27) cf. (29) to yield traces of α -chloroisobutyric acid (3:0235) or carbon monoxide + acetone (28), while \bar{C} with solid KOH gives (27) methacrylic acid [Beil. II-421, II₂-(398)], and \bar{C} in MeOH with alk. or tertiary org. bases, or mineral acids, yields (29) methyl methacrylate [Beil. II₂-(398)]

 \ddot{C} with conc. H_2SO_4 (10 wt. pts.) evolves $CO + CO_2 + HCl$ (25) (26); the CO presumably results from the usual action of H_2SO_4 on some α -hydroxy-isobutyric acid (1:0431) first formed by hydrolysis; for the other reactions see (25).

[\bar{C} with PCl₅ at 100° is claimed (30) (31) (21) to yield both bis- $(\beta,\beta,\beta$ -trichloro-ter-butyl) ether [Beil. I-383, I₁-(193)], b.p. 156° (30), and 1,1,1,2-tetrachloro-2-methylpropane (3:4725), m.p. and b.p. both at 167° (30), but later workers (26) could obtain no reaction at all between \bar{C} and PCl₅. — \bar{C} with PBr₅ at 60° (not above because of dissociation of PBr₅) gives (32) cf. (21) 2,3-dibromo-1,1,1-trichloro-2-methylpropane, b.p. 243° (32).]

 $\bar{\rm C}$ with P₂O₅ in dimethylaniline (1) or quinoline (50) htd. at 200° under ord. press. gives (yield: 30-43% (50), 15% (33)) 1,1,1-trichloro-2-methylpropene-2 (3:5605), b.p. 132°, + 57% yield of its synionic isomer 1,1,3-trichloro-2-methylpropene-1 (3:5025), b.p. 45-46°, accompanied by some α -chloroisobutyric acid (3:0235) cf. (50).

[Various reactions of \bar{C} have been employed in prepn. of pharmaceutical prods.: \bar{C} with adipic anhydride (see text of 1:0775) at 160-180° for 8 hrs. (35), or \bar{C} with adipic acid (1:0775) + SOCl₂ grad. htd. to 150-160° (36), gives β,β,β -trichloro-ter-butyl hydrogen

adipate, cryst. from pet. ether, m.p. 70° (35). — \bar{C} with 5-ethyl-5-phenyl-barbituric acid ("Luminal") does not (37) show evidence of molecular cpd. forms. but forms a eutectic, m.p. 70.4°, contg. 90% \bar{C} . — \bar{C} with 2,3-dimethyl-1-phenylpyrazolone-5 ("Antipyrine") does not (38) form a molecular cpd. but gives a eutectic contg. 60 mole % \bar{C} . — \bar{C} with 2,3-dimethyl-4-dimethylamino-1-phenylpyrazolone-5 ("Pyramidone") gives (39) a molecular cpd., m.p. 61-63°. — \bar{C} with chloral (3:5210) or chloral hydrate (3:1270) gives (40) a molecular cpd., m.p. 65°. — See also above (paragraph 4) and below (under $\bar{\mathbb{Q}}$'s).]

[For reactn. of \bar{C} + AlCl₃ (in Friedel-Crafts sense) with benzene, toluene, and *p*-xylene see (31); for reactn. of \bar{C} with ethyl sodio-acetoacetate see (25).]

[\bar{C} with aniline in alc. KOH gives according to conditions (41) either β (or α)-anilinoiso-butyranilide [Beil. XII-558], cryst. from alc., m.p. 155-157° (41), or β -anilinoisobutyric acid [Beil. XII-497], cryst. from alc., m.p. 185° (41). — For study of reactions of \bar{C} with p-ethoxyaniline (p-phenetidine) + alc. KOH see (42); of \bar{C} with o-phenylenediamine + alc. KOH see (41).]

- Carbylamine test:
 Ö with aniline + aq. alk. on warming gives characteristic odor of phenyl isocyanide (phenyl carbylamine).
- Dodoform reaction: C
 in aq soln. (1/200) treated with aq. NaOH + I₂/KI soln. gives
 yel. ppt. of iodoform (m.p. 119°) with its characteristic odor.
- —— β₁β₂β-Trichloro-ter-butyl acetate: oil, b.p. 191° (21), 190–191° (4), 151–152° at 237 mm. (43). [From C̄ (1 pt.) with Ac₂O (2 pts.) + anhyd. NaOAc (1 pt.) refluxed 2 hrs. (85% yield (43)), or from C̄ (1 mole) with AcCl (1 mole) under reflux (37% yield (21)).] [Note that this ester, although unaffected by 10% aq. NaOH at 100° for 20 min. (dif. from C̄ which is hydrolyzed), is rapidly saponified by boilg. with 3–4 vols. conc. HNO₃ for a few minutes, and upon dilution with aq ppts. C̄ (43).]
- ⑤ β,β,β-Trichloro-ter-butyl benzoate: cryst. from alc. upon addn. of aq, m.p. 34-35° (44) (45). [From C̄ with BzCl at 100° until evoln. of HCl stops (6 hrs.) (44) (45), or from C̄ + benzoic acid (1:0715) in pres. of ZnCl₂ (45).] [Note that this ester on boilg, with conc. HNO₃ is not hydrolyzed (dif. from esters of C̄ with aliphatic acids, e.g., acetate (above)), but nitrated (46) yielding mainly β,β,β-trichloro-ter-butyl m-nitrobenzoate (see below).]
- β,β,β-Trichloro-ter-butyl o-nitrobenzoate: pl. from alc., m.p. 91° (46) (47). [From C with o-nitrobenzoyl chloride on warming (46) (47).]
- $\bigoplus \beta_{,\beta,\beta}$ -Trichloro-ter-butyl p-nitrobenzoate: ndls. from alc., m.p. 145° (46) (47). [From \bar{C} with p-nitrobenzoyl chloride on warming (46) (47).]
- \bigcirc β,β,β -Trichloro-ter-butyl 3,5-dinitrobenzoate: unreported.
- β,β,β-Trichloro-ter-butyl carbamate: pl. from C₆H₆, m.p. 102° (48) (49). [From C with Na in C₆H₆ at room temp. for 4 hrs., followed by conversion of the presumably resultant metal alcoholate with phosgene (3:5000) in toluene to β,β,β-trichloro-ter-butyl chloroformate (not isolated), and reaction of the latter in the C₆H₆/toluene soln. with dry NH₃ gas (55% yield (48)) (49); note that earlier attempts (26) to obtain a metal alcoholate in toluene had led to serious explosions (cf. alkali metals with CHCl₃) (3:5050).]
- $\beta_1\beta_1\beta_2$ -Trichloro-ter-butyl N-phenylcarbamate: ndls. from C_6H_6 , m.p. 118° (48). [From \bar{C} as in the preceding case except that aniline was used in place of NH₃ in last step; yield is poor (48).]
- β,β,β -Trichloro-ter-butyl N-(α -naphthyl)carbamate: unreported.

3:2662 (1) Cameron, Holly, J. Phys. Chem. 2, 322-335 (1898). (2) Willgerodt, Ber. 14, 2451-2458 (1881). (3) Sinton, J. Assoc. Official Agr. Chem. 22, 730-732 (1939); 21, 557-560 (1938). (4) Taffe, Roczniki Farmacçi 2, 99-107 (1923); Cent. 1924, II 304; C.A. 18, 2328 (1924). (5) Sah, Lei, Ma, Sci. Repts. Natl. Tsing Hua Univ. A-1, 209-214 (1932). (6) Perrins, Pharm. J. 128, 265, 271 (1932); Cent. 1932, II 1039; C.A. 26, 4416 (1932). (7) Smelt, Pharm. J. 128, 493 (1932); Cent. 1932, II 3741, C A. 26, 4416 (1932). (8) Aldrich, J. Biol. Chem. 34, 263-267 (1918). (9) Hamilton, Am. J. Pharm. 91, 643-648 (1919). (10) Anon., Chem. Ztg. 52, 611 (1928); Cent. 1928, II 1588.

(11) Fisburn, Watson, J. Am. Pharm. Assoc. 28, 491-493 (1939); Cent. 1939, II 4464; C.A. 33, 9283 (1939). (12) Carpenter (to Givaudan-Delawanna, Inc.), U.S. 1,967,287, July 24, 1934; Cent. 1935, I 2256. (13) Staud, Minsk (to Eastman Kodak Co), U.S. 1,994,597, March 19, 1935; Cent. 1935, II 2605, C.A. 29, 3156 (1935). (14) Kodak-Pathé, Fiench 741,975, Feb. 24, 1933; Cent. 1934, I 2684. (15) Bader, Dickie (to Am. Cellulose and Chem. Mfg. Co.), U.S. 1,536,052, May 5, 1925, Cent. 1925, II 1926. (16) Bader, Dickie (to Brit Cellulose and Mfg. Co.), Brit. 195,849, May 3, 1923; Cent. 1923, IV 343. (17) Dreyfus, Brit. 205,195, Nov. 8, 1923; Cent. 1924, I 716. French 562,056, Nov. 3, 1923; Cent. 1924, I 599. (18) Willgerodt, Ber. 16, 1585 (1883). (19) Vastagh, Pharm. Zentralhalle 78, 497-499 (1937); Cent. 1937, II 3626; C.A. 31, 7595 (1937). (20) Henry, Compt. rend. 142, 131 (1906); Bull. soc. chrm Belg. 20, 152-156 (1906); Cent. 1906, II 1178.

(21) Willgerodt, Durr, J. prakt. Chem. (2) 39, 283-289 (1889).
(22) Bruyne, Davis, Gross, Physik. Z. 33, 720, Note 2 (1932).
(23) Iocitsch, J. Russ. Phys.-Chem. Soc. 30, 920-924 (1889).
(26) Willgerodt, Ber. 15, 2307-2308 (1882).
(25) Willgerodt, Schiff, J. prakt. Chem. (2) 41, 515-526 (1890).
(26) Wolffenstein, Loewy, Bachstez, Ber. 48, 2039-2040 (1915).
(27) Ostropiatow, J. Russ. Phys.-Chem. Soc. 28, 47-56 (1896), Ber. 29, Referate 908-909 (1896).
(28) Bressani, Segre, Gazz. chim. ital. 41, I 673-674 (1911).
(29) Thomas, Oxley (to Celanese, Ltd.), Brit. 505,103, June 1, 1939; Cent. 1939, II 3635, C.A. 33, 7821 (1939).
(30)

Willgerodt, Dürr, Ber. 20, 539-540 (1887).

(31) Willgerodt, Genieser, J. prakt. Chem. (2) 37, 365-371 (1888). (32) Swarts, Bull. soc. chim. Belg. 36, 204-205 (1927). (33) Jacob, Bull. soc. chim. (5) 7, 581-586 (1940), C.A. 36, 3507 (1942). (34) Kirrmann, Jacob, Compt. rend. 203, 1528-1529 (1936). (35) Chem. Fabrik Dr. J. Wiernik & Co., Ger. 576,002, Oct. 16, 1934; Cent. 1935, I 440, C.A. 29, 890 (1935). (36) Chem. Fabrik Dr. J. Wiernik & Co., Ger. 583,852, April 27, 1934, Cent. 1934, II 283. (37) Mossini, Boll. chim. farm. 77, 573-574 (1938); Cent. 1939, I 1530, C.A. 33, 1875 (1939). (38) Rychterowna, Wiadomości Farm. 61, 95-97 (1934); Cent. 1934, II 3647; C.A. 28, 2983 (1934). (39) Callsen (to I.G.), Ger. 442,719, April 6, 1927; Brit. 257,816, Sept. 30, 1926, Cent. 1927, I 2950. (40) Hofmann-La Roche & Co., Ger. 151,188, May 11, 1904, Cent. 1904, I 1506.

(41) Banti, Gazz. chim. ital. 59, 819-824 (1929), Cent. 1930, I 1292, C.A. 24, 1632 (1930), (42) Passerini, Ragni, Gazz. chim. ital. 64, 910-912, 916-917 (1934); Cent. 1935, II 44; C.A. 29, 3322 (1935). (43) Aldrich, J. Am. Chem. Soc. 37, 2720-2723 (1915). (44) Aldrich, J. Am. Chem. Soc. 42, 1502-1507 (1920). (45) Aldrich (to Parke, Davis & Co), U S. 1,443,552, Jan. 30, 1923; Cent. 1923, IV 802. (46) Aldrich, Blanner, J. Am. Chem. Soc. 44, 1759-1762 (1922). (47) Aldrich (to Parke, Davis & Co.), U.S. 1,451,357, April 10, 1923; Cent. 1925, II 1803. (48) Yoder, J. Am. Chem. Soc. 45, 478 (1923). (49) Dox, Yoder (to Parke, Davis & Co.), U.S. 1,658,231, Feb. 7, 1928; Cent. 1928, I 1914. (50) Price, Marshall, J. Org. Chem. 8, 532-535 (1943).

M.P. 97° (1) (2) (3) (5) B.P. 110° at 12 mm. (1) (2) 100° at 12 mm. (5)

Colorless cryst. with camphoraceous odor. — Sublimes; eas. volatile with steam. — Insol. aq.

[For prepn. of C from pentaerythritol (1:5850) with 4 moles SOCl₂ + 4 moles pyridine (3) cf. (4) (5) or with conc. HCl in s.t. at 150° followed by PCl₃ (2) or on htg. the trichlorohydrin (1) with PCl₅ at 150° see indic. refs. (1).] [Note that pentaerythritol (1:5850) on htg. in s.t. with conc. HCl at 120-180° gives (1) a mixt. of mono-, di-, and trichloro-

hydrins: the monochlorohydrin, $(HOCH_2)_3C.CH_2Cl$, m.p. 141°, b.p. 190° at 12 mm., is sol. in aq.; the dichlorohydrin, $(HOCH_2)_2C(CH_2Cl)_2$, m.p. 95°, b.p. 160° at 12 mm., is sol. in aq. $+ C_6H_6$; the trichlorohydrin, $HOCH_2_CE(CH_2Cl)_3$, m.p. 80°, b.p. 136° at 12 mm., is sol. in C_6H_6 + pet. ether (1); note also that pure dichlorohydrin has recently (6) been reported as m.p. 79–80°.]

3:2675 (1) Fecht, Ber. 40, 3888-3889 (1907). (2) Wagner, Dengel, Z. physik. Chem. B-16, 384 (1932). (3) Ballaus, Wagner, Z. physik. Chem. B-45, 173 (1939). (4) Govaert, Hansens, Beyaert, Versl. gewone Vergadering Afdeel. Naturkunde 52, 135-137 (1943); Cent. 1943, II 1358; C.A. 38, 5201 (1944). (5) Mooradian, Cloke, J. Am. Chem. Soc. 67, 943 (1945). (6) Rapoport, J. Am. Chem. Soc. 68, 341 (1946).

3:2690 2-CHLORORESORCINOL OH
$$C_6H_5O_2Cl$$
 Beil. S.N. 554 OH

[See also 4-chlororesorcinol (3:3100) and 5-chlororesorcinol (3:3530).]

Colorless cryst. purified by sublimation.

[For prepn. of $\bar{\mathbb{C}}$ from 2,4-dihydroxy-5-nitrobenzoic acid (5-nitro- β -resorcylic acid) [Beil. X-382, X₁-(179)] via chlorination with SO₂Cl₂ in AcOH to 3-chloro-2,4-hydroxy-5-nitrobenzoic acid, reduction of the latter with SnCl₂/HCl in AcOH to 3-chloro-2,4-dihydroxy-5-aminobenzoic acid, with final removal of the amino group by diazotization and use of alk. SnCl₂, see (1)

[\bar{C} is formed in small amt. together with 4-chlororesorcinol (3:3100) from resorcinol (1:1530) by actn. of N,N-dichlorourea (2).]

[Note that attempts (3) cf. (1) to prepare C from 2-aminoresorcinol [Beil. XIII-782] by diazotization and use of Sandmeyer reactn. have failed because the actn. of nitrous acid yields 4-nitroso-2-diazoresorcinol.]

[The prod., m.p. 89°, b.p. 255-256°, obtained (4) from resorcinol (1:1530) with SO₂Cl₂ in ether may have contained \bar{C} .]

3:2696 (1) Milligan, Hope, J. Am. Chem. Soc. 63, 544 (1941). (2) Likhosherstov, J. Gen. Chem. (U.S.S.R.) 3, 164-171 (1933); Cent. 1934, I 1476; C.A. 28, 1675 (1934). (3) Likhosherstov, Zhabotinskaya, J. Gen. Chem. (U.S.S.R.) 2, 761-769 (1932); Cent. 1933, II 1180; C.A. 27, 2677 (1933). (4) Reinhard, J. prakt. Chem. (2) 17, 322-325 (1878).

M.P. 97-98° (1)

Ndls. from pet. ether. — Eas. sol. ether, C6H6, or CHCl3; spar. sol. alc. or pet. ether; insol. aq.

[For prepn. of C from 2,3,4,6-tetrachlorobenzal (di)chloride (3:6980) by hydrolysis with conc. H₂SO₄ at 96° see {1}.]

Č with NaHSO₃ forms the corresp. addn. cpd.; spar. sol. cold aq. (1); for use in sepn. of Č from 2,3,4,5-tetrachlorobenzaldehyde (3:3140) see (2).

[For use of C in prepn. of dyes of the triphenylmethane series see (3).]

3:2700 (1) Cassella and Co., Ger. 290,209, Feb. 8, 1916; Cent. 1916, I 396-397, not in C.A. (2) Chem. Fabrik Griesheim Elektron, Brit. 251,511, May 27, 1926; Cent. 1926, II 2355; C.A. 21, 1361 (1927) French 603,650, April 20, 1926, Cent. 1926, II 2355, not in C.A. (3) Cassella and Co., Ger. 302,138, Nov. 28, 1917; Cent. 1918, I 250; not in C.A.

3:2705 5-CHLORO-3,4-DIMETHYLPHENOL OH
$$C_8H_9OCl$$
 Beil. VI — VI₁— VI₂—(456)

M.P. 98° (1) (2)

Ndls. from lt. pet. — Volatile with steam.

[For prepn. of Č from 5-chloro-3,4-dimethylaniline (6-chloro-o-4-xylidine) (1) via diazotization and hydrolysis (yield not stated) see (1); from 6-amino-5-chloro-3,4-dimethylphenol (6-chloro-5-amino-o-4-xylenol) (2) via diazotization and elimination of original amino group using Cu₂Cl₂ reaction (unusual) (yield not stated) see (2)]

 \bar{C} with $\bar{C}l_2$ in CHCl₃ gives (1) 2,5,6-truchloro-3,4-dimethylphenol (3:4747), m.p. 182.5°. The nitration of \bar{C} has not been reported, and neither of the two possible mononitro derivs. nor the corresp. dinitro deriv. is known.

Č in alk. soln. couples with benzenediazonium chloride giving (2) the corresp. azo cpd., red ndls. from alc., m.p. 143° (2).

- --- 5-Chloro-3,4-dimethylphenyl acetate: unreported.
- **D** 5-Chloro-3,4-dimethylphenyl benzoate: m.p. 42° (1).

3:2705 (1) Hinkel, J. Chem. Soc. 125, 1853 (1924). (2) Hinkel, Ayling, Bevan, J. Chem. Soc. 1928, 2532.

3:2710 2,3,4,5-TETRACHLOROTOLUENE

Ndls. from MeOH.

[For prepn. of \bar{C} from 3,4,5-trichloro-2-aminotoluene (3) or from 2,4,5-trichloro-3-aminotoluene [Beil. XII-872] (2) (3) via diazotization and use of Cu₂Cl₂ reactn. see indic. refs.; from 3,4,5-trichlorotoluene (3:0580) with Cl₂ in pres. of Al/Hg (2) (3) or with SO₂Cl₂ + AlCl₃ + S (35% yield (1)) see indic. refs.]

[C at b.p. with Cl₂ yields (4) 2,3,4,5-tetrachlorobenzal (di)chloride (3:9397).]

 \bar{C} on nitration with 6 pts. of a mixt. of 2 pts. HNO₃ (D=1.48) + 4 pts. H₂SO₄ (D=1.84) at 105° for ½ hr. (1) yields 2,3,4,5-tetrachloro-6-nitrotoluene, m.p. 159.6° cor. (1), 159° (3).

3:2710 (1) Silberrad, J. Chem. Soc. 127, 2682-2683 (1928). (2) Cohen, Dakin, J. Chem. Soc. 85, 1280, 1285 (1904). (3) Cohen, Dakin, J. Chem. Soc. 89, 1453-1455 (1906). (4) Chem. Fabrik Griesheim-Elektron, Brit. 251,511, May 27, 1926; French 603,650, April 20, 1926; Cent. 1926, II 2355.

[See also 4-chlorophthalic acid (3:4390).]

Cryst. from CCl₄ (5) (4), from Ac₂O (2), from ether, or from alc. (For crystallographic consts. see (2).) — Eas. sol. alc., ether, CHCl₃; less sol. CS₂; spar. sol. lgr.

[For use of \bar{C} with glycerol or ethylene glycol in prepn. of glyptal type resins see (26).] [For prepn. of \bar{C} from 4-chlorophthalic acid (3:4390) by htg. or sublimation (6) (7) (8) (1) (9) or by htg. with AcCl (2) see indic. refs.; from NaH \bar{A} with conc. H₂SO₄ at 100° see (10); from phthalic anhydride (1:0725) with Cl₂ in pres. of Fe or Fe salts at 160-260° see (11) (note that crude \bar{C} obtd. by chlorination methods or from 4-chlorophthalic acid obtd. by chlorination methods may cont. dichlorophthalic anhydrides from which \bar{C} is separable by its greater soly. in toluene (4)); from 4-nitrophthalic anhydride [Beil. XVII-486, XVII₁-(250)] with Cl₂ at 240° see (12)]

[C with Cl₂ in fumg. H₂SO₄ in pres. of I₂ gives (13) mixt contg. much 3,4-dichlorophthalic anhydride (3:3695), m.p. 120-121°, b.p. 329°, and little 4,5-dichlorophthalic anhydride (3:4830), m.p. 187°.]

[\bar{C} with SOCl₂ + ZnCl₂ in s.t. at 240° yields (27) 4-chlorophthalyl (di)chloride [Beil. IX-817], b.p. 275-276° (6)]

[C in MeOH satd. with dry HCl yields (6) dimethyl 4-chlorophthalate, ndls. from lgr., m.p. 38° (5), m.p. 37° (6), b.p. 186–187° at 32 mm. (5); C in EtOH similarly gives (6) diethyl 4-chlorophthalate, b.p. 173–174° at 16 mm. (14), 300–305° (6).

Č fused and treated with dry NH₃ gas (6) or Č htd. with urea (28) yields 4-chlorophthalimide [Beil. XXI-503, XXI₁-(391)], m.p. 210-211° (6) (3). [Ring opening of this prod. with NaOCl yields (9) 3 pts. 4-chloro-2-aminobenzoic acid (4-chloroanthranilic acid) [Beil. XIV-365, XIV₁-(548)], m.p. 235-236° (9), and 1 pt. 5-chloro-2-aminobenzoic acid as "anhydride," m.p. 178-179° (9).] [For use of 4-chlorophthalimide in prepn. of pigments of phthalocyanine type see (28).]

[C fused with aminoacetonitrile hydrochloride or sulfate yields (15) 4-chlorophthalimidoacetamide, ndls. from hot aq., m p. 241° (15); C htd. with methyleneaminoacetonitrile until evoln. of CH₂O ceases yields (15) 4-chlorophthalimidoacetonitrile, ndls. from dil. AcOH, m.p. 146.5° (15); C htd. with glycine yields (15) 4-chlorophthalimidoacetic acid, yel. pl. from hot aq. or dil. alc., m.p. 205° (15).]

[C with 2 moles phenol htd. with ZnCl₂ at 115-130° for 48 hrs. as directed (2) gives 76% yield phenol (di)chlorophthalein, m.p. 214-233°, and prob. a mixt. of isomers; C with resorcinol htd. with trace conc. H₂SO₄ yields (6) a prod. behaving as dichlorofluorescein.

— Note, however, that C with hydroquinone (1:1590) + AlCl₃ + NaCl htd. at 200-220°

(4) or \bar{C} with p-chlorophenol (3:0475) + fumg. $H_2SO_4 + H_3BO_3$ htd. 20 hrs. at 175-195° gives (95% yield (4)) 6-chloro-1,4-dihydroxyanthraquinone (6-chloroquinizarin), tbls. from toluene, m.p. 188° (diacetate, m.p. 213°, dimethyl ether, m.p. 168.5° (4)).]

[C with C6H6 + AlCl3 yields (6) (3) 4-chloro-2-(benzoyl)benzoic acid [Beil. X-750, X₁-(356)], cryst. from xylene, m.p. 180.5° (3), from C₆H₆, m.p. 170° (6) (this on ring closure with conc. H₂SO₄ at 160-170° for 10 min. gives 2-chloroanthraquinone (3:4922), m.p. 204° (3). — \bar{C} with chlorobenzene (3:7903) + AlCl₃ yields (3) (17) 4-chloro-2-(pchlorobenzovl) benzoic acid [Beil. X_1 -(357)], cryst. from xylene, m.p. 195.5° (3) (this on ring closure as above gives (3) 2,6-dichloroanthraquinone [Beil. VII-788, VII₁-(413)], m.p. 278° (3)). — For similar condensations of \tilde{C} + AlCl₃ with p-dichlorobenzene see (3), with bromobenzene see (18), with naphthalene see (25) (19), with toluene see (19) (20), with perylene see (21) (22), with 2,2'-dinaphthyl see (23)]

[For use of C in prepn. of pigments of the phthalocyanine type see (24) (28).]

C on warming with aq. readily hydrolyzes; C on saponification with standard alk. (Sap. Eq. = 91.3) followed by acidification yields 4-chlorophthalic acid (3:4390) q.v.

3:2725 (1) Miersch, Ber. 25, 2116 (1892). (2) Blicke, Smith, J. Am. Chem. Soc. 51, 1871–1872, 1874 (1929). (3) Egerer, Meyer, Monatsh. 34, 81–83, 86, 90 (1913). (4) Waldmann, J. prakt. Chem. (2) 126, 254–255 (1930). (5) Ayling, J. Chem. Soc. 1929, 255 (6) Rée, Ann. 233, 236– (6) Rée. Ann. 233, 236-240 (1886). (7) Alén, Bull soc. chim. (2) 36, 434 (1881). (8) Claus, Dehne, Ber. 15, 320 (1882). (9) Moore, Marrack, Proud, J. Chem. Soc. 119, 1788-1789 (1921). (10) Scottish Dyes, Ltd., Bangham, Thomas, Brit. 347,666, May 28, 1931; Cent. 1931, II 1195.

(11) Dvornikoff (to Monsanto Chem. Co.), U.S. 2,028,383, Jan. 21, 1936; Cent. 1936, I 2830; C.A. 30, 1394 (1936). (12) Imperial Chem. Ind., Ltd., Shaw, Thomas, Brit. 357,165, Oct. 15, 1931; Cent. 1931, II 3663. (13) Villiger, Ber. 42, 3594 (1909). (14) von Braun, Larbig, Kredel, Ber. 56, 2338 (1923). (15) Stephen, J. Chem. Soc. 1931, 871-873. (16) Scottish Dyes, Ltd., Bangham, Hooley, Thomas, Brit. 339,589, Jan. 8, 1931, Cent. 1932, I 2095, C.A. 25, 2859 (1931). (17) Muller (to I.G.), Ger. 495,447, April 7, 1930; Cent. 1931, I 1675. (18) Waldmann, J. prakt. Chem. (2) 126, 74-75 (1930). (19) B.A S.F., Ger. 234,917, May 26, 1911; Cent. 1911, II 114. (20) B.A.S.F., Ger. 211,927, July 14, 1909; Cent. 1909, II 396.

(21) Zinke, Gorbach, Shimka, Monatsh. 48, 593-598 (1927). (22) Nawiasky, Grosskinsky (to I.G.), Ger. 642,650, March 11, 1937; Cent. 1937, I 5057. (23) Neresheimer, Kacer (to I.G.). Ger. 565,425, Nov. 30, 1932; Cent. 1933, I 1358. (24) Imperial Chem. Ind., Ltd., French 808,845, Feb. 16, 1937; Brit. 464,126, April 12, 1937; Cent. 1937, II 3820; C.A. 31, 6255 (1937). (25) Schwenk, Waldmann, J. prakt. Chem. (2) 128, 320-326 (1930). (26) Kogan, Ponomarenko, Org. Chem. Ind. (U.S.S.R.) 7, 382-385 (1940); C.A. 35, 4118 (1941). (17) Kyrides (to Monsanto Chem. Co.), U.S. 1,951,364, March 20, 1934; Cent. 1934, II 333. (28) Imperial Chem. Ind., Ltd., Heilbron, Irving, Linstead, Thorpe, Brit. 410,814, June 21, 1934; French 763,993, May 12, 1934; Cent. 1935, I 1305.

(10) [See also a-chloroisocrotonic acid (3:1615).]

96°

Ndls. from aq. (4) (20) or pet. eth. (8). — \bar{C} is sol. in 47.1 pts. aq. at 19° (13); 100 pts. satd. aq. soln. at 12.5° cont. 1.97 pts. \bar{C} (9). — \bar{C} is less (9) (5) volatile with steam than the isomeric α -chloroisocrotonic acid (3:1615). — Eas. sol. alc. or ether (10). — Readily sublimes (10). — Note that the m.p. of mixts. of \bar{C} with β -chlorocrotonic acid (3:2625) is depressed far below either (4).

[For thermal anal. of system $\tilde{C}+2,6$ -dimethylpyrone see (12); with conc. H_2SO_4 see (14).]

Preparation. For prepn. of \bar{C} from α,α,β -trichloro-n-butyric acid (3:1280) [itself readily obtd. from α,α,β -trichloro-n-butyraldehyde (butylchloral) (3:5910) by oxidn. with HNO₃] by removal of two halogen atoms with Zn dust + aq (83% yield on initial butylchloral hydrate (3)) (10), or with Zn + HCl (15), see indic. refs.; from the higher-melting form of α,β -dichloro-n-butyric acid ("isocrotonic acid dichloride") (3:1903) by splitting out HCl with alc. KOH see (17) (18); from the lower-melting form of α,β -dichloro-n-butyric acid ("crotonic acid dichloride") (3:1375) by splitting out HCl with excess aq. NaOH (5) (18) or with pyridine at 100° for 3 hrs. (4) or with 1% Am₃N refluxed at 160-180° for 16 hrs. (85% yield (28)) (note, however, that with NaOH the yield is low and much of the isomeric α-chloroisocrotonic acid (3:1615) is formed); from α-chloro-β-hydroxy-n-butyric acid [Beil., III-309, 310] by elimination of H₂O with warm 80% H₂SO₄ see (17).]

[For prepn. of \bar{C} from α,α,β -trichloro-n-butyraldehyde (butylchloral) (3:5910) by simultaneous oxidn. and elimination of HCl with aq. K₄Fe(CN)₆ (yield 44.3% (3)) (19) see indic. refs.]

[For form. of \bar{C} from crotonic acid (1:0425) by actn. of Cl_2 and distillation of product see (20); from α -chloroisocrotonic acid (3:1615) by htg. in s.t. at 150–160° for 12 hrs. (21), with pyridine HCl in pyridine 7 days at room temp. (4), or to small extent even on steam distn. (22) see indic. refs.; from the methyl, ethyl, or n-propyl esters of α -chloro- α -vinylacetic acid or from α -chloro- α -vinylacetonitrile (or amide) on hydrolysis with alkali (note shift of double bond from β , γ to α , β position) see (11); from ethyl α -chlorocrotonate (3:8523) by hydrolysis with conc. HCl see (23).]

Chemical behavior. [C on reduction with Na/Hg is dehalogenated yielding (10) crotonic acid (1:0425), m.p. 72°; note, however, that C does not readily absorb H₂ even in pres. of Pt black (11).]

 \bar{C} with Cl_2 in CS_2 adds 1 mole halogen yielding (24) α, α, β -trichloro-n-butyric acid (3:1280), m.p. 59.5-60°. — \bar{C} adds Br_2 readily (15) yielding (10) α, β -dibromo- α -chloro-n-butyric acid [Beil. II-286], m.p. 92° (10).

 \bar{C} with fumg. HCl in s.t. at 100° for 5 hrs. adds 1 HCl to double bond yielding (17) (18) the higher-melting α,β -dichloro-n-butyric acid (3:1903), m.p. 78°.

 $\bar{\rm C}$ behaves as a monobasic acid; dissociation const. at 25° is 7.2 \times 10⁻⁴ (25); Neut. Eq. 120.5.

[Salts: NH₄ \bar{A} , lfts. or hexag. tbls., sublimable (10); Na \bar{A} (10); K \bar{A} , lfts. from alc. in which it is spar. sol. (1 pt. K \bar{A} in 736.4 pts. 99% alc. at 16.5° (5)) (use in sepn. of \bar{C} from the isomeric α -chloroisocrotonic acid (3:1615) (4) (18) (17); Ag \bar{A} , ndls., spar. sol. aq. (10) (17); Ca \bar{A}_2 , pr. spar. sol. cold aq. (10) (17); Ba \bar{A}_2 , more sol. aq. than Ca \bar{A}_2 (10) (17); Cu \bar{A}_2 , blue ndls., converted by warm aq. to a basic salt (10); Pb \bar{A}_2 -H₂O (10).]

[\bar{C} with NaOEt is unchanged even at 215° (20), but \bar{C} with 10 N KOH at 190–200° decomposes with form. of AcOH (1:1010), oxalic acid (1:0445), CO₂ + H₂ + other prods. (20).]

[For study of rate of reactn. of C with K₃AsO₃ see (2).]

[\tilde{C} with PCl_5 on warming gives (10) α -chlorocrotonoyl chloride, liq. with sharp odor, b.p. 142° (10).]

— Methyl α-chlorocrotonate: b.p. 161-162° (see 3:5870). [For study of rate of esterification of C with MeOH see (26) (27).]

294

- Ethyl α -chlorocrotonate: b.p. 176° (see 3:8523).
- Φ α-Chlorocrotonamide: lfts., spar. sol. cold aq., eas. sol. alc.; m.p. 113.5° (8), 111.5-112.5° (11), 107° (10). [From α-chlorocrotonyl chloride (above) (10) or ethyl α-chlorocrotonate (11) with conc. aq. NH₄OH; also by other routes such as from α,α,β-trichloro-n-butyraldehyde (3:5910) with NH₄OH + KCN (93% yield (8)).]
- ---- α-Chlorocrotonanilide: unreported.
- ---- α -Chlorocroton- α -naphthalide: unreported.

3:2760 (1) Stelling, Z. physik. Chem. B-24, 423 (1934).
 (2) Backer, van Oosten, Rec. trav. chim. 59, 57-58 (1940).
 (3) Roberts, J. Chem. Soc. 1938, 779.
 (4) Pfeiffer, Ber. 43, 3041-3042.
 (5) Wislicenus, Ann. 248, 288, 293, 295 (1888).
 (6) Wislicenus, Ber. 20, 1008-1010 (1887).
 (7) von Auwers, Ber. 56, 724 (1923).
 (8) Chattaway, Irving, J. Chem. Soc. 1929, 1046.
 (9) Kahlbaum, Ber. 12, 2338-2339 (1879).
 (10) Sainow, Ann. 164, 94-105 (1872).

(11) Rambaud, Bull. soc. chim. (5) 1, 1352-1355 (1934). (12) Kendall, J. Am. Chem. Soc. 38, 1232 (1914). (13) Michael, Browne, Am. Chem. J. 9, 284 (1887). (14) Kendall, Carpenter, J. Am. Chem. Soc. 36, 2505 (1914). (15) Kramer, Pinner, Ann. 158, 51 (1871). (16) Pinner, Ber. 8, 1563 (1875). (17) Melikoff, Ann. 234, 200, 203-204 (1886). (18) Michael, Schulthess, J. prakt. Chem. (2) 46, 256, 260-262 (1892). (19) Wallach, Ber. 10, 1530 (1877). (20) Friedrich, Ann. 219, 351-356, 371-373 (1883).

(21) Michael, Pendleton, J. prakt. Chem. (2) 38, 4 (1888). (22) Wislicenus, Ann. 248, 337 (1888). (23) Wallach, Ann. 173, 301 (1874). (24) Valentin, Ber. 28, 2661-2662 (1895). (25) Ostwald, Z. physik. Chem. 3, 244 (1889). (26) Sudborough, Roberts, J. Chem. Soc. 87, 1845-1846 (1905). (27) Michael, Oechslin, Ber. 42, 322 (1909). (28) Long (to Wingfoot Corp.), U.S. 2,376,067, May 15, 1945, C.A. 39, 3550 (1945).

3:2800 5-CHLORO-2-HYDROXY- Cl $C_7H_5O_2Cl$ Beil. VIII_-53 CHO CHO OH

Colorless tbls. from alc.; long flat ndls. from C_6H_6 (1). — Insol. aq.; sol. alc., ether. — Sol. in alk. with yel. color.

[For prepn. of \bar{C} from salicylaldehyde (1:0205) by chlorination with Cl₂ (10) (11) in AcOH (2), or with SO₂Cl₂ (1) (8), see indicated refs.; from 5-chloro-2-hydroxybenzyl alcohol by oxidn. with $K_2Cr_2O_7 + H_2SO_4$ see (6); from 5-chlorosalicylic acid (3:4705) by reduction (poor yield) see (3); from p-chlorophenol (3:0475) via Reimer-Tiemann reactn. (4) or via hexamethylenetetramine (7) see indicated refs.]

C on reduction with Raney Ni (Al/Ni alloy) in 10% aq. alk. at 90° gives (75% yield (16)) o-cresol (1:1400).

Č on oxidn. with CrO₃ gives (in poor yield (1)) 5-chlorosalicylic ac. (3:4705), m.p. 172° (1).

 \tilde{C} yields with satd. aq. NaHSO₃ soln. a cpd. \tilde{C} .NaHSO₃ (12) (use in purification of \tilde{C} (4)). — \tilde{C} with NH₃ gives 5,5',5"-trichloro-hydrosalicylamide, yel. scales from ether, m.p. unrecorded (10). — \tilde{C} in alk. gives on oxidn. with H₂O₂ good yield (13) of 4-chloropyrocatechol (3:2470).

Č in AcOH treated with conc. HNO₃ as directed (14) gives 5-chloro-3(?)-nitrosalicylaldehyde, yel. ndls. from et. pet., m.p. 105-107° (14).

Č htd. with chloroacetic ac. (3:1370) and slightly more than 2 moles KOH in s.t. at 160° yields (15) 4-chlorocoumarone (oil, volatile with steam) and 5-chloro-2-formyl-phenoxyacetic ac. (not volatile with steam from alk. soln.), cryst. from aq., m.p. 169-170° (15).

- © 5-Chlorosalicylaldoxime: ndls. from aq., m.p. 128° (15) (7); 123-124° (9); 122°. (11) (6) [use in inorganic analysis (9)].
- 5-Chlorosalicylaldehyde phenylhydrazone [Beil. XV-189]: m.p. 150-152° (15), 148° (11).
- **5-Chlorosalicylaldehyde** *p*-nitrophenylhydrazone: unreported.
- --- 5-Chlorosalicylaldehyde 2,4-dinitrophenylhydrazone: unreported.
- D 5-Chlorosalicylaldehyde semicarbazone: ndls. from AcOII, m.p. 286-287° (11) (4).
- 3:2800 (1) Durrans, J. Chem. Soc. 123, 1426 (1923). (2) Bradley, Dains, Am. Chem. J. 14, 295 (1892). (3) Weil, Traun, Marcel, Ber. 55, 2665 (1922). (4) Sen, Ray, J. Indian Chem. Soc. 9, 176 (1932). (5) Hanus, J. prakt. Chem. 158, 265 (1941). (6) Visser, Arch. Pharm. 235, 547 (1897). (7) Duff, J. Chem. Soc. 1941, 547-550. (8) Peratoner, Gazz. chim ital. 28, I, 235 (1898). (9) Flagg, Furman, Ind. Eng. Chem., Anal. Ed. 12, 529-531 (1940). (10) Piria, Ann. 30, 169 (1839).
- (11) Biltz, Stepf, Ber. 37, 4024 (1904). (12) Bertagnini, Ann. 85, 196 (1853). (13) Dakin, Am. Chem. J. 42, 488 (1909). (14) Lovett, Roberts, J. Chem. Soc. 1928, 1978. (15) Stoermer, Ann. 312, 325-326 (1900). (16) Schwenk, Papa, Whitman, Ginsberg, J. Org. Chem. 9, 1-8 (1944).

3:2825 p-XYLYLENE DICHLORIDE
$$C_8H_8Cl_2$$
 Beil. V - 384 $(\omega,\omega'\text{-Dichloro-}p\text{-xylene})$ $ClCH_2$ — CH_2Cl V_1 -(186) V_2 -(300) M.P. 100° (1) (2) B.P. 240–245° dec. (2) 98–99° (3) 135° at 16 mm. (1) 98–100° (6)

Lfts. or tbls (from alc.). — Volatile with steam.

[For prepn. from p-xylylene glycol by distn. with conc. HCl see (4); for prepn. from benzyl chloride (3:8535) + trioxymethylene + ZnCl₂ see (1) (42% yield (6)); for prepn. of \bar{C} from p-xylene (1:7415) with SO₂Cl₂ + Br₂O₂ refluxed in sunlight 4 hrs. (58% yield) see (6).]

 \bar{C} on htg. with 30 pts. aq. in s.t. at 170–180° yields (1) (4) p-xylylene glycol [Beil. VI-919], ndls., very sol. aq., alc. or ether, mp 112–113°.

C boiled with Pb(NO₃)₂ soln. yields (5) terephthalaldehyde [Beil. VII-675], fine ndls. from boilg. aq., m.p. 115°.

 \bar{C} htd. with benzyl alc. (1:6480) + KOH gives good yield (1) of p-xylylene glycol dibenzyl ether, cryst. from alc., m.p. 67° (1).

3:2825 (1) Quelet, Bull. soc. chim. (4) 53, 222-229 (1934). (2) Lauth, Grimaux, Bull. soc. chim. (2) 7, 235 (1867); Ann. 145, 117-118 (1868). (3) Wishcenus, Penndorf, Ber. 43, 1838 (1910). (4) Grimaux, Ann. 155, 339-340 (1870). (5) Grimaux, Compt. rend. 83, 825 (1876). (6) Kulka, Can. J. Research 23-B, 106-110 (1945).

95-96°

[See also 2,3-dichlorohydroquinone (3:4220).]

(4)

Yel. ndls. from aq. (2) or alc. (1). — C has characteristic quinone odor.

[For prepn. of \tilde{C} from 2,3-dichlorohydroquinone (3:4220) by oxidn. with MnO_2+ dil. H_2SO_4 (yields: 88% (1), 60% (3)) (4), or with $CrO_3/AcOH$ (2) see indic. refs.; for formn. of \tilde{C} from p-benzoquinone (1:9025) in HCl or H_3PO_4 with Cl_2 see (6).]

[For study of oxidn.-reductn. potential of system $\bar{C} + 2,3$ -dichlorohydroquinone (3:4220) see (1) (5).]

[C with butadiene-1,3 gives an adduct which upon oxidn. yields (7) 2,3-dichloronaphthoquinone-1,4 (3:4857); similarly C with 2,3-dimethylbutadiene-1,3 gives an adduct which upon oxidn. yields (7) 2,3-dichloro-6,7-dimethylnaphthoquinone-1,4.]

[For use of C as accelerator for vulcanization of rubber see (8).]

[\bar{C} in alc. with p-nitrosodimethylaniline gives (60% yield (9)) corresp. nitrone; for condens. of \bar{C} with other nitroso cpds. and use of prods. as dye intermediates see (10).]

[Č in CHCl₃ with Cl₂ is not attacked at low temps., but at ord. temp. yields (4) tetra-chloro-p-benzoquinone (chloranil) (3:4978).]

 \bar{C} on reductn. (presumably with SO_2+H_2O) yields 2,3-dichlorohydroquinone (3:4220) q.v.

3:2855 (1) Conant, Fieser, J. Am. Chem. Soc. 45, 2204-2205 (1923). (2) Eckert, Ender, J. prakt. Chem. (2) 104, 82 (1922). (3) Peratoner, Geneo, Gazz. chim. ital. 24, II 375-396 (1894). (4) Oliveri-Tortorici, Gazz. chim. ital. 27, II 584-585 (1897). (5) Kvalnes, J. Am. Chem. Soc. 56, 668-669 (1934). (6) Chelintsev. Compt. rend. acad. sci. (U.S.S.R.) 14, 289-291 (1937); Cent. 1937, II 381; C.A. 31, 7350 (1937). (7) I.G., Brit. 324,661, Feb. 27, 1930; French 677,296, March 6, 1930; French 677,781, March 14, 1930; Cent. 1930, II 810. (8) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; Cent. 1933, I 3133. (9) Gündel, Pummerer, Ann. 529, 31 (1937). (10) Gündel (to I.G.), Ger. 563,968, Nov. 11, 1932; Cent. 1933, II 619.

3:2885 3,4,5-TRICHLOROPHENOL OH C₆H₂OCl₃ Beil. VI — VI₁— VI₂-(181)

Ndls. from lgr. — Volatile with steam. — Ionization const. at 25° is 4.5×10^{-9} (4); \bar{C} is too weakly acidic to be titrated (1) although sol. in alk.

[For prepn. from 3,4,5-trichloroaniline via diazo react. (51% yield) see (1) (2); by cleavage of 3,4,5-trichloroanisole see (3).]

Č treated with large excess Br₂ yields 2,6-dibromo-3,4,5-trichlorophenol, ndls. from AcOH, m.p. 180° (3).

The methyl ether of C, 3,4,5-trichloroanisole, prepared indirectly, has m.p. 63° (3).

3,4,5-Trichlorophenyl benzoate: from Č + BzCl + 20% NaOH; ndls. from alc., m.p. 120° (3).

3:2885 (1) Tiessens, Rec. trav. chim. 50, 113 (1931). (2) Herzberg, Scharfenberg, Ger. 367,362, Jan. 20, 1923; Cent. 1923, II 1254. (3) Kohn, Kramer, Monatsh. 49, 163-165 (1928). (4) Tiessens, Rec. trav. chim. 48, 1066-1068 (1929).

3:2910 4,5-DICHLORO-2-METHYLPHENOL (4,5-Dichloro-o-cresol)

OH C₇H₆OCl₂

Beil. VI —
VI₁-(174)
VI₂-(333)

M.P. 101° (1)

Ndls. from pet. ether; spar. sol. pet. ether, eas. sol. alc., AcOH, C6H6.

[For prepn. of C from 4-chloro-2-methylphenol (3:0780) with Cl₂ in CHCl₃ see (1).]

 \tilde{C} in 2 pts. ice-cold HNO₃ (D=1.48) stood for 12 hrs. gives (75% yield (1)) a prod. of compn. $C_7H_6O_8N_3Cl_2$, white ndls. from dry ether by addn. of pet. ether, m.p. 110° dec. (1).

Č in AcOH on mononitration yields (1) 4,5-dichloro-6-nitro-2-methylphenol [Beil. VI₁-(179)], yel. ndls. from pet. ether, m.p. 69° (1).

\$\text{\text{\$\text{\$\delta}\$}}\$ 4,5-Dichloro-2-methylphenyl benzoate: ndls. from \$\text{\$\text{\$C\$}\$}\$ from \$\text{\$\text{\$C\$}\$}\$ in alk. soln. on shaking with benzoyl chloride (1).]

3:2910 (1) Zincke, Ann. 417, 207, 231-233 (1918).

3:2935 2,3-DICHLORONAPHTHOL-1 OH $C_{10}H_6OCl_2$ Beil. VI - 612 $VI_{1} VI_{2}-$

M.P. 101° (1)

Subl. in ndls.; spar. sol. cold aq., mod. sol. hot aq.; eas. sol. alc., ether, AcOH, CHCl3, C_6H_6 .

[For prepn. from sodium 1-naphtholsulfonate-2 by htg. with PCl₅ at 100-120° see (1).]

C dis. in hot Na₂CO₃ yielding sol. Na salt.

Č htd. with PCl₅ at 130-140° yields 1,2,3-trichloronaphthalene (3:2125), colorless ndls. from alc., m.p. 90° (1).

 \bar{C} on oxidn. in s.t. at 200° with dil. HNO₃ (D=1.15) yields (1) phthalic ac. (1:0820), converted in m.p. tube to phthalic anhydride (1:0725), m.p. 128° (1).

Č on oxidn. with CrO₃ in AcOH or dil. H₂SO₄ gives (although in poor yield (1)) 2,3-dichloronaphthoquinone-1,4 (3:4857), gold-yel. ndls. (from alc.), m.p. 190°.

3:2935 (1) Claus, Knyrim, Ber. 18, 2926-2929 (1885).

3:2965 8-CHLORONAPHTHOL-2

Ndls. from lgr.; very eas. sol. alc., ether, AcOH, C₆H₆, CHCl₃; spar. sol. pet. ether. — Volatile with steam. — \bar{C} depresses m.p. of 6-chloronaphthol-2 (3:3500) to 79-88° (5).

[For prepn. of \bar{C} from sodium 2-hydroxynaphthalenesulfonate-8 [Beil. XI-286, XI₁-(67)] with 2 moles PCl₅ at 150–160° see (1) (note that some 1,7-(2,8)dichloronaphthalene (3:1385) is also formed and that its proportion increases with more PCl₅ or at higher temps. (1)); from 8-aminonaphthol-2 [Beil. XIII-685] via diazotization and use of Cu₂Cl₂ reactn. see (2); for formn. of \bar{C} (20% yield (3)) from β -naphthol (1:1540) by treatment with soln. of Na₂CO₃ + Cl₂ see (3) (note that 30% of 2,2'-dhydroxybinaphthyl-1,1' [Beil. VI-1051, VI₁-(519)] together with a tar is also formed (3)).]

- [C (2 pts.) with benzaldehyde (1 pt.) with 7 pts. HBr/AcOH soln. stood for 24 hrs. gives (75% yield (2)) meso-phenyl-dichlorodibenzoxanthane, colorless ndls. from acetone, m.p. 213-214.5° (2).]
- [\bar{C} (as sodium salt) treated with CO_2 under press. at elevated temp. as directed gives (4) 8-chloro-2-hydroxynaphthoic acid-3, pale yel. ndls. from hot C_6H_6 , m.p. 250° (4).]
 - 8-Chloro-2-naphthyl m-nitrobenzoate: citron-yel. ndls. from hot C₆H₆ on addn. of
 4 vols. hot alc., m.p. 176° ⟨5⟩. [From C̄ in warm dil. aq. NaOH on shaking with
 m-nitrobenzoyl chloride ⟨5⟩.]

3:2965 (1) Claus, Volz, Ber. 18, 3157-3158 (1885). (2) Dilthey, Quint, Heinen, J. prakt. Chem. (2) 152, 73-75 (1939). (3) Tishchenko, J. Russ. Phys.-Chem. Soc. 60, 153-162 (1928); Cent. 1928, II 767; C.A. 22, 3397 (1928). (4) Lange, Luce, Jacobs (to I.G.), Ger. 564,128; Nov. 14, 1932; Cent. 1933, II 446. (5) Ruggli, Knupp, Metz, Zimmerman, Helv. Chem. Acta 12, 1050 (1929).

3:2990 p-CHLOROPHENACYL CHLORIDE
$$C_8H_6OCl_2$$
 Beil. VII - 282 (Chloromethyl p-chlorophenyl ketone) Cl. CO.CH₂Cl VII₁-(152)

Ndls. (from alc.).

[For prepn. from p-chloroacetophenone (3:6735) by chlorination in CS_2 see (1); from chloroacetyl chloride (3:5235) + chlorobenzene (3:7903) + CS_2 + AlCl₃ see (2).]

C on oxidn. with alk. KMnO₄ yields p-chlorobenzoic ac. (3:4940).

C on treatment with Br₂ gives (3) ω-bromo-p-ω-dichloroacetophenone, cryst. from alc., m.p. 83-83.5° (3). — C with KCN yields (4) p-chlorobenzoylacetonitrile, m.p. 129.5-130° (4). — C with KSCN yields (4) p-chlorophenacyl thiocyanate, m.p. 138.6-139.2° (4). — C with Na₂S at 60° gives (5) bis-(p-chlorophenacyl) sulfide, m.p. 121-121.6° (5).

 \bar{C} in MeOH treated with NH₂OH.HCl yields (6) corresponding oxime, chloromethyl p-chlorophenyl ketoxime, m.p. 100.5-101° (6). [Note that although this deriv. has m.p. too similar to that of original \bar{C} to be used as identification itself, upon htg. at 100° with conc. H₂SO₄ and pouring into aq. it is converted by Beckmann rearr. to chloroaceto-p-chloroanilide [Beil. XII-612], m.p. 168° (6), ndls. from alc., m.p. 169° (7).]

- C (1 mole) in alc. gradually added to phenylhydrazine (2 moles) in alc. with cooling ppts. (8) 1-phenyl-3-chlorophenyl-Δ²-diazene-1,2, yel. ndls. from alc., m.p. 164-164.5° (8).
- 3:2990 (1) Gautier, Ann. chim. (6) 14, 395-396 (1888). (2) Collet, Compt. rend. 125, 718 (1897).
 (3) Rabcewicz-Zubkowski, Roczniki Chem. 9, 532-537 (1929); C.A. 24, 92 (1930). (4) Rabcewicz-Zubkowski, Kaflinska, Roczniki Chem. 10, 541-569 (1930); C.A. 25, 505 (1931). (5) Chrzaszczewska, Chwalinski, Roczniki Chem. 7, 67-73 (1927), Cent. 1927, II 415; C.A. 22, 1339 (1928). (6) Collet, Bull. soc. chim. (3) 27, 540 (1902). (7) Beckurts, Frerichs, Arch. Pharm. 253, 241 (1915). (8) Bodforss, Ber. 52, 1762, 1772-1773 (1919).

CHAPTER VIII

DIVISION A. SOLIDS

(3:3000-3:3499)

3:3005 5,6-DICHLORO-3,4-DIMETHYLPHENOL

(5,6-Dichloro-o-4-xylenol)

CI CH₃

C₈H₈OCl₂ Beil. S.N. **529**

M.P. 102.5° (1) 102° (2)

Cryst. from lt. pet. - Very sol. most organic solvents. - Volatile with steam.

[For prepn. of \bar{C} from 5,6-dichloro-3,4-dimethylaniline (5,6-dichloro-o-4-xylidine) (3) via diazotization and hydrolysis (yield not stated) see (1); for formn. of \bar{C} from 4,5,6-trichloro-1,1-dimethylcyclohexen-4-one-3 with conc. H_2SO_4 at $110-120^\circ$ (yield not stated) see (2).]

 \bar{C} with Cl_2 in lt. pet. readily gives (2) 2,5,6-trichloro-3,4-dimethylphenol (3:4747), m.p. 182°.

The nitration of C has not been reported, and the expected 2-nitro-5,6-dichloro-3,4-dimethylphenol is unknown.

- —— 5,6-Dichloro-3,4-dimethylphenyl acetate: unreported.
- **D** 5.6-Dichloro-3.4-dimethylphenyl benzoate: m.p. 97.5° (1), 94° (2).

3:3005 (1) Hinkel, Ayling, Bevan, J. Chem. Soc. 1928, 2532-2533. (2) Hinkel, J. Chem. Soc. 125, 1851 (1924). (3) Hinkel, Ayling, Bevan, J. Chem. Soc. 1928, 1877.

3:3015 1,3,5-TRICHLORONAPHTHALENE

Cl C₁₀H_sCl₃ Beil. V - 545 V₁-(263) V₂-(446)

M.P. 103° (1) (2) (4) 102-103° (3) 94° (8)

[For prepn. of \tilde{C} from 1,3-dichloronaphthalenesulfonyl chloride-5 [Beil. XI-163] (4) (5), from 1,5-dichloronaphthalenesulfonyl chloride-3 [Beil. XI-182] (1), from 1-chloron-5-nitronaphthalenesulfonyl chloride-3 [Beil. XI-182] (6), or from 1-chloronaphthalene-3,5-bis-(sulfonyl chloride) [Beil. XI-215] (7), each with PCl₅ as directed, see indic. refs.; from 1,7-dichloronaphthylamine-3 (8) via diazotization and use of Cu₂Cl₂ reactn. see (8); for formn. of \tilde{C} (together with other products) from 1-nitronaphthalene [Beil. V-553, V₁-(264)] with Cl₂(2) in pres. of I₂ + FeCl₃ (3) see indic. refs.]

[Č treated with ClSO₂H in CS₂ and reactn. prod. conv. to K salt as directed (1) yields potassium 1,3,5-trichloronaphthalenesulfonate-7 (corresp. sulfonyl chloride, m.p. 152° (1)).]

3:3015 (1) Turner, Wynne, J. Chem. Soc. 1941, 247, 253. (2) Atterberg, Ber. 9, 317 (1878). (3) Buffle, Corbas, Arch. sci. phys. nat. 14, 149-158 (1932); Cent. 1932, II 3394. (4) Widman, Ber. 12, 2230 (1879). (5) Armstrong, Wynne, Chem. News 61, 274 (1890). (6) Cleve, Chem. Ztg. 17, 758 (1893). (7) Armstrong, Wynne, Chem. News 62, 162 (1890). (8) Friedländer, Karamessinis, Schenk, Ber. 55, 48-49 (1922).

3:3045 4-CHLORONAPHTHOL-2

C₁₀H₇OCl Beil. S.N. 538

Ndls. from lgr. or 30% aq. alc.

[For prepn. of C from 1,4-dichloronaphthol-2 (3:3840) by partial reduction with SnCl₂ in AcOH/HCl at 100° in s.t. for 8 hrs. (74% yield (2)) (1) see indic. refs.; from 4-chloronaphthol-2-sulfonic acid-1 (2) (see also under 3:3840) by hydrolysis of the sulfonic acid group (91% yield) see (2); from 4-chloronaphthalene-1,2-diazo-oxide (itself obtd. in 95% yield (3) from 4-chloro-2-nitronaphthylamine-1 with HNO₂) on boilg. with Al powder in EtOH for 19 hrs. (84% yield (4)) or (less advantageously) with Na₂SnO₂ (4) see indic. refs.] NaĀ is spar. sol. in cold aq. 10% NaOH (4).

[C with alc. NaOH + CHCl₃ (3:5050) undergoes Reimer-Tiemann reaction giving (but in very small yield (2)) 4-chloro-2-hydroxynaphthaldehyde-1, m.p. 118° (2).]

 \bar{C} (in alk. soln.) with diazotized aniline gives (4) 4-chloro-1-benzeneazonaphthol-2, or -red ndls. from acetone, or crimson ndls. from chlorobenzene, m.p. 165° (4) (note that after fusion and resolidification this prod. has m.p. 151° but after a second resolidification (at about 155°) remelts on slow htg. at 165° (4)). [For use of \bar{C} in prepn. of azo dyes by coupling with o-hydroxydiazonium salts see (5).]

- 4-Chloro-2-naphthyl methyl ether: pl. from lt. petroleum, m.p. $44-45^{\circ}$ (4). [From \bar{C} with Me₂SO₄ + aq. NaOH (4).]
- 4-Chloro-2-naphthyl acetate: pl. from aq. MeOH or lt. petroleum, m.p. 58-59° (2),
 56° (4). [From C with excess Ac₂O refluxed 30 min. (90-100% yield (2)).]
- (2).

3:3045 (1) Fries, Schimmelschmidt, Ann. 484, 293 (1930). (2) Burton, J. Chem. Soc. 1945, 280-283. (3) Hodgson, Birtwell, J. Chem. Soc. 1943, 322. (4) Hodgson, Birtwell, J. Chem. Soc. 1943, 468-469. (5) Herzberg, Wunderlich (to I.G.), Ger. 459,889, May 18, 1928; Cent. 1928, II 395; not in C.A.

3:3070 3,4-DICHLOROBENZOPHENONE (3,4-Dichlorophenyl phenyl ketone) C

C₁₃H₈OCl₂ Beil. S.N. 652

M.P. 104-105° (1) 102-103° (2) (3)

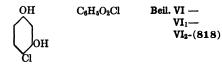
Cryst. (from alc. (1)).

[For prepn. (79.5% yield) from o-dichlorobenzene (3:6055) + BzOH (1:0715) + AlCl₃ see (1); for prepn. from o-dichlorobenzene (3:6055) + BzCl (3:6240) + AlCl₃ see (2) (3).]

3,4-Dichlorobenzophenone oxime: m.p. 153-154° (1). [This oxime upon Beckmann rearr. with H₂SO₄ gives (1) 3,4-dichlorobenzanilide which can be hydrolyzed to 3,4dichlorobenzoic ac. (3:4925), m.p. 207-208° (1), and aniline.]

3:3070 (1) Newton, Groggins, Ind. Eng. Chem. 27, 1398 (1935). (2) Böeseken, Rec. 27, 15 (1908). (3) Kraay, Rec. trav. chim. 49, 1085 (1930).

3:3100 4-CHLORORESORCINOL



302

The nature of the cpd., m.p. 89°, and formerly (3) thought to be C, is still in doubt, cf. (1). \bar{C} is very sol. in aq. and not volatile with steam (1); eas. sol. aq., alc., ether, C_6H_6 , and CS₂ (4).

[For prepn. of C from resorcinol (1:1530) by actn. of SO₂Cl₂ in ether (95% yield (1)) see (1) (4).1

- C with FeCl₃ gives a blue-violet soln. becoming brown on warming (4).
- C reduces NH₄OH/AgNO₃ on warming (4).
- C on further chlorination with SO₂Cl₂ (no details) gives (96% yield (1)) of 4,6-dichlororesorcinol (3:3380).
- \tilde{C} (10 g.) refluxed with KHCO₃ (40 g.) in aq. (50 ml.) for $1\frac{1}{2}$ hrs. gives (76% yield (5)) of 5-chloro-2,4-dihydroxybenzoic acid (6), cryst. from hot aq., m.p. 224-225° cor. (6), 215-216° (Maguenne bloc) after drying at 100-105° (5) (6).

Č in AcOH treated with xanthydrol (1:5205) yields 4-chloro-2-(?)-xanthydrylresorcinol, cryst. from C₆H₆, m.p. 215° (7).

[For studies on prepn. of alkyl ethers of 4-chlororesorcinol for use as antiseptics and germicides see (8); for use of \bar{C} in prepn. of purpurin (1,2,4-trihydroxyanthraquinone) by reaction with phthalic anhydride, H₂SO₄ + H₃BO₃, see (9).]

[For coupling of C with diazotized aniline, p-nitroaniline, or p-toluidine see (11).]

- **4-Chlororesorcinol diacetate:** m.p. 46-47° (10).
- **D** 4-Chlororesorcinol dibenzoate: m.p. 66° (10).

3:3100 (1) Moore, Day, Suter, J. Am. Chem. Soc. 56, 2456-2458 (1934). (2) Likhosherstov, J. Gen. Chem. (U.S.S.R.) 3, 164-171 (1933); Cent. 1934, I 1476; C.A. 28, 1675 (1934). (3) Clark, (3) Clark, 1876, 1676, 1876, 1 Chem. (U.S.S.R.) 14, 203-210 (1944); C.A. 39, 2285 (1945).

(11) Petyunin, J. Gen. Chem. (U.S.S.R.) 14, 303-311 (1944); C.A. 39, 4060 (1945).

3:3130 2-CHLOROHYDROQUINONE OH
$$C_6H_5O_2Cl$$
 Beil. VI - 849 VI₁-(417) VI₂-(844)

[See also 2-chlorobenzoquinone-1,4 (3:1100).]

Colorless lfts. from CHCl₃ in which \tilde{C} is eas. sol. hot but spar. sol. cold. — Very eas. sol. aq., alc., or ether; sol. in warm C_6H_6 (dif from hydroquinone (1:1590) and use in sepn. from latter (1)). — Not sublimable (5).

[For prepn. of \tilde{C} from 2-chlorobenzoquinone-1,4 (3:1100) by reductn. with aq. SO_2 (2) (9) see indic. refs. (note, however, that in dil. aq. NaOH under N_2 both reductn. and sulfonation occur (10)); from benzoquinone-1,4 (1:9025) with conc. HCl (11) (2) or in CHCl₃ with HCl gas (100% yield (12)) (2); from sodium benzoquinonesulfonate (5) with conc. HCl below 20° (55% yield (5)) in CO₂ see indic. refs.; from p-benzoquinone dichloride (2,3-dichlorocyclohexen-5-dione-1,4) [Beil. VII-573] by reductn. with $SnCl_2 + HCl$ at 0° see (4); from hydroquinone (1:1590) in CCl₄ with Cl₂ see (13).]

 $[\bar{C}]$ is used as a photographic developer under name "Adurol" (for identification of \bar{C} in developers see (1)); \bar{C} forms an addn. cpd. (14) with 2 moles p-(methylamino)phenol also used as developer under name Chloranol; for use of \bar{C} as vulcanization accelerator see (15); for use of \bar{C} as antioxidant (16) and as gum inhibitor in cracked gasoline (17) or in aq. emulsion as insecticidal spray (18) see indic. refs.; for study of bactericidal actn. see (19).]

 \bar{C} on oxidn. with NaClO₃ + H₂SO₄ + V₂O₅ in AcOH (92% yield (20)), with K₂Cr₂O₇ + H₂SO₄ (yield: 89% (21), 84% (8)) (2), with MnO₂ + dil. H₂SO₄ (56% yield (8)), or with PbO₂ in C₆H₆ (22) gives 2-chlorobenzoquinone-1,4 (3:1100). [For studies of oxidn-reductn. potential of this system and also for the intermediate quinhydrone see under the quinone (3:1100).]

[For reactn. of \tilde{C} with phthalic anhydride + conc. H_2SO_4 at $130-135^\circ$ see (2); for reactn. of \tilde{C} with naphthalene-1,2-dicarboxylic acid anhydride (23) or with naphthalene-2,3-dicarboxylic acid anhydride (24) each fused with $AlCl_3$ + NaCl see indic. refs.]

 \tilde{C} in AcOH with xanthydrol (1:5205) yields (25) 2-chloro-3-xanthydrylhydroquinone, cryst. from C_6H_6 , m.p. 236-237° (25).

 \bar{C} gives no effervescence with aq. 10% Na₂CO₃ but soln. darkens on stdg. (1); \bar{C} with aq. 5% AgNO₃ scarcely reduces in cold but does so rapidly on warming (1); \bar{C} with 10% aq. FeCl₃ gives red-brown color in cold and on boilg, pronounced quinone-like odor (1).

- ② 2-Chlorohydroquinone diacetate: pr. from dil. alc., m.p. 99° (1) (26), 72° (2), 71-72° (27), 70.5° cor. (3). [From C with Ac₂O (2) or AcCl (26).] [Note that a monoacetate, m.p. 62° (28) has been reported, but the reason for the wide divergence in the m.p.'s reported for the diacetate has not been explained.]
- ② 2-Chlorohydroquinone dibenzoate: fine woolly ndls. from mixt. of alc. + ether, m.p. 130° (2). [From C on refluxing with BzCl (2).]

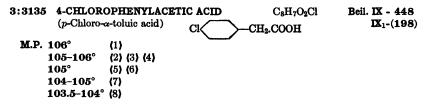
3:3130 (1) Clarke, J. Ind. Eng. Chem. 10, 891-895 (1918). (2) Levy, Schultz, Ann. 210, 137-144 (1881). (3) van Erp, Ber. 58, 663-665 (1925). (4) Dimroth, Eber, Wehr, Ann. 446, 144 (1926). (5) Seyewetz, Compt. rend. 156, 902 (1913); Seyewetz, Paris, Bull. soc. chim. (4) 13, 490 (1913). (6) Schulz, Ber. 15, 654 (1882). (7) La Mer, Baker, J. Am. Chem. Soc. 44, 1956, 1960 (1922). (8) Conant, Fieser, J. Am. Chem. Soc. 45, 2201-2202 (1923). (9) Städeler, Ann. 69, 302-309 (1849). (10) Dodgson, J. Chem. Soc. 1939, 2498-2502.

304

(11) Wöhler, Ann. 51, 155 (1844). (12) Clark, Am. Chem. J. 14, 571 (1892). (13) von Bramer, Zabriskie (to Eastman Kodak Co.), U.S. 1,912,744, June 6, 1933; Cent. 1933, II 2090. (14) Union Phot. Ind. Étab. Lumière & Jougla Réunis, Ger. 345,471, Dec. 12, 1921; Cent. 1922, II 604. (15) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; Cent. 1933, I 3134. (16) Christmann (to American Cyanamide Co.), U.S. 1,806,671, May 26, 1931; Cent. 1931, I 1207. (17) Clarke, Towne (to Texas Co.), U.S. 2,023,871, Dec. 10, 1935; Cent. 1936, I 2671; C.A. 30, 851 (1936). (18) Yates (to Shell Development Co.), U.S. 1,778,240, Oct. 14, 1930; Cent. 1931, I 2799; C.A. 24, 5928 (1930). (19) Cooper, Woodhouse, Biochem. J. 17, 600–612 (1923). (20) Underwood, Walsh, J. Am. Chem. Soc. 58, 646–647 (1936).

(21) Den Hollander, Rec. trav. chim. 39, 483-484 (1920). (22) Hunter, Northley, J. Phys. Chem. 37, 885-886 (1933). (23) Waldmann, J. prakt. Chem. (2) 131, 77 (1931). (24) Waldmann, Ber. 64, 1721 (1931). (25) Fabre, Ann. chim. (9) 18, 111-112 (1922). (26) Scheid, Ann. 218, 216-217 (1883). (27) Thiele, Winter, Ann. 311, 344 (1900). (28) Clermont, Chautard,

Compt. rend. 102, 1072 (1886).



Colorless ndls. from aq.; eas. sol. aq., alc., ether, C_6H_6 . — Odor faintly like that of phenylacetic acid. — [For study of ioniz. const. of \bar{C} see (6); for fate in animal body see (13).]

[For prepn. of $\bar{\mathbf{C}}$ from p-chlorobenzyl bromide (?) [Beil. V-307] by conversion to p-Cl.C₆H₄.CH₂MgX and subsequent carbonation with CO₂ at 0° (74% yield) see (9); from p-chlorophenylacetonitrile (p-chlorobenzyl cyanide) [Beil. IX-448] by hydrolysis (80% yield (3)) with boilg. aq. KOH (6) (10) or with boilg. dil. H₂SO₄ (8) see indic. refs.; from p-aminophenylacetic acid [Beil. XIV-456, XIV₁-(589)] via diazotization and use of Cu₂Cl₂ reactn. see (5) (2) (11); from 2-phenyl-4-(4-chloro-benzal)oxazolone-5 (the azlactone from p-chlorobenzaldehyde + N-benzoylglycine + Ac₂O) (7) [Beil. XXVII₁-(299)] on boilg. with aq. NaOH and afterwards treated with H₂O₂ see (7); from 3-chloro-1,5-bis-(p-chlorophenyl)pentadiene-1,3 (3) in acetone soln. by oxidn. with KMnO₄ see (3); for formn. from phenylacetic acid (1:0665) with Cl₂ in sunlight see (12); from ethyl p-chlorophenylacetate (see below) by alk. hydrolysis see (19).]

[For reactions of closely related p-Cl.C₆H₄.CH₂.COOMgCl with large excess of isopropyl MgCl or o-tolyl MgBr yielding p-chlorophenylmalonic acid (14), cryst. from alc., m.p. 163° (14), see (14); for quite dif. behavior with other RMgX cpds. see (22).]

[\tilde{C} with benzaldehyde htd. in s.t. for 20 hrs. at 300° not only condenses but also loses CO₂ yielding (6) 4-chlorostilbene (1-(p-chlorophenyl)-2-phenylethylene) [Beil. V-633], white lfts. from AcOH, m.p. 129° (6) (for corresp. reactns. of \tilde{C} with p-methoxybenzaldehyde (1:0240), or with salicylaldehyde (1:0205), see (6)); \tilde{C} (as K salt) with o-nitrobenzaldehyde + Ac₂O htd. 24 hrs. at 100° undergoes Perkin condens. yielding (45–50% yield (15)) α -(4-chlorophenyl)-o-nitrocinnamic acid, colorless cryst. from AcOH, m.p. 186–186.5° u.c. (190.2–190.7° cor.) (15).]

- [C on dinitration with HNO₃ + fumg. H₂SO₄ yields (19) 4-chloro-2,6-dinitrophenylacetic acid, pale yel. ndls. from boilg. aq., m.p. 167° (19).]
- [Č with PCl₅ in CHCl₅ yields (2) (13) p-chlorophenylacetyl chloride, yellowish oil, b.p. 120° at 14 mm. (2); this prod. with aminoacetic acid (glycine) in dil. aq. alk. gives (65-75% yield (13)) (2) p-chlorophenylaminoacetic acid (p-chlorophenylaceturic acid), lfts. from aq., m.p. 165° u.c. (2), 164-165° (13).]
- [Č conv. to Pb salt, latter dried at 110°, and distilled yields (16) 4,4′-dichlorodibenzyl ketone, ndls. from alc., m.p. 93° (oxime, m.p. 135–136°, semicarbazone, m.p. 118° (16)).]—
 [For CaĀ₂.H₂O and AgĀ see (10).]
 - Methyl p-chlorophenylacetate: oil, b.p. 114-115° at 6 mm. (17). [From C in MeOH satd. with dry HCl gas (6).] [For study of rate of reactn. with NH₃ in MeOH at 25° see (17).]
 - Ethyl p-chlorophenylacetate: m.p. 34° (18), 32° (1) (6), b.p. 253-254° at 749 mm. (1), 260° (6). [From \bar{C} in EtOH with dry HCl gas (6).] [This ester melted and treated with sodium evolves H₂ and yields a pale red sodium cpd. (19); the ester with Na sand in dry ether refluxed 8 hrs., then treated with BzCl, gives (poor yield (19)) ethyl α-(4-chlorophenyl)benzoylacetate, ndls., m.p. 97-98° (19); the ester does not (19) condense with itself in pres. of NaOEt but upon treatment with isopropyl MgX gives (93% yield (9)) the desired condens. prod., viz., ethyl α,γ-(p-chlorophenyl)-acetoacetate, white cryst. from alc., m.p. 119-120° (9); for reactn. of ethyl p-chlorophenylacetate with diethyl ethoxymethylenemalonate [Beil. III-469, III₁-(162), III₂-(300)] yielding ethyl 7-chloronaphthol-1-dicarboxylate-2,4 (20) and α-(p-chlorophenyl)glutaconic acid (20) see (20).] [For study of rate of hydrolysis of ethyl p-chlorophenylacetate see (18).]
 - p-Chlorophenylacetamide: tbls. from alc., m.p. 175° (10). [Obtd. indirectly from p-chlorophenylacetonitrile by partial hydrolysis (10).]
 - ① (p-Chlorophenylacet)anilide: lfts. from abs. alc., m.p. 164.5° (19). [From $\bar{C} + 1\frac{1}{2}$ moles aniline at 180–190° for $\frac{1}{2}$ hr. (19).]
 - \bigcirc (4-Chlorophenylacet)-*m*-chloroanilide: colorless ndls. from dil. alc., m.p. 137.5° cor. (21). [From \bar{C} + *m*-chloroaniline (1 mole) on htg. at 180-190° for 1 hr. (21); also from *p*-chlorobenzyl *m*-chlorophenyl ketoxime by Beckmann rearr. with PCl₅ in ether (21).]
 - (4-Chlorophenylacet)-p-toluidide: white ndls. from C_6H_6 , m.p. 189.5° (18). [From $\tilde{C} + p$ -toluidine htd. as for the anilide (above) (19).]
 - (4-Chlorophenylacet)hydrazide: ndls. from alc., m.p. 170° (1). [From ethyl p-chlorophenylacetate (above) with hydrazine hydrate in boilg. alc. (1); for its further condens. prods. with acetone, benzaldehyde, salicylaldehyde see (1); note also that with I₂ in hot alc. the (mono)hydrazine gives (1) N,N'-bis-(p-chlorophenylacetyl)-hydrazine, ndls. from alc., m.p. 255° (1).]
 - (4-Chlorophenylacet)phenylhydrazide: white ndls. from C_0H_0 , m.p. 166° (19). [From \bar{C} with excess phenylhydrazine on htg. as above (19).]

3:3135 (1) Curtius, J. prakt. Chem. (2) 89, 527-530 (1914). (2) Friedmann, Maase, Biochem. Z.
 27, 107 (1910). (3) Straus, Ann. 393, 316-317 (1912). (4) Schotten, Z. physiol. Chem. 7, 27, Note (1882). (5) Dippy, Williams, J. Chem. Soc. 1934, 161-166. (6) van Walther, Wetzliich, J. prakt. Chem. (2) 61, 195-198 (1900). (7) Mauthner, J. prakt. Chem. (2) 95, 60 (1917). (8) Jackson, Field, Am. Chem. J. 2, 89-91 (1880/81). (9) Ivanov, Spassov, Bull. soc. chim. (4) 49, 376-377 (1931). (10) Beilstein, Kuhlberg, Neuhoff, Ann. 147, 347-350 (1868).

(11) Petrenko-Kritschenko, Ber. 25, 2240 (1892). (12) Radziszewski, Ber. 2, 208 (1869). (13) Cerecedo, Sherwin, J. Biol. Chem. 62, 218-221 (1924/25). (14) Ivanov, Spassov, Bull. soc. chim. (4) 49, 22 (1931). (15) Nylén, Ber. 53, 158-159 (1920). (16) Kenner, Morton, J.

Chem. Soc. 1934, 680. (17) Betts, Hammett, J. Am. Chem. Soc. 59, 1568-1572 (1937). (18) Kindler, Ann. 452, 108 (1927). (19) Mehner, J. prakt. Chem. (2) 62, 560-565 (1900). (20) Menon, J. Chem. Soc. 1936, 1775-1777.

(21) Jenkins, J. Am. Chem. Soc. 55, 2898 (1933). (22) Ivanov, Bull. soc. chim. (5) 4, 686 (1937).

3:3140 2,3,4,5-TETRACHLORO-BENZALDEHYDE

C7H2OCl4 Beil. S.N. 635

M.P. 106-106.5° (1)

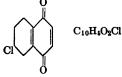
[For prepn. of \bar{C} from 2,3,4,5-tetrachlorobenzal (di)chloride (3:9397) by hydrolysis (presumably with strong H_2SO_4) see (1).]

Č with NaHSO₃ forms the corresp. addn cpd. which may be used as means of sepn. of Č from 2,3,5,6-tetrachlorobenzaldehyde (3:2700).

[For use of C in prepn. of dyestuffs see (1).]

3:3140 (1) Chem. Fabrik Griesheim-Elektron, Brit. 251,511, May 27, 1926; Cent. 1926, II 2355; [C.A. 21, 1361 (1927)]: French 603,650, April 20, 1926, Cent. 1926, II 2355; not in C.A.

3:3145 6-CHLORONAPHTHO-QUINONE-1,4



Beil. S.N. 674

M.P. 106-107° (1)

[For prepn. of \bar{C} from benzoquinone-1,4 (1:9025) by addition of 2-chlorobutadiene-1,3 ("Chloroprene") (3:7080) and subsequent oxidation of the resulting Diels-Alder type adduct see (2); for formn. of \bar{C} by oxidation of various dichloronaphthalenes see (1).

3:3145 (1) Kozlov, Talybov, J. Gen. Chem. **9,** 1827–1836 (1939); C.A. **34,** 4067 (1940). (2) Carothers, Collins (to du Pont Co.), U.S. 1,967,862, July 24, 1934; Cent. **1936**, I 2209; C.A. **28,** 5994–5995 (1934).

3:3155 1,1,2,3,4,4-HEXACHLORO-BUTANE

M.P. 107° (1) (2)

[For isolation of \bar{C} from the high-boilg, fraction resulting in the preparation of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see (1) (2); long refluxing (20 days) of freshly distilled samples of the latter compound also yields (1) \bar{C} .]

C on boilg. with alc. Ca(OH)₂ or with alk. at room temp. loses 2 HCl yielding (1) the liquid stereoisomer (3:6150) of 1,2,3,4-tetrachlorobutadiene-1,3. [The solid stereoisomer (3:0870) was not obtained from C (1).]

3:3155 (1) Müller, Hüther, Ber. 64, 589-600 (1931); C.A. 25, 3956-3957 (1931). (2) Ghighi, Ann. chim. applicata 28, 363-368 (1938); Cent. 1939, I 86; C.A. 33, 6792 (1939).

(" Hexachlorophenol ")

Cryst. from CHCl3 or CS2; white ndls. from pet. eth. (1). — Insol. aq., spar. sol. cold alc., mod. sol. C₆H₆, very eas. sol. CHCl₃ or pet. eth. (4).

[For prepn. by various methods see Beil. VII-144 + Beil. VII₁-(96); for comml. prepn. by chlorination of phenol sec (2).]

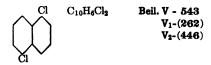
Č with aq. KI (1), or Zn dust in boil. alc. (4), or SnCl₂ + HCl in AcOH (100% yield) (5) (6) or even with conc. aq. or alc. KOH (4), yields pentachlorophenol (3:4850).

C (4 g.) grad. added to conc. HNO₃ (20 g.) with warming, and the resultant soln. poured into aq., ppt. recrystd. from nitrobenzene, yields (5) tetrachlorobenzoquinone (chloranil) (3:4978), m.p. 292° (5).

C melted with conc. H₂SO₄, then htd. cautiously with shaking until reaction suddenly begins, evolves HCl, and on cooling chloranil (see above) separates (5).

3:3180 (1) Buchan, McCombie, J. Chem. Soc. 1931, 144. (2) Britton, Martin, Alquist, Heindel (to Dow Chem. Co.), US. 1,969,686, Aug. 7, 1934, Cent. 1935, I 3046. (3) Langer, Ann. 215, 121 (1882). (4) Hugounenq, Ann. chim. (6) 20, 560-562 (1890). (5) Biltz, Ber. 37, 4009 (1904). (6) Biltz, Giese, Ber. 37, 4018 (1904). (7) Ter Horst (to U.S. Rubber Co.), U.S. 2,378,597, June 19, 1945; C.A. 39, 4188 (1945).

3:3200 1,5-DICHLORONAPHTHALENE



M.P. 107° (1) (6) (7) (9) (10) 106.5-107° (2) 106.5° (3) (24)106-107° **(4)** 105-107° (5)

Lfts. from alc. or AcOH. — Sublimes in very broad thin pr. — [For use as wood impregnant see (22).]

[For prepn. of C from 1,5-dinitronaphthalene [Beil. V-558, V₁-(264)] (6) (2), from naphthalene-1,5-bis-(sulfonyl chloride) [Beil. XI-213] (36% yield (4)) (7) (8), from 1-chloronaphthalene-5-sulfonyl chloride [Beil. XI-161] (9) (5), from 5-chloronaphthol-1 [Beil. VI-612| (10) by htg. with PCl₅ see indic. refs.; from 5-sulfonaphthylamine-1 [Beil. XIV-744. XIV₁-(733)] by htg. corresp. diazonium salt with 2 moles PCl₅ see (1) (11); from 1,5dichloro-7-aminonaphthalene by replacement of -NH₂ by -H see (12); from 1,5-dichloronaphthalenesulfonic acid-2 [Beil. XI-181] by hydrolysis of -SO₃H group see (13) (14); from 4,5-dichloronaphthalene-2-sulfonyl chloride [Beil. XI-182] or from 1,8-dichloronaphthalene (3:2435) by htg. with conc. HCl in s.t. at 290° see (15); from naphthalene (1:7200) in CCl₄ at -10 to 0° with Cl₂ in pres. of Fe (together with other products) (16) or from 1nitronaphthalene [Beil. V-553, V_1 -(264)] with Cl_2 (together with other products) (17) (2) see indic. refs.]

[Č in CHCl₃ soln. satd. with Cl₂ gives (25) both 1,5-dichloronaphthalene tetrachloride, m.p. 84°, and a trichloronaphthalene dichloride, m.p. 94° (separated by spar. soly. of latter in MeOH).]

[Č on mononitration yields (10) 1,5-dichloro-8-nitronaphthalene [Beil. V-556], yel. pr. from AcOH, m.p. 142° (10) (17) (23); note that the isomeric 1,5-dichloro-3-nitronaphthalene, m.p. 132°, has been reported indirectly (23) (12).]

[Č on monosulfonation (18) (13) gives chiefly 1,5-dichloronaphthalenesulfonic acid-3 [Beil. XI-183, XI₁-(41)] (corresp. sulfonyl chloride, m.p. 143° (13), corresp. sulfonamide, m.p. 204° (24)) accompanied by a smaller amt. 1,5-dichloronaphthalenesulfonic acid-2 [Beil. XI-181] (corresp. sulfonyl chloride, m.p. 125° (13)).]

[C with pieric acid yields a cpd. C.PkOH, m.p. 87° (10).]

[Č on oxidn. with CrO₃/AcOH yields (19) 3-chlorophthalic acid (3:4820) but on oxidn. with dil. HNO₃ yields (20) a nitro-chloro-phthalic acid.] [Č on cat. vapor-phase oxidn. (21) gives 80% yield 3-chlorophthalic anhydride (3:3900) + 20% phthalic anhydride (1:0725).]

3:3200 (1) Erdmann, Ann. 247, 353-354 (1888). (2) Weissberger, Sängewald, Hampson, Trans. Faraday Soc. 30, 890 (1934). (3) Krollpfeiffer, Ann. 430, 198 (1923). (4) Beattie, Whitmore, J. Am. Chem. Soc. 55, 1546-1548 (1933). (5) Ferrero, Bolliger, Helv. Chim. Acta 11, 1146-1147 (1928). (6) Atterberg, Ber. 9, 1188 (1877). (7) Armstrong, Ber. 15, 205 (1882). (8) Armstrong, Wynne, Chem. News 61, 93 (1890); 62, 163 (1890). (9) Cleve, Bull. soc. chim. (2) 26, 540 (1876). (10) Erdmann, Kirchhoff, Ann. 247, 378 (1888).

(11) Erdmann, Ber. 20, 3185-3186 (1887). (12) Kalle and Co., Ger. 343,147, Oct. 28, 1921; Cent. 1922, II 143. (13) Turner, Wynne, J. Chem. Soc. 1941, 253. (14) Cleve, Chem. Ztg. 17, 398 (1893). (15) Armstrong, Wynne, Chem. News 76, 69-70 (1897). (16) B.A.S.F., Ger. 234,912, May 26, 1911; Cent. 1911, II 63. (17) Atterberg, Ber. 9, 316-318, 926-928 (1877). (18) Armstrong, Wynne, Proc. Chem. Soc. 1890, 81. (19) Guareschi, Gazz. chim. ital. 17, 120 (1887). (20) Atterberg, Ber. 10, 547-548 (1877).

(21) Pongratz, Bassi, Fuchs, Süss, Wüstner, Schober, Angew. Chem. 54, 22-25 (1941). (22) Röchling'sche Eisen und Stahlwerke, Ger. 415,228, June 16, 1925; Cent. 1925, II 1239. (23) Friedländer, Karamessinis, Schenk, Ber. 55, 47-50 (1922). (24) Armstrong, Wynne, Chem. News 61, 274 (1890). (25) Wynne, J. Chem. Soc. 1946, 61.

3:3220 PARA-α-CHLORO-ISOBUTYRALDEHYDE (2,4,6-trus-(α-Chloroisopropyl)-trioxane-1,3,5) CH HC—C(CH₃)₂ HC—C(CH₃)₂ CH HC—C(CH₃)₂ HC—C(CH₃)₂

ClC(CH₈)₂

M.P. 107° (1) (2)

Odorless tasteless ndls. (from distn. with steam); pr. (from ether); insol. aq.; sol. alc., ether, pet. ether. — Sublimes above m.p.

[For prepn. from α -chloro-isobutyraldehyde (3:7235) by shaking with $\frac{1}{2}$ vol. conc. H_2SO_4 see (1) (2).]

3:3220 (1) Brochet, Ann. chim. (7) 10, 357-359 (1897). (2) Brochet, Bull. soc. chim. (3) 7, 643-644 (1892).

3:3250 2,4-DICHLORONAPHTHOL-1

Ndls. (from dil. alc. or lgr.); from AcOH \bar{C} separates in pr. with 1 mole of AcOH rapidly lost at 40-50° (1). — \bar{C} is volatile with steam; eas. sol. abs. alc. ether or C_6H_6 . — \bar{C} on htg. to 180° decomposes with loss of HCl.

[For prepn. from β -naphthol (1:1500) (1) (2) or 4-chloronaphthol-1 (3:3720) (4) by chlorination see (1) (2) (3); from naphthalene 1,2,3,4-tetrachloride (3:4750) by oxidn. with CrO₃ in AcOH see (5); for other methods see Beil. VI-612.]

 \ddot{C} dissolves in NaOH or Na₂CO₃ but on warming (or even long stdg. in cold) yields (6) ultramarine flocks which impart to ether a violet, and to benzene a deep blue violet, color (6). [Same result obtd. with K₃Fe(CN)₆ but not with pyridine (6).]

Č on boil. with dil. HNO₃ is oxidized (1) to phthalic ac. (1:0820); but with CrO₃ in AcOH yields 2-chloronaphthoquinone-1,4 (3:3580), volatile with steam, golden-yel. ndls. from aq., alc., or AcOH, m.p. 116° (1).

 \tilde{C} is not affected by Sn + alc. HCl (3), or Na/Hg (3), but on htg. in AcOH with conc. HI (D=1.7) for 10 hrs. gives (3) α -naphthol (1:1500).

C dislvd. in 20 pts. 15% aq. KOH and shaken with 4 pts. (CH₃)₂SO₄ gives (94% yield (3)) of the methyl ether, methyl 2,4-dichloro-1-naphthyl ether, colorless ndls. from alc., m.p. 58° (3).

D 2,4-Dichloro-1-naphthyl acetate: from C by htg. with AcCl (2); ndls. (from alc.), m.p. 74-76° (2).

3:3250 (1) Cleve, Ber. 21, 891–893 (1888). (2) Zincke, Ber. 21, 1035–1036 (1888). (3) Franzen, Stäuble, J. prakt. Chem. (2) 103, 384–385 (1921/22). (4) Reverdin, Kauffmann, Ber. 28, 3053 (1895). (5) Helbig, Ber. 28, 506 (1895). (6) Willstatter, Schuler, Ber. 61, 370 (1928).

3:3275 6-CHLORO-2-METHYL-BENZOIC ACID

Beil. S.N. 941

M.P. 108°

102° (2)

[91.5° (3)]

Long slender colorless ndls. from hot aq. (2) or from HCl (1).

[For prepn. of C from 6-chloro-2-methylbenzamide (see below) (itself obtd. from 6-chloro-2-methylbenzonitrile, m.p. 82-83° (2)) by actn. of nitrous acid see (2); from 6-amino-2-methylbenzoic acid (1) via diazotization and use of Cu₂Cl₂ reactn. see (1) (3).]

Č on htg. with aniline, K₂CO₅, and copper powder yields (1) 3-methyldiphenylamine-carboxylic acid-2, cryst. from 50% alc., m.p. 145° dec. (1).

[C melted and treated with Br₂ evolves HBr, and the prod. on warming with dil. NaOH yields (3) 3-chloro-\alpha-hydroxyphthalide, colorless pl. from dil. alc., m.p. 138° (3).]

----- 6-Chloro-2-methylbenzamide: scales from boilg. aq., m.p. 167° (2). [Prepd. indirectly as above.]

3:3275 (1) Gleu, Nitzsche, J. prakt Chem. (2) 153, 213 (1939). (2) Kenner, Witham, J. Chem. Soc. 119, 1458 (1921). (3) Levy, Stephen, J. Chem. Soc. 1930, 2788.

3:3295 3,4-DICHLORONAPHTHOL-2

M.P. 108° (1) (2).

Small colorless ndls. from lgr. Sol. in cold K₂CO₃ soln. (2).

[For prepn. from β -naphthol (1:1540) via 1-nitrosonaphthol-2, chlorination with SO₂Cl₂ in tetrachloroethane to 1-nitroso-3,4-dichloronaphthol-2, reduction to 1-amino-3,4-dichloronaphthol-2 and thence via diazo reaction to \bar{C} see (1); for prepn. from 1,3,4-tri-chloronaphthol-2 by reduction with FeSO₄ + NaOH see (2).]

Č treated with 1 mole HNO₂ yields 1-nitroso-3,4-dichloronaphthol-2, golden-yel. cryst. from AcOH, m.p. not given (1).

3:3295 (1) Marschalk, Bull. soc. chim. (4) 43, 1367 (1928). (2) Herzberg, Spengler, Schmidt (to I.G.), Ger. 431,165, June 30, 1926; Cent. 1926, II 1196.

M.P. 108.5-109 (26) 108-109° (1) cor. (27) (29) 108° (2) (28) 107-108° cor. (3) 107° (4) 106-107° (17) 105-106° (5) 105° (6)

[See also 1,1-dichloro-2,2-bis-(p-chlorophenyl)ethane, "DDD" (3:3320).]

Note that \bar{C} is the remarkable insecticide to which so much publicity is currently being given. Despite the general fanfare the amount of real scientific data which has been released at this writing is small, although very rapid publication is inevitable in the near future. No attempt can be made in this text to cover the utilization of \bar{C} , but attention is drawn to two bibliographies (7) (8) containing respectively 174 and 418 references, although most of these are to general and nontechnical reports. For an extensive review of chemistry of \bar{C} see (30).

[For patents on utilization of "DDT" as insecticide see (9) (10). — For studies of toxicology and pharmacology of "DDT" see (11) (12) (13) (14). — Note that \bar{C} is by rabbits in part excreted as di-(p-chlorophenyl)acetic acid (3:4612), m.p. 166-166.5° u.c. (24).]

Colorless cryst. from 95% alc. — \overline{C} is spar. sol. in 95% alc.; viz., 0.8 wt. % at 0°, 3.9 wt. % at 48° (3); spar. sol. pet. ether of b.p. 30-60° (3); \overline{C} is moderately sol. in CCl₄, ether, or CHCl₃ (3); eas. sol. in pyridine, dioxane, C₆H₆, or acetone (3); for data and graph of wt. % solubility/temp. over range 0-48° see (3) cf. (25); for soly. of \overline{C} in kerosenes see (31). [For detn. of \overline{C} in technical samples, i.e., in pres. of "DDD" (3:3320), by recrystn. from satd. alc. soln. of "DDT" see (26).]

Note that technical \bar{C} may contain some of the isomeric 1,1,1-trichloro-2-(p-chlorophenyl)-2-(o-chlorophenyl)ethane (3:1820) and /or polymers of chloral (3:5210); in fact, technical \bar{C} of setting point 88° contains about 70% \bar{C} accompanied by 18% of the o-p isomer +6% of the o-p isomer (25). — For extensive report on the compn. of technical grade \bar{C} see (29).

[For optical crystallographic props. of C see (28).]

PREPARATION OF C

 \bar{C} is universally prepd. by condensation of chloral or chloral hydrate with chlorobenzene. From chloral hydrate. [For prepn. of \bar{C} from chloral hydrate (3:1270) with chlorobenzene (3:7903) + fumg. H₂SO₄ (8-10% SO₃) (70% yield (2) (4)) or ClSO₃H (77% yield (32)) see indic. refs.]

From chloral. [For prepn. of \bar{C} from anhydrous chloral (3:5210) with chlorobenzene (3:7903) + conc. H_2SO_4 see (6) (15) (16)]

CHEMICAL BEHAVIOR OF C

Reduction of \tilde{C} . \tilde{C} on reduction with Na/alc. gives up all its chlorine quant. detn. of which comprises a method for the quant. detn. of \tilde{C} (14).

[\bar{C} on hydrogenation with $H_2 + Pd/CaCO_3$ in various solvents on slight warming gives according to conditions (18) various products of bimolecular reduction; these include 2,2,3,3-tetrachloro-1,1,4,4-tetra-(p-chlorophenyl)butane, cryst. from AcOEt, m.p. 271.5° (28% yield (18)), both higher-melting (229°) and lower-melting (174°) stereoisomers of 2,3-dichloro-1,1,4,4-tetra-(p-chlorophenyl)butene-2 (former 36% yield, latter in traces) (18), and perhaps other products; for much further study of these reaction products see the original reference (18)]

[C on electrolytic reduction in ale. HCl soln. gives (13% yield (19)) at the cathode 1,1,4,4-tetra-(p-chlorophenyl)butyne-2, pr. from AcOEt, m.p. 174° (19); note that this prod. on oxidn. with CrO₃/AcOH gives (91% yield (19)) 4,4'-dichlorobenzophenone (3:4270), m.p. 145°.]

Oxidation of C. Attempts to oxidize C with CrO₃/AcOH have given (5) no identifiable products.

Dehydrochlorination of C. C under various conditions can be caused to split out 1 HCl yielding 1,1-dichloro-2,2-bis-(p-chlorophenyl)ethylene.

C with alc. KOH refluxed 10 hrs. (5) (6) or 15-20 min. (24) (for study of rate see (20) (27)) gives (yields: almost 100% (24), 81% (5)) 1,1-dichloro-bis-(p-chlorophenyl)ethylene (3:2438) [for use of this reaction by detn. of ionized chlorine as means for detn. of C in spray deposit see (21).]

 \bar{C} with excess Ba(OH)_{2.8}H₂O in ethylene glycol refluxed 10-12 hrs. gives (33% yield (24)) di-(p-chlorophenyl)acetic acid (3:4612), m.p. 166-166.5° u.c.; this results by initial loss of HCl as above and further degradation.

 \ddot{C} in the pres. of minute amts. (e.g., 0.01%) of FeCl₃ or AlCl₃ at 110-120° loses HCl giving (22) cf. (34) 1,1-dichloro-2,2-bis-(p-chlorophenyl)ethylene (3:2438). (See also below under behavior of \ddot{C} with AlCl₃ + C₆H₆.)

SUBSTITUTION REACTIONS OF C

Bromination. No study of the behavior of \bar{C} toward Br₂ appears yet to have been reported.

Chlorination. \tilde{C} in CCl₄ soln. with Cl₂ + trace of PCl₃ in light at b.p. of mixture for 3 hrs. gives (73% yield (5)) 1,2,2,2-tetrachloro-1,1-bis-(p-chlorophenyl)ethane (3:2477), m.p. 91-92° (5).

Nitration. C on introduction of two nitro groups (no details) gives (6) a prod., ndls. from alc., m.p. 148.0-148.3° (29), which is presumably 1,1,1-trichloro-1,2-bis-(4-chloro-2-nitrophenyl)ethane; note that this dinitro compd. has same m.p. as corresp. dinitro deriv. from "o,p-DDT" (3:1820) but m.p. of a mixt. of the two is depressed (29).

Č on tetranitration with a mixt. (1:1 by volume) of fumg. HNO₃ and conc. H₂SO₄ at 100° for 1 hr. gives (23) 1,1,1-trichloro-2,2-bis-(4-chloro-3,5-dinitrophenyl)ethane, m.p. 223.5-224.5° cor. (23). — [Note that similar tetranitration of "DDD" (1,1-dichloro-2,2-bis-(p-chlorophenyl)ethane (3:3320) gives (23) 1,1-dichloro-2,2-bis-(4-chloro-3,5-dinitrophenyl)ethane, m.p. 224.5-225.5° cor. (23); similar tetranitration of the o-p isomer of "DDT" (viz., 1,1,1-trichloro-2-(o-chlorophenyl)ethane) (3:1820) gives a prod., m.p. 229.5-230° cor. (23). — For color reactions of these tetranitro derivs. with MeOH/NaOMe and its use in detn. of Č see {23} (33).]

Behavior with AlCl₃ + C₆H₆. \bar{C} with anhydrous AlCl₃ (1 mole) in large excess of C₆H₆ reacts at room temp. evolving 2 moles HCl and giving (10% yield (1)) 1,1,2,2-tetraphenylethane [Beil. V-739, V₁-(371), V₂-(673)], m.p. 211°. [Note that the mechanism of this surprising result has not yet been explained; that by similar treatment the same tetraphenylethane is also obtd. in 25% yield from 1,1-dichloro-2,2-bis-(p-chlorophenyl)-ethane (3:3320), in 10% yield from 1,1,1-trichloro-2,2-diphenylethane (3:1420), and from the o-p isomer of "DDT" (viz., 1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)-ethane) (3:1820), but not at all from 1,1-dichloro-2,2-bis-(p-chlorophenyl)ethylene (3:2438); and that if chlorobenzene is substituted for C₆H₆ no tetraphenylethane results from any of them (1).]

3:3298 (1) Fleck, Preston, Haller, J. Am. Chem. Soc. 67, 1419-1420 (1945). (2) Darling, J. Chem. Education 22, 170 (1945). (3) Gunther, J. Am. Chem. Soc. 67, 189-190 (1945). (4) Iris, Leyva, Rev. inst. salubridad enfermedad tróp. (Mex.) 5, 71-74 (1944); C.A. 39, 495 (1945). (5) Grummitt, Buck, Jenkins, J. Am. Chem. Soc. 67, 155-150 (1945). (6) Zeidler, Ber. 7, 1181 (1874). (7) Roark, U.S. Dept. Agr., Bur. Entomology and Plant Quarantine, 12 pp. (June 1944). (8) Roark, U.S. Dept. Agr., Bur. Entomology and Plant Quarantine, 27 pp. (May 1945). (9) Müller (to J. R. Geigy, A.G.), U.S. 2,329,074, Sept. 7, 1944; C.A. 38, 1056 (1944). (10) Hughes (to J. R. Geigy, A.G.), Brit. 547,874, Sept. 15, 1942; C.A. 37, 6400 (1943).

(11) Draize, Woodard, Fitzhugh, Nelson, Smith, Calvery, Chem. Eng. News 22, 1503-1504 (1944). (12) Lillie, Smith, U.S. Pub. Health Repts. 59, 979-984 (1944). (13) Nelson, Draize, Woodard, Fitzhugh, Smith, U.S. Pub. Health Repts. 59, 1009-1020 (1944). (14) Smith, Stohlman, U.S. Pub. Health Repts. 59, 984-993 (1944); 60, 289-301 (1945). (15) Callaham, Chem. Met. Eng. 51, No. 10, 109-114 (Oct. 1944). (16) Breckenridge, Can. Chem. Process Ind. 28, 570 (1944). (17) Stohlman, U.S. Pub. Health Repts. 60, 350-353 (1945). (18) Brand, Bausch, J. prakt. Chem. (2) 127, 222-224, 231-233 (1930). (19) Brand, Horn, Bausch, J. prakt. Chem. (2) 127, 240-241, 244-246 (1930). (20) Brand, Busse-Sundermann, Ber. 75, 1828 (1942).

127, 240-241, 244-246 (1930). (20) Brand, Busse-Sundermann, Ber. 75, 1828 (1942).
 (21) Gunther, Ind. Eng. Chem., Anal. Ed. 17, 149-150 (1945). (22) Fleck, Haller, J. Am. Chem. Soc. 66, 2095 (1944). (23) Schechter, Haller, J. Am. Chem. Soc. 66, 2129-2130 (1944).
 (24) White, Sweeney, U.S. Pub. Health Repts. 60, 66-71 (1945). (25) Gunther, J. Chem. Education 22, 238-242 (1945). (26) Cristol, Hayes, Haller, Ind. Eng. Chem., Anal. Ed. 17, 470-473 (1945). (27) Cristol, J. Am. Chem. Soc. 67, 1494-1498 (1945). (28) Gooden, J. Am. Chem. Soc. 67, 1616-1617 (1945). (29) Haller, Bartlett, Drake, Newman, Cristol, et al., J. Am. Chem. Soc. 67, 1591-1602 (1945). (30) Cristol, Haller, Chem. Eng. News 23, 2070-2075 (1945).

(31) Fleck, Haller, Ind. Eng. Chem. 38, 177-178 (1946). (32) Rueggeberg, Torrans, Ind. Eng. Chem. 38, 211-214 (1946). (33) Schechter, Soloway, Hayes, Haller, Ind. Eng. Chem., Anal. Ed. 17, 704-709 (1945). (34) Fleck, Haller, J. Am. Chem. Soc. 68, 142-143 (1946).

3:3300 2,3,5-TRICHLORO-NAPHTHALENE

M.P. 109.5° (1) (2)

[For prepn. of C from 2,3-dichloronaphthol-8 (3:4315) (2) or from 2,3-dichloronaphthalenesulfonyl chloride-8 [Beil. XI-164] (1) (2) (3) with PCl₅ see indic. refs.]

[C treated with ClSO₃H in CS₂ and reactn. prod. conv. to salts as directed (1) gives salts of 2,3,5-trichloronaphthalenesulfonic acid-8 (corresp. sulfonyl chloride, m.p. 164° (1)).]

3:3300 (1) Turner, Wynne, J. Chem. Soc. 1941, 247, 255-256. (2) Armstrong, Wynne, Chem. News 61, 275 (1890). (3) Armstrong, Wynne, Proc. Chem. Soc. 1890, 83; 1895, 79.

This compd. is closely related to "DDT" (3:3298) and occurs (4) as minor impurity in technical grades of this compound.

[For prepn. of \bar{C} from dichloroacetaldehyde (3:5180) or from 2,2-dichloro-1-(p-chlorophenyl)ethanol (4) with chlorobenzene (3:7903) + conc. H_2SO_4 + fumg. H_2SO_4 (63% yield) see (4).]

C with alc. KOH refluxed 3 hrs. loses 1 HCl giving (77% yield (4)) (5) 1,1-dichloro-2,2-bis-(p-chlorophenyl)ethylene (3:1430).

C on dinitration with 10 vols. fumg. HNO₃ at 50° for ½ hr. gives (90% yield (4)) a dinitro deriv.; cryst. from alc., m.p. 178-179° (4).

 \bar{C} on tetranitration with a mixt. (1:1 by volume) of fumg. HNO₃ + conc. H₂SO₄ at 100° for 1 hr. gives (1) a prod., m.p. 224.5–225.5° cor., which presumably has the structure 1,1-dichloro-2,2-bis-(4-chloro-2,6-dinitrophenyl)ethane.

 \bar{C} with anhydrous AlCl₃ (1 mole) + excess C_6H_6 at ord. temp. evolves HCl and gives (25% yield (2)) 1,1,2,2-tetraphenylethane, m.p. 211° (2).

3:3320 (1) Schechter, Haller, J. Am. Chem. Soc. 66, 2129-2130 (1944). (2) Fleck, Preston, Haller, J. Am. Chem. Soc. 67, 1419-1420 (1945). (3) Cristol, Hayes, Haller, Ind. Eng. Chem., Anal. Ed. 17, 470-473 (1945). (4) Haller, Bartlett, Drake, Newman, Cristol, et al., J. Am. Chem. Soc. 67, 1596, 1600 (1945). (5) Cristol, J. Am. Chem. Soc. 67, 1494-1498 (1945).

[For prepn. from m-chlorophenol (3:0255) by htg. with chloroacetic ac. (3:1370) and aq. alk. see (1) (2).]

3:3325 (1) Koelsch, J. Am. Chem. Soc. 53, 304-305 (1931). (2) Hayes, Branch, J. Am. Chem. Soc. 65, 1555-1557 (1943)

Colorless ndls. from dil. AcOH (1). — Very slowly volatile with steam (1). — \bar{C} has pronounced sternutatory props. (1) (3).

[For prepn. from m-hydroxybenzaldehyde (1:0055) via direct chlorination see (2); via 4-nitro-3-hydroxybenzaldehyde, reductn. to corresp. amino cpd., and use of appropriate diazo reactn. see (1); for prepn. from o-chlorobenzaldehyde (3:6410) via nitration to 2-chloro-5-nitrobenzaldehyde, m.p. 78-79°, oximation, reduction to 2-chloro-5-aminobenzaldoxime, m.p. 159-160°, and finally diazotization and hydrolysis see (1); for prepn. from 4-chloro-3-methylphenol (3:1535) see (3); for prepn. from p-chlorophenol (3:0475) by condensation with chloral (3:5210) and subsequent alk. hydrolysis see (4)

Č in 50% AcOH mononitrated as specified (1) gives mixt. of 2-nitro and 4-nitro products eas. sepd. by volatility of latter with steam (1) 2-Nitro-6-chloro-3-hydroxybenzaldehyde: yel. ndls. from dil. AcOH, m.p. 136° (5), 138° (3). [Corresp p-nitrophenylhydrazone, deep or.-red ndls. from AcOH, m.p. 256-257° dec. (5); semicarbazone, yel. ndls. from alc., m.p. 249-250° dec. (5).] 4-Nitro-6-chloro-3-hydroxybenzaldehyde: deep yel. ndls. from AcOH, m.p. 104° (5) (3). [Corresp. p-nitrophenylhydrazone, brick-red ndls. from AcOH, m.p. 284-286° dec. (5); semicarbazone, yel. pl. from alc., m.p. 266-267° dec. (5)]

Č in aq. contg. NaHCO₃ treated (1) with Me₂SO₄ yields 6-chloro-3-methoxybenzalde-hyde, m.p. 62° (1). [Corresp. oxime, ndls., m.p. 101.5° (1); p-nitrophenylhydrazone, old-gold ndls., m.p. 229° (1)] [This methyl ether on oxidn. with KMnO₄ (1) yields 6-chloro-3-methoxybenzoic acid, ndls. from ddl. AcOH, m.p. 170-171° (1).]

- 6-Chloro-3-hydroxybenzaldoxime: colorless ndls. of monohydrate from dil. alc., from abs. alc. in anhydrous ndls., m.p. 146-147° (1).
- --- 6-Chloro-3-hydroxybenzaldehyde phenylhydrazone: unrecorded.
- 6-Chloro-3-hydroxybenzaldehyde p-nitrophenylhydrazone: red ndls. from dil. alc., m.p. 250-251° (1).
- ---- 6-Chloro-3-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.
- ⑥ 6-Chloro-3-hydroxybenzaldehyde semicarbazone: pale yel. ndls., m.p. 236° (1).

3:350 (1) Hodgson, Beard, J. Chem. Soc. **1926**, 151–154. (2) Bissell, Kranz (to National Aniline and Chem. Co.), U.S. 1,776,803, Sept. 30, 1930; Cent. **1931**, I 159; C A. **24**, 5768–5769 (1930). (3) Friedlander, Schenck, Ber. **47**, 3046–3047 (1914). (4) Haakh, Smola, Austrian **141**,159, March **25**, 1935; Cent. **1935**, II 439. (5) Hodgson, Beard, J. Chem. Soc. **1926**, 2034.

M.P. 112-113° (1) 110-111° (2)

Colorless ndls. from cone. alc. soln. (1). — Insol. boilg. aq. but volatile with steam. — Eas. sol. alc., ether, C₆H₆, CHCl₃, CS₂.

[For prepn. of \tilde{C} from 2,4,5-trichlorobenzal (di)chloride (3:6910) by hydrolysis with fumg. H₂SO₄ (1), with warm conc. H₂SO₄ (3), or with aq. in s.t. at 260° (2) see indic. refs.]

- [\bar{C} on oxidn. with KMnO₄ should yield 2,4,5-trichlorobenzoic acid (3:4630), m p. 164°, but this reaction is not actually reported in the literature; note that \bar{C} in air oxidizes only slowly (1).]
- $[\bar{C} \text{ with Na}_2SO_3 \text{ under press. gives (4) 5-chlorobenzaldehydedisulfonic acid-2,4 [Beil. XI-325].]}$
- [C with anhydrous NaOAc on htg. (Perkin synthesis) gives (1) 2,4,5-trichlorocinnamic acid, m.p. 200-201°.]

[For use of C in prepn. of dyestuffs see (5) (3).]

- ---- 2,4,5-Trichlorobenzaldoxime: unreported.
- ---- 2,4,5-Trichlorobenzaldehyde phenylhydrazone: unreported.
- 2.4.5-Trichlorobenzaldehyde p-nitrophenylhydrazone: unreported.
- ---- 2,4,5-Trichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.

3:3375 (1) Seelig, Ann. 237, 147-149, 151 (1887). (2) Beilstein, Kuhlberg, Ann. 152, 238-239 (1869). (3) Fischer Ger. 25,827, June 23, 1883, Friedländer 1, 42 (1877-87). (4) Geigy and Co., Ger. 198,909, June 1, 1908; Cent. 1908; II 214; [C A. 2, 2733-2734 (1908)]. (5) Perkin, Clemo (to British Dyestuffs Corp.), Brit. 165,658, July 28, 1921, C.A. 16, 835 (1922).

3:3380 4,6-DICHLORORESORCINOL

Cryst. from lgr. — \bar{C} is very sol. aq. (forms hydrate, m.p. 70°) (1); \bar{C} is eas. sol. alc., ether (1). — [For bactericidal action of \bar{C} see (3).]

[For prepn. of \bar{C} from resorcinol (1:1530) with N,N'-dichlorourea see (1); from 4-chlororesorcinol (3:3100) with SO_2Cl_2 (96% yield) see (3) cf. (4); (the prods. of m.p. 77°, b.p. 249° (5), and m.p. 101°, b.p. 254° (6), may have been impure samples of \bar{C}).]

- [C with N, N'-dichlorourea + KBr gives (2) 2-bromo-4,6-dichlororesorcinol, m.p. 101°.]
- |C with N,N'-dichlorourea + KI gives (7) 2-iodo-4,6-dichlororesorcinol, m.p. 94°.
- $[\bar{C}]$ with ethyl α -ethoxyacetoacetate in alc. NaOEt gives (4) 6,8-dichloro-3-acetyl-5-hydroxycoumarin, m.p. 236°.]

Note that \bar{C} does not (6) (9) condense with phthalic anhydride.

4,6-Dichlororesorcinol dimethyl ether: ndls. from alc., m.p. 118° (8), 117-118° (9), 116-117° (3). [From C with Me₂SO₄ + aq. alk. (3) (9).]

3:3380 (1) Likhosherstov, J. Gen. Chem. (U.S.S.R.) 3, 164-171 (1933); Cent. 1934, I 1476;
 C.A. 28, 1675 (1934) (2) Likhosherstov, J. Gen. Chem. (U.S.S.R.) 3, 172-176, Cent. 1934,
 I 1476; C.A 28, 1676 (1934). (3) Moore, Day, Suter, J. Am. Chem. Soc. 56, 2458-2459 (1934).
 (4) Weiss, Kratz, Monatsh. 51, 395 (1929). (5) Reinhard, J. prakt. Chem. (2) 17, 328-329 (1878).
 (6) Mettler, Ber. 45, 802-803 (1912). (7) Likhosherstov, J. Gen. Chem. (U.S.S.R.) 3, 177-182 (1933); Cent. 1934, I 1477; C.A. 28, 1676-1677 (1934). (8) Hönig, Ber. 11, 1039-1040 (1878).
 (9) Jacobs, Heidelberger, Rolf, J. Am. Chem. Soc. 41, 463 (1919).

3:3400 1.3.7-TRICHLORONAPHTHALENE

$$CI$$
 CI
 CI

C10H5Cla

Beil. V-545 V₁---V₂---

Ndls. from alc.

[For prepn. of \tilde{C} from 1,3-dichloronaphthalenesulfonyl chloride-7 [Beil. XI-183] (5), from 1,7-dichloronaphthalenesulfonyl chloride-3 [Beil. XI-182] (6), from 3,7-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-162] (5), from 3-chloronaphthalene-1,7-bis-(sulfonyl chloride) [Beil. XI-215] (7), from 7-chloronaphthalene-1,3-bis-(sulfonyl chloride) [Beil. XI-212] (1) (3) (6) (7), from 1-nitronaphthalenedisulfonic acid-3,7 [Beil. XI-216] (3) (4), or from 7-chloro-3-naphtholsulfonic acid-1 (2), each with PCl₅ as directed, see indic. refs.; for formn. of \tilde{C} from β -chloronaphthalene tetrachloride (1,2,3,4,6-pentachlorotetralin) [Beil. V-493] with alc. KOH see (8).]

[Č treated with ClSO₃H in CS₂ and reactn. prod. conv. to sodium salt as directed (1) yields sodium 1,3,7-trichloronaphthalenesulfonate-7 (corresp. sulfonyl chloride, m.p. 138° (1).]

3:3490 (1) Turner, Wynne, J. Chem. Soc. 1941, 247, 253-254. (2) Battegay, Silbermann, Kienzle, Bull. soc. chim. (4) 49, 718-719 (1931). (3) Armstrong, Wynne, Chem. News 61, 93 (1890). (4) Alén, Ber. 17, Referate, 437 (1884). (5) Armstrong, Wynne, Chem. News 61, 275 (1890). (6) Armstrong, Wynne, Chem. News 76, 69 (1879). (7) Armstrong, Wynne, Chem. News 62, 165 (1890). (8) Armstrong, Wynne, Chem. News 61, 285 (1890).

Colorless (12) or pale greenish-yellow (7) (8) cryst. from hexane + AcCl (1), dry ether (9), lgr. (7) (8), or dry $C_0H_0 + \text{pet.}$ ether (12) (17). — Ord. \tilde{C} frequently conts. two kinds of crysts., white and yellow, both melting at 110-112° (13). — \tilde{C} from CCl₄ cryst. with

1 mole solvent; \bar{C} from acetone cryst. with $\frac{1}{2}$ mole solvent; in both cases solvent is lost at 92° but not readily in air at ord. temp. (24). — [For study of x-ray crystallography of \bar{C} see (25).] — Note that \bar{C} cannot be recrystd. from MeOH or EtOH without more or less complete conversion to the corresp. trityl ethers (see also below under behavior of \bar{C} with alcohols).

 \bar{C} may be stored satisfactorily in ord. screw-top bottles, provided they are well sealed with paraffin (7). — On long exposure to moist air, however, \bar{C} is hydrolyzed (see also below) to triphenylcarbinol (1:5985), m.p. 161-162°; for f.p./compn. diagram of system \bar{C} + triphenylcarbinol, eutectic, m.p. 100°, contg. 90% \bar{C} , see (26). — Samples of partially hydrolyzed \bar{C} may be purified by recrystn. from $\frac{1}{2}$ wt. of C_6H_6 contg. 5-25% acetyl chloride, the latter reconverting the triphenylcarbinol to \bar{C} (7).

 \bar{C} is eas. sol. in other, C_6H_6 (100 g. C_6H_6 dis. 85.8 g. \bar{C} at 25° (35)), CCl₄, CHCl₅, or CS₂, but is much less sol. in pet. ether (19). — Solns. of \bar{C} in acetyl chloride (27) (29), benzoyl chloride (27), hot 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (27) (28), dichloroethylene (28), nitrobenzene (27), SOCl₂ (27), SO₂Cl₂ (29) are yellow; for study of effect of temp. see (27). — Solns. of \bar{C} in liq. SO₂ are also yellow (29) and conduct electric current (30) (31) (32); for study of molecular weight of \bar{C} in liq. SO₂ see (33). — \bar{C} is very sparingly sol. in liq. NH₃ but soln. conducts elect. current (34).

[The protracted arguments on the constitution of \tilde{C} and of trityl derivatives in general (controversy over carbonium and quinonoid forms, etc.) cannot be detailed within the scope of this book; however, for leading references since 1920 see (36) (37) (38) (39) (40) (41) (42) (43) (44) (45); for earlier references see Beil. V-700.]

PREPARATION OF C

The two best-studied preparations of \bar{C} are those from triphenylcarbinol (1:5985) with AcCl (3:7065) in C_6H_6 (93-95% yield (12)) and from CCl₄ (3:5100) with $C_6H_6 + AlCl_3$ (84-86% yield on AlCl₃ used (7) (8)). Note, however, that many other methods have also been used as recorded below.

From triphenylcarbinol (1:5985). [For prepn. of \bar{C} from triphenylcarbinol with AcCl (3:7065) directly (79% yield (46)) or in C_6H_6 soln. (93-95% yield (12)); with oxalyl (di)chloride (3:5060) (47); with HCl gas in dry C_6H_6 (48) (for study of equilibrium see (49)) contg. C_6C_1 (9) or in dioxane at 50° for 22 hrs. (86% yield (14)); with conc. HCl in AcOH (79% yield (50)) or in C_6H_6 + Z_0C_1 (85% yield (51)); with PCl₆ directly (52) or in lgr. (53) or in C_6H_6 (29) or in C_6H_6 + Z_0C_1 (90% yield (51)); with PCl₃ + Z_0C_1 in C_0C_1 (92% yield (51)); with SOCl₂ in C_0C_1 (97% yield (51)); with SiCl₄ in C_0C_1 or lgr. at 40° (54), or with COCl₂ (3:5000) in C_0C_1 (5) see indic. refs.]

From other triphenylcarbinol derivatives. [For prepn. of C from K triphenylcarbinolate with COCl₂ (3:5000) in toluene (5); from triphenylmethoxy—MgBr, (C_6H_5)₃C—OMgBr (from benzophenone + C_6H_5 MgBr), with AcCl in C_6H_6 (37% yield (55)) or with COCl₂ in toluene (14% yield (55)); from triphenylcarbinol ethyl ether (see also below) with AlCl₃ in CS₂ (56) or with AcCl (46) (57) see indic. refs.]

From various other trityl derivatives and relatives. [For prepn. of \bar{C} from α -bromotriphenylmethane (trityl bromide) with AgCl in C_6H_6 in s.t. at 200° for several days (50% yield (57)); from α -aminotriphenylmethane (tritylamine) [Beil. XII-1343, XII₁-(557)] with NH₄Cl in liq. NH₃ (34); from triphenylmethylphosphinic acid [(C_6H_5)₃C(PO)(OH)₂] with PCl₅ (3 moles) at 70° (91% yield (20)); from triphenylmethane (1:7220) with PCl₅ at 160° for 2 hrs. (65% yield (58)) or with NOCl at 150° (59) see indic. refs.]

[For prepn. of \bar{C} from triphenylacetyl chloride [Beil. IX-713, IX₁-(309)] by loss of CO on htg. at 120-150° (60) or at 170-180° (61); from bis-(triphenylmethyl) peroxide [Beil.

VI-716, VI₁-(350)] with $Cl_2 + a$ little I_2 in boilg. CCl_4 soln. for 3 hrs. (40% yield (23)) see indic. refs.

From benzene with various polyhalogenated methanes. [For prepn. of \bar{C} from C_6H_6 (1:7400) with CCl₄ (3:5100) in pres. of AlCl₃ (84-86% yield on AlCl₃ used (7) (8); 70-85% yield (18)) cf. (62) (63) (64) in CS₂ (97% yield (19)) see indic. refs.; for use of FeCl₃ (31% yield against 77% with AlCl₃ under otherwise same conditions (10) cf. (65)) see indic. refs.]

[For prepn. of \bar{C} from C_6H_6 (1:7400) with CHCl₃ (3:5050) + AlCl₃ at 50° see (22).]

[For formn, of \bar{C} from C_6H_6 with dichloro-diffuoro-methane ("Freon") + AlCl₃ see (66).] From various chlorotoluenes. [For formn, of \bar{C} from benzotrichloride (3:6540) with C_6H_6 in pres. of metallic U (67), Ti (68), Ce (69), or Cr (21) see indic. refs.; from benzal (di)chloride (3:6327) with C_6H_6 + AlCl₃ see (22).]

From various chlorodiphenylmethanes. [For formn. of \bar{C} from α -chlorodiphenylmethane (benzohydryl chloride) (3:0060) (22) or from α,α -dichlorodiphenylmethane (benzophenone chloride) (3:6960) (70) with $C_6H_6+AlCl_3$ see indic. refs.]

From other miscellaneous sources. [For formn. of C from pentaphenylethane [Beil. V-755, V_1 -(386), V_2 -(711)] with PCl₅ at 170° for 2 hrs. or refluxed in C₆H₆ (58), or (together with other products) with HCl at 150° (71) or on evapn. of soln. in SO₂Cl₂ (72).]

CHEMICAL BEHAVIOR OF C

Pyrolysis of \bar{C} . \bar{C} on htg. at 200° (52) (73) or 250° (53) or at 150° in pres. of P_2O_5 (74) loses HCl and yields both triphenylmethane (1:7220), m.p. 92°, and 9-phenylfluorene [Beil. V-720, V-1(355), V₂-(630)], m.p. 147-148°; note that 9-phenylfluorene is also formed from \bar{C} in various other reactions such as with POCl₃ on distriction. (23) or with $\frac{1}{10}$ wt. of mossy zinc refluxed in C_6H_6 for 5 hrs. (75).

Reduction of \bar{C} . \bar{C} is reduced to triphenylmethane by many different types of reducing agent [e.g., \bar{C} in anhydrous formic acid (1:1005) at 100° evolves CO_2 + HCl and gives (yield: 79% in 30 min., 90% in 2 hrs (4)) triphenylmethane (1:7220); \bar{C} in EtOII treated with cone. H_2SO_4 at 70–80° gives (76) (17) triphenylmethane accompanied by acetaldehyde (1:0100); \bar{C} is reduced by diethyl ether in the presence of AlCl₃ (56) (77), FeCl₃ (65), or ZnCl₂ (78) to triphenylmethane (1:7220), acetaldehyde (1:0100) and ethyl chloride (3:7015) also being formed; other reagents which effect reduction of \bar{C} to triphenylmethane (1:7220) include hydrazobenzene in boiling C_6H_6 (79), cyclohexadiene-1,3 (dihydrobenzene) + HgCl₂ (80); Zn + AcOH (50) (reaction here is complex, and various other prods. may be formed according to conditions), and dry H_2S at 150° (81)].

Oxidation of \tilde{C} . \tilde{C} is not readily oxidized: \tilde{C} with silver oxide in dry C_6H_6 or ether gives (78) a little fuchsone, $(C_6H_5)_2=C_6H_4=O$ [Beil. VII-520, VII₁-(290)], m.p. 168°, together with other amorphous products difficult to purify; note, however, that \tilde{C} in alcohol-free acetone with KMnO₄ in same solvent instantly reduces the KMnO₄ and gives (100% yield (85)) triphenylcarbinol (1:5985).

Hydrolysis of \tilde{C} . \tilde{C} with aq. hydrolyses to triphenylcarbinol (1:5985) + HCl: e.g., \tilde{C} on shaking with aq. at ord. temp. is 85% hydrolysed in 48 hrs. (26) cf. (82) (83) (in this connection note m.p./compn. diagram (26) of \tilde{C} + triphenylcarbinol); \tilde{C} with boilg. aq. rapidly and completely yields only triphenylcarbinol.

[For study of hydrolysis of \bar{C} by aq. in acetone (84), in dioxane (14), or by aq. HCl (35) see indic. refs.]

 \bar{C} dissolves in cold conc. H_2SO_4 yielding (86) (48) (87) a golden-yellow soln. with evolution of HCl (88) (86) (48) and formn. of triphenylcarbinyl hydrogen sulfate; dilution of this soln. with aq. ppts. (99% yield (86) (48)) triphenylcarbinol (1:5985).

[C dissolves in phenol with deep brown color; on dilution of the freshly prepd. soln. with aq. it becomes colorless and both HCl and triphenylcarbinol are detectable; if, however, the phenol soln. has stood for some time prior to dilution some p-tritylphenol [Beil. VI-731, VI₁-(364)], m.p. 282°, is also formed (89) (see also below under behavior of C with phenols).]

BEHAVIOR OF C WITH OTHER INORGANIC REACTANTS

WITH SALTS OF VARIOUS INORGANIC ACIDS

With Salts of Hydrogen Peroxide

[\bar{C} in acetone with 30% H₂O₂ in freezing mixt. treated with 50% KOH gives (90) trityl hydroperoxide, (C₆H₅)₃C—O—OH (isolated as its addn. cpd. with pyridine hydrochloride, viz., (C₆H₅)₃C—O—OH.C₅H₅N HCl, cryst. from alc., m.p. 133° dec.), accompanied by some triphenylcarbinol (1:5985).]

[\bar{C} in C_6H_6 with aq. Na_2O_2 as directed (91) gives (5-11% yield) bis-trityl peroxide, (C_6H_6)₃C—O—O—C(C_6H_6)₃, cryst. from hot CS₂, m.p. 185-186°, accompanied by much triphenylcarbinol; the bis-trityl peroxide is also obtainable from the trityl hydroperoxide (above) by reaction with \bar{C} in C_6H_6 on addn. of aq. alk. (90).]

With Salts of Halogen Hydrides

With alkali or alkaline-earth salts. [C with alkali fluorides seems not to have been studied; note, however, that trityl fluoride, cryst. from CCl₄, m.p. 104° (6), has been prepd. by other means, viz., from triphenylcarbinol with HF (6) or with acetyl fluoride (85).]

[\overline{C} with anhydrous CaBr₂ in C₆H₆ at room temp. for 5-6 hrs. (92) or \overline{C} with HBr in C₆H₆ at room temp. for 20 hrs. (92) is largely converted to trityl bromide [Beil. V-704, V₁-(348), V₂-(617)], m.p. 152°.]

[For study of rate of reaction of \bar{C} with KI in dry acetone at 0° see (93); note, however, that, although trityl iodide [Beil. V-706], m.p. 132°, is doubtless formed, yet more or less sepn. of I₂ and formn. of triphenylmethyl (or its reaction prods.) occurs also.]

With metal chlorides. \bar{C} with many metallic chlorides forms double salts [e.g., \bar{C} with AlCl₃ forms (19) (87) a cpd., \bar{C} .AlCl₃, dark-yellow very hygroscopic cryst. from nitrobenzene + CS₂, dec. abt. 122-125°; \bar{C} in nitrobenzene with SnCl₄ gives on addn. of dry CS₂ or.-yel. cryst. of a cpd., \bar{C} .SnCl₄ (30) (57) (87) (94); \bar{C} with SbCl₅ gives (57) a cpd., \bar{C} .SbCl₅, red cryst.; \bar{C} with BCl₃ gives a cpd., \bar{C} .BCl₃ (6), etc.].

With Salts of Hydrogen Sulfide

[\bar{C} with alc. NaSH (from alc. NaOEt satd. with H₂S) (81) cf. (95) (96), or \bar{C} with KSH in C₆H₆ (96), gives triphenylthiocarbinol [Beil. VI₁-(352)], cryst. from abs. alc. or alc. + CHCl₃, m.p. 107° (81) (95). — \bar{C} with alc. Na₂S as directed gives (21% yield (95)) bistrityl sulfide, m.p. 182° dec. — Note also that bis-trityl disulfide, cryst. from C₆H₆ + pet. ether, m.p. 157° dec. (95) [Beil. VI₁-(353)], is also known but prepd. indirectly (81) (95) (96).]

With Other Salts of Inorganic Acids

[\bar{C} with Ag₂SO₄ in liq. SO₂ (23), C₆H₆ (97), or at 120-130° for 15-20 min. (98) cf. (48) gives di-trityl sulfate [Beil. VI-717, VI₁-(351)]. — \bar{C} with AgClO₄ in nitrobenzene + C₆H₆ gives (99) trityl perchlorate [Beil. VI-717, VI₁-(351)]. — \bar{C} with AgCrO₄ in C₆H₆ gives (48) cf. (100) di-trityl chromate [Beil. VI-717]; note that this salt is also obtd. from \bar{C} with CrO₃ in C₆H₆ or CCl₄ (101).]

[\bar{C} with NaN₃ in C₆H₆ refluxed 20 hrs. gives (100% yield (102)) trityl azide [Beil. V-708, V₁-(349), V₂-(618)], colorless cryst., m.p. 64° (102), 65° (103). — For study of reaction of \bar{C} with silver hyponitrite and decompn. of the transient trityl hyponitrite see (104).]

WITH METAL OXIDES

[\bar{C} with HgO in dry C_6H_6 , ether, CS_2 , or CHCl₃ as directed (78) cf. (105) (106) gives (50-85% yield (78)) di-trityl oxide, cryst. from xylene, m.p. 237-238° (106), 235-237° (78) (105). — Note that \bar{C} with Ag_2O in C_6H_6 undergoes oxidation (cf. above); note that \bar{C} with CrO_3 in C_6H_6 or CCl_4 gives (101) di-trityl chromate [Beil. VI-717].]

WITH METALS

With alkali metals (or their amalgams). [\bar{C} in dry ether with 1% Na/Hg on shaking at room temp. (2) (8) (107) (108) (109) or \bar{C} with Na in liq. NH₃ (112) gives tritylsodium (sodium triphenylmethyl) [Beil. XVI₁-(589)]. \bar{C} with K in liq. NH₃ gives (112) tritylpotassium. — \bar{C} in dry ether with excess Li/Hg, Rb/Hg, or Cs/Hg in absence of air gives (113) corresp. trityllithium, tritylrubidium, or tritylcesium. — For behavior of \bar{C} with calcium in liq. NH₃ see (112). — In this connection note that \bar{C} in dry ether, C₆H₆, or CS₂ in absence of air and under CO₂ with molecular Ag (91) cf. (117), Hg (91), Zn (91) (114) (115), or \bar{C} with Cu bronze in C₆H₆ + EtOAc (116) or in s.t. at 80–110° in dark (117) gives triphenylmethyl (trityl); note also that \bar{C} with Zn + AcOH in the cold gives (50) triphenylmethane (1:7220) + trityl, but the same mixture if heated gives triphenylmethane + 1-benzohydryl-4-tritylbenzene [Beil. V-761], m p. 231° (118), 230° cor. (119), the latter under certain conditions attaining as high as 70% (50) (118).]

With Zn. [\bar{C} with $\frac{1}{10}$ wt. of mossy zinc refluxed in C_6H_6 for 5 hrs. gives (75) 9-phenyl-fluorene (see also above under pyrolysis of \bar{C}). — For behavior of \bar{C} with Zn in EtOAc see (120).]

With Mg (in dry ether). \bar{C} with Mg in dry ether in the pres. of I₂ as directed gives (96% yield (13)) cf. (121) of corresp. R—Mg—Cl cpd., viz., trityl—Mg—Cl [Beil. XVI-942, XVI₁-(556)]. — [The former controversy as to whether this can exist in a more reactive quinonoid structure (α) or a relatively less reactive carbonium (β) structure cannot be reported here (for references see above Beilstein citation), nor can space be taken for a full account of its reactions.] — Note, however, that this RMgCl cpd. with CO₂ gives (yields: 91% (2), 87.5% (121)) (122) (59) triphenylacetic acid [Beil. IX-712, IX₁-(309)], m.p. 264-265° dec. (122); for study of adverse influence of triphenylcarbinol or of benzaldehyde see (121).

WITH NITROGENOUS INORGANIC REACTANTS

[\bar{C} dislvd. in C_6H_6 and satd. with dry NH₃ gas (123) (124) repeatedly (125), or \bar{C} in naphthalene with dry NH₃ gas at 130° (126), gives (45% yield (126)) tritylamine (triphenylmethyl-amine) [Beil. XII-1343, XII₁-(557)], pr. from abs. alc., m.p. 102° (126), 103-104° (124), 105° (127) (corresp. B.HCl, spar. sol. aq., m.p. 244° (127)).]

[\bar{C} with NH₂OH (from NH₂OH.HCl in MeOH/NaOMe) in C₆H₆ gives (73–75% yield (3)) (128) cf. (129) N-tritylhydroxylamine [Beil. XV-33, XV₁-(11)], pr. from C₆H₆/pet. ether, m.p. 130–135° (3), 124–135° u.c. (128); for study of rearr. of this prod. see (129). — For study of N-methyl ether of this prod., viz., N-trityl-N-methylhydroxylamine (similarly prepd. from \bar{C} with N-methylhydroxylamine) see (130) (131); for study of the isomeric O-methyl ether, viz., N-trityl-O-methylhydroxylamine (from \bar{C} with methoxyamine), see (132).]

[\bar{C} with hydrazine hydrate (2 moles) in alc. at ord. temp. (232) or in dry ether under reflux (233) or in dry pyridine at 45–50° (234) gives (63% yield (234)) N,N'-di-tritylhydra-

zine $(\alpha,\alpha'$ -hydrazotriphenylmethane) [Beil. XV-582, XV_I-(184)], m.p. 212° (234), 219–220° dec. (235), often accompanied (232) (233) by some N-tritylhydrazine [Beil. XV-581, XV_I-(184)].

BEHAVIOR OF C WITH ORGANIC REACTANTS

WITH ORGANIC HYDROXY OR MERCAPTO COMPOUNDS

With Alcohols

Č with alcohols gives the corresp. ethers of triphenylcarbinol. With the lower monohydric alcs. this conversion can occur merely on solution and warming, but higher alcs. usually require htg., use of metal alcoholate, use of an acid acceptor (pyridine), etc.

With methyl alcohol. \bar{C} with MeOH (1:6120) in C_6H_6 for 10 min. (133), or \bar{C} with MeOH/NaOMe refluxed 4 hrs. (134), gives (55% yield (134)) triphenylcarbinyl methyl ether (α -methoxytriphenylmethane), cryst. from MeOH, m.p. 83.5-84° (133), 82.5-83° (134), 82.6-82.9° (134) (136), 82° (64); note, however, that this product exists in dimorphous forms; the lower-melting form just mentioned sometimes (134) (135) changes to a higher-melting form, m.p. 96.0-96.5° (134) (135); note also that the m.p. of this methyl ether close to that of the ethyl ether (see below) but that a mixed m.p. of the two is depressed (136). —[For studies of hydrolysis of the methyl trityl ether to triphenylmethane (1:7220) and formaldehyde (1:0145) see (134) (136); for prepn. of its addn. cpd., m.p. 90-91°, with PkOH see (138)]

With ethyl alcohol. \bar{C} with abs. EtOH (1:6130) on warming (1) (4) (5) (52) or even shaking 1 min. at ord. temp. (139), or \bar{C} with abs. EtOH/NaOEt (9) (56) (134) (139), gives (yields: 83% (138), 50% (134)) triphenylearbinyl ethyl ether (a-ethoxytriphenyl-methane), cryst. from abs. alc., ether, or pet. ether, m.p. 84° (5), 83° (1) (9), 81.2-81.8° (134), 81.3° (56), 81° (4). — Note that the m.p. of this prod. is almost identical with that of triphenylearbinyl methyl ether (above) but that a mixed m.p. of the two is depressed (137). — [For study of pyrolysis of this ethyl trityl ether yielding triphenylmethane (1:7220) and acetaldehyde see (134) (136); for study of its cleavage with AcCl (3:7065) (57) (46), with AlCl₃ in CS₂ (56), or with EtOH/HCl (26) see indic. refs.; for conversion with boilg. anhydrous formic acid to triphenylmethane (1:7220) see (4).]

With other monohydric alcs. $|\bar{C}|$ with n-PrOH (1:6150) in dry pyridine at room temp. for 20 hrs. (140), or \bar{C} with n-PrOH/NaO n-Pr refluxed 4 hrs. (134), gives (10% yield (134)) trityl n-propyl ether, cryst. from n-PrOH/pet. ether, m.p. 55° (140), 50.5-52.5° (134). — \bar{C} with isopropyl alc. (1:6135) in dry pyridine at room temp. for 20 hrs. (140) or \bar{C} with isopropyl alc./Na isopropylate under reflux gives (50% yield (134)) trityl isopropyl ether, m.p. 113° (140), 112.9-113.8° (134), 111.7° (56). — \bar{C} with n-BuOH (1:6180) + sodium n-butylate gives (40% yield (134)) trityl n-butyl ether, oil, b.p. 196-198° at 5 mm. (134). — For prepn. of corresp. trityl ethers from sec.-butyl alc. (1:6155) (134), isobutyl alc. (1:6200) (134), cetyl alc. (1:5945) (140), allyl alc. (1:6145) (140), benzyl alc. (1:6480) (134), cyclohexanol (1:6415) (140), see indic. refs.]

[For prepn. of corresp. trityl ethers from l-menthol (1:5940) (152) (153) (154), d-borneol (1:5990) (152) (153), or cholesterol (1:5975) (152) see indic. refs.]

[Note, however, that \bar{C} with K triphenylcarbinolate does not give the expected prod. but rather (96) p-hydroxytriphenylcarbinol in the form of its anhydride fuchsone; the expected ditrityl ether has been obtd. from \bar{C} by action of HgO (see above).]

With various important substituted monohydric alcohols. [\bar{C} with β -methoxyethanol (methyl "cellosolve") (1:6405) in pyridine gives (80-85% yield (141)) trityl β -methoxyethyl ether, m.p. 105.5-106.0° u.c. (141), 104° (142). — \bar{C} with β -ethoxyethanol ("cellosolve") (1:6410) in pyridine at 100° for 5 hrs. gives (92% yield (141)) trityl β -ethoxyethyl

ether, m.p. 79.0–79.5° u.c. (141), 77–78° (143). — $\bar{\rm C}$ with β -isopropoxyethyl alc. (isopropyl "cellosolve") (1:6413) in pyridine gives (50–60% yield (141)) trityl β -isopropoxyethyl ether, m.p. 71.0–71.5° u.c. (141). — $\bar{\rm C}$ with β -benzyloxyethyl alc. (benzyl "cellosolve") (1:6533) in pyridine gives (50–70% yield (141)) trityl β -benzyloxyethyl ether, m.p. 76–77° u.c. (141). — $\bar{\rm C}$ with β -phenoxyethyl alc. (phenyl "cellosolve") (1:6518) in pyridine gives (75–85% yield (141)) trityl β -phenoxyethyl ether, m.p. 123.5–124.0 u.c. (141).

[C with β -(β -methoxyethoxy) ethyl alc. (methyl "carbitol") (1:6458) in pyridine gives (55-60% yield (141)) trityl β -(β -methoxyethoxy) ethyl ether, m.p. 58-59° u.c. (141). — Note that the trityl ethers of β -(β -ethoxyethoxy) ethyl alc. ("carbitol") (1:6470) and of β -(β -n-butoxyethoxy) ethyl alc. (butyl "carbitol") (1:6517) are unreported.]

With various polyhydric alcohols. (For \bar{C} with carbohydrates see separate section below.)

[Č with ethylene glycol (1.6465) in pyridine may according to conditions (141) give either or both of the two possible ethers, viz., ethylene glycol monotrityl ether, m.p. 105-105.5° u.c. (141), 104.5-105.5° (144), 102-103° (143), 98-100° (140) (corresp. benzoyl deriv. m.p. 58.5-59.5° (144); corresp. p-nitrobenzoyl deriv., m.p. 155-156° (144)), and/or ethylene glycol ditrityl ether, m.p. 190° u c. (145), 187-188° u.c. (141), 185-186° (140).]

[C with propylene glycol (propanediol-1,2) (1:6455) in pyridine gives (146) propylene glycol ditrityl ether, m.p. 176.5-177.0° u.c. (146).]

[Č (2 moles) with diethylene glycol (1:6525) in pyridine gives (60-70% yield (141)) diethylene glycol ditrityl ether, m.p. 157.5-158.0° u.c. (141); note that corresp. diethylene glycol monotrityl ether has m.p. 112.5-113.5° u.c. (141).]

[C (2 moles) with triethylene glycol (1:6538) in pyridine gives (45-60% yield (141)) triethylene glycol ditrityl ether, mp. 142.0-142.5° u.c. (141); note that this prod. is dimorphous, and an unstable form, m.p. 130.5-131.5° u.c., sometimes obtd. can be converted to the stable higher-melting form by htg. at 125° or by grinding in acetone (141).]

[Č with glycerol (1:6540) may give mono-, di-, or tritrityl ethers acc. to conditions; glycerol α -monotrityl ether, m p. 93-94° (147), 92-94° (140), but also sometimes in another form of m.p. 108-110° (147) (148), 109-110° (149); glycerol α , α' -ditrityl ether, m.p. 174-177° (150), 174-176° cor. (151), 170-171° (140); glycerol α , α' , β -tris-trityl ether, m.p. 196-197° (147) (150). — Note that the relationships of these three ethers are subtle; e.g., the monoether at 180-190° is converted (147) into the α , α' -diether; the latter in turn at 260° gives (147) the triether.]

[\bar{C} (4 moles) with pentaerythritol (1:5850) in pyridine gives (145) a tetratrityl ether m.p. above 350°.]

With carbohydrates and their relatives. $\bar{\mathbf{C}}$ has recently been much employed as a tritylating agent for compounds of the carbohydrate group. This use started from the original (erroneous) impression that $\bar{\mathbf{C}}$ etherified hydroxyl groups only if the latter were primary. However, although $\bar{\mathbf{C}}$ does in general react preferentially with such primary hydroxyls, and this reaction has been proposed (155) as a means for the detection of primary alcs. in the presence of secondary and/or tertiary alcohols, yet such primary tritylation is *not* specific. Abundant evidence is already available (156) (157) (158) (159) that secondary hydroxyl groups undergo tritylation. Although the scope of this book cannot be extended to a detailed treatment of the use of $\bar{\mathbf{C}}$ as tritylating agent in the carbohydrate group, yet a few brief citations may be of service as leading references.

With various tetrahydric alcohols. [For behavior of \tilde{C} with meso-erythritol (1:5825) and pentaerythritol (1:5850) see [145].]

With various pentahydric alcohols and pentoses. [For behavior of \bar{C} with adonitol, arabitol, xylitol, fucitol, rhamnitol, and epirhamnitol see (145); with arabinose, ribose, and xylose see (160); with various derivatives of these see (158) (167) (168).]

With various hexahydric alcohols and hexoses. [For behavior of \bar{C} with mannitol (145) (161), sorbitol (145), dulcitol (162) see indic. refs.; with d-glucose (163) (164) (165), with d-galactose (165), with fructose (160) (166); with various derivs. of these see (159) (169) (152) (170) (171) (172) (173).]

With various disaccharides. [For behavior of \bar{C} with sucrose (174), maltose (174), turanose (175) see indic. refs.]

With various polysaccharides. [For behavior of C with raffinose (174), glycogen (176), starch (177), cellulose (177), and arabogalactan (178) see indic. refs.]

With thiols (for thiophenols see below). \bar{C} with mercaptans yields the corresp. trityl thioethers [e.g., \bar{C} with MeSH in dry ether or C_6H_6 gives (179) (180) trityl methyl sulfide [Beil. VI₁-(352)], lfts. from MeOH, m.p. 105° (179); \bar{C} with EtSH similarly gives (179) (180) trityl ethyl sulfide [Beil. VI₁-(353)], m.p. 125° (179). — \bar{C} with Na triphenylthiocarbinolate in alc. on htg. gives (95) ditrityl sulfide, m.p. 182° dec. (also obtd. from \bar{C} + abs. alc. Na₂S) — For tritylation with \bar{C} of SH groups in mercaptoacetic acid, α -mercaptopropionic acid (thiolactic acid), β -mercaptopropionic acid (thiohydracrylic acid, α -mercaptosuccinic acid (thiomalic acid) see (180)].

With phenols. Č with phenols (as with alcohols) gives in general the corresp. trityl ethers; however, with phenols there is a further complication in that either rearrangement of the trityl radical of the ether or direct nuclear alkylation by the trityl radical of Č (or both) may occur according to the conditions employed, the latter reaction being profoundly favored by dissociating solvents.

With phenol (or its salts). [Č with KOC₆H₆ (89) (181) cf. (182) or NaOC₆H₅ (139) (182) in dry ether gives (yields: 90% (139), 71% (181), 70% (182)) trityl phenyl ether (α-phenoxytriphenylmethane) [Beil. VI-716, VI₁-(350)], mp 103° (89) (165) (181), 102° (139) accompanied by some p-tritylphenol (4-hydroxytetraphenylmethane) [Beil. VI-731, VI₁-(364)], m.p. 282° (182), 280° (179); note that the latter, which under favorable circumstances may represent as much as 74% yield (182), may be separated from the former by use of "Claisen's alkali" (182), was originally (89) overlooked; note, also, that Č with phenol (1:1420) in pyridine at 100° for 3½ hrs. gave 28% yield (165) trityl phenyl ether, while Č with phenol at 130-140° for 4 hrs. gave (182) cf. (179) only 1.5% of this product and 98.5% of the isomeric p-tritylphenol.]

With the 3 cresols. [\bar{C} with o-cresol (1:1400) in pyridine at 110° for 5-6 hrs. (183) (181) (184) or \bar{C} with sodium o-cresolate in dry ether refuxed 2 hrs. (183) gives (yields: 31-53% (183) trityl o-tolyl ether, m.p. 112-113° (183) (181), 112 5° (184), accompanied by as much as 26% (183) of the isomeric nuclear tritylation prod., 4-trityl-2-methylphenol, m.p. 186° (185), 185° (181), 183° (183) (186), 182-183° (187); \bar{C} with sodium o-cresolate in excess o-cresol at 120° for $3\frac{1}{2}$ hrs. (183) or \bar{C} with o-cresol at 180° for 5 hrs. (181) or in pres. of $ZnCl_2$ at 180° for $\frac{1}{2}$ hr. (181) gives (33% yield (183)) 4-trityl-2-methylphenol. — Note that this latter cryptophenol was originally (181) (183) (184) supposed to possess the structure α -(o-hydroxyphenyl)- β , β , β -triphenylethane, but this erroneous view has since (186) (187) cf. (188) (189) (195) been corrected.]

[\overline{C} with the sodium salt of *m*-cresol (1:1730) in dry ether under reflux 2 hrs. gives (53% yield (185)) trityl *m*-tolyl ether, m.p. 101° (185), none of the expected nuclear tritylation prod., viz., 4(or 2)-trityl-3-methylphenol being found although the latter has subsequently (190) (186) been otherwise obtained and found to have m.p. 213-214° (190), 213° (186).]

[\overline{C} with p-cresol (1:1410) in dry pyridine at 100° for 7 hrs. (181) or 5 hrs. (191) (26) or \overline{C} with sodium p-cresolate in dry ether refluxed 2 hrs. (185) gives (yields: 80% (191), 50-60% (185)) trityl p-tolyl ether, the latter being definitely trimorphous and occurring in three forms; viz., m.p. 114° (185), 113-114° (191) (192) (26); m.p. 95° (193) (194); and m.p. 81° (181) (193) (194) (note that the lower-melting forms tend to convert to the 114°

type (194)) accompanied by a trace of a cryptophenol, presumably 2-trityl-4-methylphenol, m.p. 182° (185) (190), also obtd. (64% yield (190)) from $\bar{\rm C}$ with sodium p-cresolate in excess p-cresol at 130-140° for 3 hrs.]

With other phenols. [For further examples of nuclear tritylation of phenols by use of C with isochavibetol and isoeugenol see (196) cf. (26); with 2-hydroxynaphthoquinone-1,4 see (197). — For form. of di-trityl ethers from pyrocatechol (1:1520) (140) or from hydroquinone (1:1590) (198) see indic. refs.]

With thiophenols. \tilde{C} with thiophenol on htg. (199) or in C_6H_6 soln. on refluxing $\frac{1}{2}$ hr. (180) (179), or \tilde{C} with $NaSC_6H_6$ in ether at ord. temp. for 18 hrs. (200) (201), gives (yield alm. quant. (199) (200), 96% (180)) trityl phenyl sulfide, m.p. 106.5° (180), 106° (201), 105–106° (199) (200), 105° (179); this prod. on oxidn. with $CrO_3/AcOH$ gives (199) the corresp. sulfoxide, m.p. 163°, but is unaffected by H_2O_2 (199) [for corresp. sulfone, m.p. 175–176° (210), see below under reaction of \tilde{C} with salts of organic acids (sodium benzene-sulfinate)].

[For corresp. sulfides from \bar{C} with o-thiocresol, p-thiocresol, α -thionaphthol, β -thionaphthol, 2,4-dinitrothiophenol see (201).]

With enols or enolates. [For examples of reaction of $\tilde{\mathbf{C}}$ with the enol form of diphenylacetaldehyde (202), methyl diphenylacetate (202), or with stilbenediol bis-MgI cpd. (203) see indic. refs.]

Behavior of C with Ethers

 \bar{C} with various aliphatic ethers in the pres. of suitable catalysts yields triphenylmethane and an aldehyde [e.g., \bar{C} with diethyl ether in the pres. of AlCl₃ (56) (77), FeCl₃ (65), or ZnCl₂ (78) gives triphenylmethane and acetaldehyde; although the latter is lost by polymerization the method is standard (77) for prepn. of triphenylmethane (1:7220)].

[Note, however, that with aromatic ethers nuclear tritylation occurs: e.g., \bar{C} with anisole (1:7445) + SnCl₄ at 100-110° for 1 hr. gives (45% yield (204)) 4-tritylanisole, m.p. 200.5° (204).]

BEHAVIOR OF C WITH ORGANIC ACIDS

(For salts of organic acids see below.)

 \bar{C} with AcOH even at 13° (133) (146) cf. (50) is in equilibrium with trityl acetate (see below) + HCl. — \bar{C} with thiolacetic acid (CH₃COSH) gives trityl thiolacetate [Beil. VI-721, VI₁-(353)], m.p. 138° (179). — \bar{C} with thiolbenzoic acid (C₆H₅COSH) in toluene gives (85% yield (180)) trityl thiclbenzoate [Beil. IX-422, IX₁-(170)], m.p. 187.5-188° (180). — \bar{C} with free thiocyanic acid in C₆H₆ gives (97% yield (180)) trityl thiocyanate, m.p. 139° (180) (see also below).

BEHAVIOR OF C WITH SALTS OF ORGANIC ACIDS

C with salts of organic acids normally reacts to yield the corresp. trityl esters.

 \bar{C} with AgOAc in dry ether or C_6H_6 on shaking at room temp. (57) or in C_6H_6 refluxed 2 hrs. (46), or \bar{C} shaken with NH₄OAc in C_6H_6 at ord. temp. (205), gives trityl acetate, cryst. from AcOEt + lgr., m.p. 87-88° (46) (57). — \bar{C} with AgOBz in C_6H_6 at 60° for 4 hrs. gives (96) trityl benzoate, m.p. 165-166° (96). — Note that in analogous fashion \bar{C} might be expected to react with silver salts of *p*-nitrobenzoic and 3,5-dinitrobenzoic acids to give corresp. esters, but these are unreported.

[Č with excess dry Ag₂CO₃ in dry C₆H₆ shaken 24 hrs. gives (60-80% yield (106)) (105) ditrityl carbonate, cryst. from xylene, m.p. 209° dec. (106), 205-210° (105); this prod. on htg. in xylene in pres. of Cu pdr. decomposes (106) (105) into CO₂ and ditrityl ether, m.p. 237-238° (106) (see also above under Č with HgO).]

[C with excess Hg(CN)2 at 150-170° for 1 hr. gives (alm. 100% yield (53)) on extraction

with C_6H_6 (53) (206) (207) trityl cyanide (triphenylacetonitrile) [Beil. IX-714, IX₁-(309)], pr. from AcOH, m.p. 129° (208), 127.5° (53).]

[C with mercury fulminate in dry C₆H₆ under cooling gives (65% yield (208)) trityl cyanide oxide, (C₆H₆)₃CNO, ndls. from alc., m.p. 153-154° (208).]

[Č with KSCN in dry C₆H₆ shaken at room temp. for 2 days gives (209) trityl thiocyanate [Beil. VI-721], m.p. 137° (209) (see also above under Č with organic acids (HSCN)).]

[\bar{C} with sodium benzenesulfinate in dry ether gives (210) trityl phenyl sulfone [Beil. VI-721], lfts. from ether, m.p. 175–176° (210); note that corresp. sulfoxide (see above under behavior of \bar{C} with thiophenol) has m.p. 163°. — Similarly, \bar{C} with sodium *p*-toluenesulfinate in dry C_6H_6 gives (179) trityl *p*-tolyl sulfone [Beil. VI₁-(353)], m p. 173° (179).]

BEHAVIOR OF C WITH ORGANOMETALLIC COMPOUNDS

This topic cannot be fully expanded within the scope of this book, but the following examples will serve as leading references.

With organo-alkali compounds. [\bar{C} with L₁ n-butyl in pet. ether for 9 days gives (26% yield (211)) 1,1,1-triphenylpentane, m.p. 153-154° (211). — \bar{C} with Li C_6H_5 gives (212) free trityl isolated in form of (20% yield) ditrityl peroxide.]

[\bar{C} with Na *n*-butyl or Na trityl in liq. NH₃ + toluene (112) or \bar{C} with Na trityl in dry ether (108) gives free trityl. — \bar{C} with Na + tetraphenylethylene as directed gives (213) pentaphenylethyl.]

With RMgX compounds. \bar{C} with MeMgBr (214) or \bar{C} with MeMgI (215) gives no gas (216) cf. (217) (218) but couples giving (yields: 95% (214), 70% (215)) 1,1,1-triphenylethane (α -methyltriphenylmethane) [Beil. V-709, V₁-(350)], cryst. from alc., m.p. 94-95° (214) (215), 94.8-950° (15); note that this prod. is also obtd. from MeMgBr with trityl acetate (61% yield (219)) or from K trityl with MeI in liq. NH₃ (85-94% yield (220)).

[C with EtMgBr in dry ether reacts rapidly and quant. (221) yielding (215) not only the expected 1,1,1-triphenylpropane [Beil. V-712], m.p. 51° (215), but also (215) triphenylmethane (1:7220) and ethylene]

[C with n-PrMgBr in dry ether gives (215) not only 1,1,1-triphenylbutane, m.p. 79° (215), but also considerable triphenylmethane (1:7220). — C with iso-PrMgBr in dry ether gives (215) not only 1,1,1-triphenyl-2-methylpropane, b.p. 233-234° at 21 mm. (215), but also much triphenylmethane (1:7220)]

[\bar{C} with C_6H_5MgBr in dry ether or C_6H_6 gives a small yield (25-30% (222), 10-12% (139), 5-10% (215) (223)) tetraphenylmethane [Beil. V-738, V₁-(371), V₂-(672)], m.p. 281-282° (224) (225), b p. 431° at 760 mm. (225), but the principal product (yield: 50-77% (222), 47.4% (226)) is 4-benzohydrylbiphenyl (p-phenyltetraphenylmethane) [Beil. V-738, V₂-(672)], m.p. 111° (226), 112-113° (116); for explanation and study of this reaction see (222). — Note that \bar{C} with C_6H_5MgI behaves differently giving (227) cf. (179) triphenylmethyl and biphenyl (1:7175).]

[\bar{C} in C_6H_6 with benzyl MgCl in dry ether gives (100% yield (215)) (228) 1,1,1,2-tetraphenylethane [Beil. V-740, V₁-(372), V₂-(674)], m.p. 144° (215), 143.5-143.7° (15). — \bar{C} with benzohydryl bromide + Mg in dry ether (215) cf. (230) (or better trityl MgBr + benzohydryl bromide (229) cf. (230)) gives (90% yield (229)) pentaphenylethane [Beil. V-755, V₁-(386), V₂-(711)], m.p. in air 166-178° (229), in N₂ 182-185° (229). — \bar{C} with trityl MgCl gives (230) free trityl.]

[For behavior of C with phenylacetylenyl MgBr giving trityl-phenylacetylene or with acetylene-bis-MgBr giving di-tritylacetylene (hexaphenylbutyne-2) see (231).]

BEHAVIOR OF C WITH (ORGANIC) AMINES

(For \tilde{C} with NH₃, NH₂OH, NH₂NH₂, etc., see above under \tilde{C} with inorganic nitrogen compds; for \tilde{C} with arylhydrazines see below.)

C with Primary Amines

[Č with MeNH₂ in C₆H₆ in pres. of NaOMe gives (125) trityl-N-methylamine [Beil. XII-1344, XII₁-(557)], m.p. 73° (125) (236) (corresp. B.HCl, m.p. 216° (125)).]

With aromatic prim. amines. \bar{C} in C_6H_6 with aniline in alc. refluxed 15 min. gives (80% yield (228)) (57) N-tritylanıline [Beil. XII-1344, XII₁-(557)], cryst. from alc./ether, m.p. 149-150°, (57), 148-149° (237), 146° (228) [note that this prod. with ½ its wt. ZnCl₂ at 160° for 15 min. rearranges (228) to p-tritylaniline [Beil. XII-1348], ndls. from toluene or alc., m.p. 256° cor. (225), 249° (228); note also that \bar{C} is claimed to form with aniline an addn. cpd., m.p. 189-190° (34)].

[$\bar{\mathbf{C}}$ in $\mathbf{C}_6\mathbf{H}_6$ with o-toluidine in alc. refluxed 15 min. gives (228) N-trityl-o-toluidine, m.p. 142.5° (228), 142° (237) (238), 140–142° (57); this prod. with $\mathbf{ZnCl_2}$ at 160° for 15 min. rearranges (82% yield (189)) (228) to 4-trityl-2-methylaniline, m.p. 216° (228), 215° (189) (not to α-(2-amino)- β , β , β -triphenylethane as originally supposed (228) cf. (189)). — $\bar{\mathbf{C}}$ with m-toluidine directly has not been studied nor has the other expected product, viz., N-trityl-m-toluidine, nor its rearr. prod., been reported. — $\bar{\mathbf{C}}$ in $\mathbf{C}_6\mathbf{H}_6$ with p-toluidine in alc. refluxed 15 min. gives (228) N-trityl-p-toluidine [Beil XII-1344], m.p. 180° (228), 177–178° (85), 177° (238), 176° (237): this product with $\mathbf{ZnCl_2}$ at 190° for 30 min. does not (228) rearrange.]

[Č with p-aminobiphenyl (p-xenylamine) in C_6H_6 on htg. gives (82% yield (239)) N-trityl-p-xenylamine, pr. from C_6H_6 , m.p. 179.5-180.5° (239); note that this prod. does not rearrange]

C with Secondary Amines

With aliphatic sec. amines. $[\bar{C} \text{ with } Me_2NH \text{ in } C_6H_6 \text{ gives } (65\% \text{ yield } (240)) \text{ trityl-dimethyl-amine, cryst. from abs. alc., m.p. } 95-97^{\circ} (240), 97^{\circ} (236).]$

With aromatic sec. amines. $[\bar{C}]$ with diphenylamine might first be expected to give N-trityl-diphenylamine, ndls. from toluene, m.p. 172° (241), which has actually been prepd. by other means (241) (242) (243); however, \bar{C} with diphenylamine (244) in hot C_6H_6 (243) or pyridine (165) or the above N-trityl-diphenylamine with diphenylamine HCl in C_6H_6 or in hot AcOH directly (243) gives the rearr. prod., viz., 4-trityl-diphenylamine (4-anilinotetraphenylmethane), m.p. 242° (243) (244), 240° (165). — For use of these and related prods. as antioxidants see (244) (245). —For analogous behavior of \bar{C} with di-p-tolylamine, di-p-amylamine, and di-(p-dimethylaminophenyl)amine see (243).]

[For behavior of \tilde{C} with N,N-diphenyl-p-phenylenediamine yielding a blue meriquinoid salt, m.p. 182-183°, see (246) (247) (248); with indole and with 2-methylindole giving N-trityl derive. see (196).]

With heterocyclic sec. amines. [C with piperidine in C₆H₆ yields (179) N-tritylpiperidine, ndls. from alc., m.p. 153° (179).]

C with Tertiary Amines

With aliphatic ter-amines. [\bar{C} with Me₃N in acetonitrile + CHCl₃ at room temp. ppts. a prod., m.p. 190–195° dec. (249), of compn. $2(C_6H_5)_3COH$. (CH₃)₃ N.HCl from which extraction with aq. leaves triphenylcarbinol (1:5985), m.p. 161°, or from which extraction with C₆H₆ leaves the trimethylamine HCl. — For analogous behavior of \bar{C} with Et₃N see (249).]

With aromatic ter-amines. [C with 3 wts. dimethylaniline at 100-115° for 8 hrs. gives (42% yield (250)) 4-trityldimethylaniline (4-dimethylamino-tetraphenylmethane), cryst. from alc., m.p. 204-205° (250), 208° (251).]

With heterocyclic ter-amines. [\bar{C} with pyridine does not give a simple quaternary salt; however, \bar{C} with pyridine in nitromethane + CHCl₃ (249) or in EtOAc (249), or \bar{C} in dry pyridine with exactly 1 mole H₂O (84) (252) (165), gives a definite prod., cryst. from acetone (249) or CHCl₃ (42), m.p. 176° (42), 174° (34) (253) (165), 172–174° (84), 170–175° (249); this prod. is formulated as either (C₆H₅)₃C.OH.C₅H₅N.HCl (249) or as (C₆H₅)₃CCl.-C₅H₅N.H₂O (84) (252) (42).]

BEHAVIOR OF C WITH ARYLHYDRAZINES

With monoarylhydrazines. \bar{C} with phenylhydrazine (2 moles) in dry ether at room temp. gives (90% yield (254)) N-trityl-N-phenylhydrazine [Beil. XV-581, XV₁-(184)], cryst. from boilg. abs. alc., m.p. 136-137° (254), 148° (255). [Note that this prod. is easily oxidized (dehydrogenated), e.g., with nitrous oxides (100% yield (254), 86% (256)) or Br₂/aq. (100% yield (257)) giving tritylazobenzene (C_6H_5)₃C—N=N— C_6H_5 [Beil. XVI-85], m.p. 113-114° (254), 110° (255), 110-112° (256) (for study of thermal decompn. of this prod see (258)).]

[C with p-nitrophenylhydrazine in a large vol. C_6H_6 gives (257) cf. (256) N-trityl-N-(p-nitrophenyl)hydrazine, m.p. 170° (250)]

With diarylhydrazines. [\bar{C} with N,N-(unsym.)-diphenylhydrazine (2 moles) in C_6H_6 refluxed 20 min. gives (259) N'-trityl-N,N-diphenylhydrazine, m.p. 136–137° (259). — \bar{C} with N,N'-diphenylhydrazine (hydrazobenzene) (2 moles) in dry ether under CO_2 refluxed 16 hrs. gives (259) N'-trityl-N,N-diphenylhydrazine, m.p. 107° (259) (in this connection recall also that \bar{C} with hydrazobenzene in boilg. C_6H_6 is in part reduced (79) to triphenylmethane).]

Behavior of C with Amides

[\bar{C} (2 moles) with urea (1 mole) in dry pyridine at 100° gives (165) cf. (179) N,N'-ditritylurea, cryst. from alc. with 2 EtOH not lost on air drying, m.p. 245° (165); note that N-tritylurea (prepd. indirectly (124)) has m.p. 234–235° dec (124). — \bar{C} (1 mole) + thiourea in pyridine at 100° for 1 hr. gives (165) cf. (179) N-tritylthiourea, cryst. from C_6H_6 , m.p. 222° dec. (165), 217° (179)]

BEHAVIOR OF C WITH HYDRAZIDES

[C with free semicarbazide (NH₂CONH.NH₂) in pyridine at 0° gives (88% yield (260)) 1-tritylsemicarbazide, cryst. from abs. alc. with 1 EtOH, m.p. 186-188° dec.; the solvate alc. is lost in vac. at 110° after 6 hrs. and m.p. rises to 190-192° (260).]

[C with primary hydrazides (acylhydrazine) in general reacts to give N-trityl-N-acylhydrazines which upon suitable dehydrogenation give N-trityl-N-acyl-azo compounds; the topic cannot here be expanded but for many examples see (260) (261).]

- ① Triphenylmethane (1:7220): Ifts. from alc. [From C in anhydrous formic acid (1:1005) at 100° for 2 hrs. in 90% yield (4).]
- Triphenylcarbinol (1:5985): cryst. from C₆H₆ or alc., m.p. 161-162°. [From C on boilg, with aq.]
- Trityl methyl ether: cryst. from MeOH, m.p. 82-83°. (See text above under behavior of C with alcohols.)
- Trityl ethyl ether: cryst. from EtOH, m.p. 83-84°. (See text above under behavior of C with alcohols.)

D N-Tritylphthalimide: tbls. from alc., m.p. 172° (179). [From C with K phthalimide at 200° (179).1

3:3410 (1) Nixon, Branch, J. Am. Chem. Soc. 58, 492-498 (1936). (2) Renfrow, Hauser, Org. Syntheses, Coll. Vol. 2 (1st ed.), 607-609 (1943); 19, 83-85 (1939). (3) Stieglitz, Leech, J. Am. Chem. Soc. 36, 288-289 (1914). (4) Bowden, Watkins, J. Chem. Soc. 1940, 1333-1334. (5) Bowden, J. Chem. Soc. 1939, 312-313. (6) Wiberg, Heubaum, Z. anorg. allgem. Chem. 222, 103-106 (1935). (7) Hauser, Hudson, Org. Syntheses 23, 102-107 (1943). (8) Hauser, Hudson, J. Am. Chem. Soc. 63, 3156-3157 (1941). (9) Anderson, J. Am. Chem. Soc. 50, 211 (1928). (10) Wertyporoch, Ber. 66, 1238 (1933).

(11) Smyth, Dornte, J. Am. Chem. Soc. 53, 546 (1931). (12) Bachmann, Org. Syntheses 23, 100-102 (1943). (13) Gilman, Zoellner, J. Am. Chem. Soc. 53, 3493-3496 (1929). (14) Read, Taylor, J. Chem. Soc. 1939, 478-484. (15) Smith, Andrews, J. Am. Chem. Soc. 53, 3650 (1931). (16) Bergmann, Engel, Wolff, Z physik. Chem. B-17, 89 (1932). (17) Orndorff, Gibbs, McNulty Shapiro, J. Am. Chem. Soc. 49, 1543 (1927). (18) Gomberg, Ber. 33, 3144-3149 (1900). (19)

Norris, Sanders, Am. Chem. J. 25, 54-62 (1901). (20) Hatt, J. Chem. Soc. 1929, 2421.

(21) Chakrabarty, Dutt, J. Indian Chem. Soc. 5, 516 (1928). (22) Boeseken, Rec. trav. chim. 22. 306 313 (1903). (23) Gomberg, Cone, Ber. 37, 3544-3545 (1904). (24) Norris, J. Am. Chem. Soc. 38, 711 (1916). (25) Wang, Lee, J. Am. Chem. Soc. 66, 1113-1114 (1944). (26) Funakubo, Matsui, Ber. 70, 2437-2446 (1937). (27) Hantzsch, Ber. 54, 2590-2591 (1921). (28) Hofmann, Kirmreuther, Thal, Ber. 43, 186 (1910). (29) Gomberg, Ber. 35, 2397-2408 (1902). (30) Walden, Ber. 35, 2021-2024 (1902); Z. physik. Chem. 43, 454 (1903).

(31) Gomberg, Sullivan, J. Am. Chem. Soc. 44, 1818 (1922). (32) Bowden, Thomas, J. Chem. Soc. 1940, 1246-1247. (33) Jander, Mesech, Z. physik. Chem. A-183, 292 (1939). (34) Kraus, Rosen, J. Am. Chem. Soc. 47, 2743-2745 (1925). (35) Halford, J. Am. Chem. Soc. 53, 105-112 (1931). (36) Lifschitz, Ber. 67, 1413-1417 (1934). (37) Hantzsch, Burawoy, Ber. 67, 793-798 (1934). (38) Hantzsch, Burawoy, Ber. 66, 1435-1441 (1933). (39) Hantzsch, Burawoy,

Ber. 64, 1622-1635 (1931). (40) Burawoy, Ber. 64, 1635-1646 (1931).

(41) Lifschitz, Ber. 64, 161–182 (1931). (42) Hantzsch, Burawoy, Ber. 63, 1181–1191 (1930). (43) Recsei, Ber. 60, 2378–2388 (1927). (44) Hantzsch, Ber. 54, 2569–2572 (1921). (45) Hantzsch, Ber. 54, 2573-2612 (1921). (46) Gomberg, Davis, Ber. 36, 3924-3927 (1903). Adams, Weeks, J. Am. Chem. Soc. 38, 2519 (1916). (48) Gomberg, Ber. 35, 2400-2402 (1902). (49) Halford, Reid, J. Am. Chem. Soc. 63, 1873-1878 (1941). (50) Gomberg, Ber. 36, 379-385

(51) Clark, Streight, Trans. Roy. Soc. Canada (3) 23, III, 77-89 (1929). (52) Hemilian, Ber. 7, 1207-1208 (1874). (53) E. Fischer, O. Fischer, Ann. 194, 257-261 (1878); Ber. 11, 612-613 (1878). (54) Dilthey, Ber. 36, 924 (1903). (55) Bowden, John, J. Chem. Soc. 1939, 317. (56) Norris, Young, J. Am. Chem. Soc. 46, 2580-2583 (1924). (57) Gomberg, Ber. 35, 1829, 1834-1837 (1902). (58) Cone, Robinson, Ber. 40, 2163-2166 (1907). (59) Perrot, Compt. rend. 198, 1425 (1934). (60) Schmidlin, Hodgson, Ber. 41, 442-443 (1908).

(61) Bistrzycki, Landtwing, Ber. 41, 687-688 (1908). (62) Riddell, Noller, J. Am. Chem. Soc. 54, 292 (1932). (63) Boeseken, Rec. trav. chim. 24, 209-210 (1905). (64) Friedel, Crafts. Ann. chim. (6) 1, 497-499, 501-502 (1884). (65) Meissel, Hinsberg, Ber. 32, 2422 (1899). (66) Henne, Leicester, J. Am. Chem. Soc. 60, 865 (1938). (67) Lal, Dutt, J. Indian Chem. Soc. 12. 390 (1935). (68) Sharma, Dutt, J. Indian Chem. Soc. 12, 778 (1935). (69) Lal. Dutt. J. Indian

Chem. Soc. 9, 566 (1932). (70) Boeseken, Rec. trav. chim. 23, 101-102 (1904).

(71) Tschitschibabin, Ber. 40, 368 (1907); J. Russ. Phys.-Chem. Soc. 39, 162 (1907); Cent. 1907. II, 147. (72) Norris, Thomas, Brown, Ber. 43, 2945 (1910). (73) Hemilian, Ber. 11, 837-840 (1878). (74) Lecher, Ber. 46, 2666 (1913). (75) Gilman, Kirby, Kinney, J. Am. Chem. Soc. 51, 2259 (1929). (76) Schmidlin, Garcia-Banus, Ber. 45, 3189 (1912). (77) Norris, Org. Syntheses, Coll. Vol. 1 (2nd ed), 548-550 (1941); (1st ed.), 532-534 (1932); 4, 81-83 (1925). (78) Gomberg, J. Am. Chem. Soc. 35, 202-206 (1913). (79) Aspelund, Acta Acad. Aboensis Math. et Phys. 5, No. 1, 1-119; Cent. 1929, I 2417; C.A. 24, 4033 (1930). (80) Straus, Thiel, Ann. 525, 162-163, 172-173 (1936).

(81) Vorlander, Mittag, Ber. 46, 3450-3460 (1913). (82) Straus, Dutzmann, J. prakt. Chem. (2) 103, 15, 35, 68 (1921/2). (83) Straus, Hussey, Ber. 42, 2169-2171 (1909). (84) Rebek, Kramarsic, Ber. 62, 484, 486 (1929). (85) Blicke, J. Am. Chem. Soc. 46, 1517-1518 (1924). (86) Gomberg, Am. Chem. J. 25, 328 (1901). (87) Kehrmann, Wentzel, Ber. 34, 3815-3819 (1901). (88) Norris, Am. Chem. J. 25, 119 (1901). (89) Baeyer, Ber. 42, 2624-2625 (1909). (90) Wieland, Maier, Ber. 64, 1205-1210 (1931).

(91) Gomberg, Ber. 33, 3150-3157 (1900). (92) Straus, Ann. 370, 356-358 (1909). (93) Conant, Kirner, Hussey, J. Am. Chem. Soc. 47, 498 (1925). (94) Pfeiffer, Ann. 384, 155 (1911). (95) Vorländer, Mittag, Ber. 52, 413-415 (1919).
(96) Blicke, J. Am. Chem. Soc. 45, 1967-1969 (1923).
(97) Gomberg, Ber. 40, 1849 (1907).
(98) Anderson, J. Am. Chem. Soc. 52, 4569 (1930).
(99) Gomberg, Cone. Ann. 370, 193-194 (1909).
(100) Wienbaus, Ber. 47, 322 (1914).

(99) Gomberg, Cone, Ann. 370, 193-194 (1909). (100) Wienhaus, Ber. 47, 322 (1914).
(101) Wienhaus, Trebs, Ber. 56, 1652 (1923). (102) Bergmann, Wolff, Ber. 63, 1179 (1930).
(103) Lifschitz, Girbes, Ber. 61, 1488 (1928). (104) Spielman, J. Am. Chem. Soc. 57, 1117-1119 (1935). (105) Gomberg, Ber. 46, 225-226 (1913). (106) Halford, J. Am. Chem. Soc. 51, 2157-2158 (1929). (107) Schlenk, Ochs, Ber 49, 608-610 (1916). (108) Schlenk, Marcus, Ber. 47, 1665-1667 (1914). (109) Scheibler, Schmidt, Ber. 69, 15 (1936). (110) Bachmann, Wiselogle, J. Am. Chem. Soc. 58, 1943-1945 (1936).

(111) Morton, Stevens, J. Am. Chem. Soc. 54, 1922-1924 (1932). (112) Kraus, Kawamura, J. Am. Chem. Soc. 45, 2756-2763 (1923). (113) von Grosse, Ber. 59, 2646-2654 (1926). (114) Gomberg, Ber. 34, 2726-2729 (1901). (115) Gomberg, J. Am. Chem. Soc. 23, 496-497 (1901). (116) Schlenk, Weickel, Herzenstein, Ann. 372, 17-19 (1910). (117) Morton, Peakes, J. Am. Chem. Soc. 55, 2449-2451. (1933). (118) Ullmann, Borsum, Ber. 35, 2877-2881 (1902). (119) Gomberg, Ber. 35, 3918-3919 (1902). (120) Noiris, Culver, Am. Chem. J. 29, 129-140 (1903); Gomberg, ibid. 364-371; Norris, ibid. 609-616.

(121) Kinney, Mayhue, J. Am. Chem. Soc 53, 190-199 (1931). (122) Schmidlin, Ber. 39, 634-636 (1906). (123) Stieglitz, Vosburgh, Ber. 46, 2154 (1913). (124) Brander, Rec. trav. chim. 37, 70, 83 (1918). (125) Vosburgh, J. Am. Chem. Soc. 38, 2085, 2090 (1916). (126) Nauen, Ber. 17, 442-443 (1884). (127) Elbs, Ber. 16, 1276-1277 (1883). (128) Mothwurf, Ber. 37, 3152 (1904). (129) Stieglitz, Leech, Ber. 46, 2150 (1913). (130) Stieglitz, Leech, J. Am. Chem. Soc. 36, 297-301 (1914).

(131) Stieglitz, Stagner, J. Am. Chem. Soc. 38, 2065-2067 (1916). (132) Guthmann, Stieglitz, J. Org. Chem. 1, 31-37 (1936). (133) Straus, Hussey, Ber. 42, 2175-2176 (1909) (134) Norris, Young, J. Am. Chem. Soc. 52, 755-761 (1930). (135) Hatt, J. Chem. Soc. 1938, 484. (136) Norris, Oreswell, J. Am. Chem. Soc. 55, 4946-4951 (1933). (137) Boyd, Hatt, J. Chem. Soc. 1927, 904-905. (138) Barıl, Megrdichian, J. Am. Chem. Soc. 58, 1415-1416 (1936). (139) Gomberg, Kamm, J. Am. Chem. Soc. 39, 2010-2014 (1917). (140) Helferich, Speidel, Toeldte, Ber. 56, 766-770 (1923).

(141) Seikel, Huntress, J. Am Chem. Soc. 63, 593-595 (1941). (142) Nierenstein, Ber. 69, 1821 (1927). (143) Hurd, Filachione, J. Am. Chem. Soc. 59, 1950-1951 (1937). (144) Verkade, Tollenaar, Posthumus, Rec. trav chim. 61, 373-382 (1942), Cent. 1942, II 1339; C.A. 37, 5371 (1943). (145) Valentin, Collection Czechoslov. Chem. Commun. 3, 498-511 (1931). (146) N. Green, M. W. Green, J. Am. Chem. Soc. 66, 1610-1611 (1944). (147) Hurd, Mack, Filachione, Sowden, J. Am. Chem. Soc. 59, 1952-1954 (1937). (148) Jackson, King, J. Am. Chem. Soc. 55, 679 (1933). (149) Verkade, van der Lee, Meerburg, Rec. trav. chim. 54, 721-722 (1935). (150) Verkade, van der Lee, Meerburg, Rec. trav. chim. 56, 619-622 (1937).

(151) Helferich, Sieber, Z. physik. Chem. 175, 312-313 (1928). (152) Josephson, Ann. 493, 174-180 (1932). (153) Rule, Bain, J. Chem. Soc. 1939, 1898-1899. (154) Schmidlin, Garcia-Banus, Ber. 45, 3188 (1912). (155) Sabetay, Compt. rend. 203, 1164-1166 (1936). (156) Hockett, Hudson, J. Am. Chem. Soc. 53, 4456-4457 (1931). (157) Hockett, Hudson, J. Am. Chem. Soc. 56, 945-947 (1934). (158) Hockett, Hudson, J. Am. Chem. Soc. 56, 947-949 (1934). (159) Hockett, Fletcher, Ames, J. Am. Chem. Soc. 63, 2516-2519 (1941). (160) Zeile, Kruckenberg, Ber. 75, 1135-1138 (1942).

(161) Micheel, Ber. 65, 262-265 (1932). (162) Wolfrom, Burke, Waisbrot, J. Am. Chem. Soc. 61, 1827-1829 (1939). (163) Reynolds, Evans, Org. Syntheses 22, 56-58 (1942). (164) Helferich, Klein, Ann. 456, 222 (1926). (165) Helferich, Moog, Junger, Ber. 58, 872-886 (1925). (166) Helferich, Bredereck, Ann. 465, 180-181 (1928). (167) Smith, J. Chem. Soc. 1939, 753-755. (168) Müller, Ber. 64, 1822-1823 (1931). (169) Walters, Hockett, Hudson, J. Am. Chem. Soc. 61, 1528-1530 (1939). (170) Helferich, Bigelow, J. prakt. Chem. (2) 131, 259-265 (1931).

(171) Helferich, Becker, Ann. 449, 7-8 (1924). (172) Helferich, Klein, Schafer, Ber. 59, 81 (1926). (173) Helferich, Bauerlein, Wiegand, Ann. 447, 30-34 (1926). (174) Josephson, Ann. 472, 230-240 (1929). (175) Pacsu, J. Am. Chem. Soc. 53, 3099-3104 (1931). (176) Schmid, Kotter, Monatsh. 59, 335-340 (1932). (177) Helferich, Koester, Ber. 57, 587-591 (1924). (178) Low, White, J. Am. Chem. Soc. 65, 2430-2432 (1943). (179) von Meyer, Fischer, J. prakt. Chem. (2) 82, 521-526 (1910). (180) Biilmann, Due, Bull. soc. chem. (4) 35, 384-390 (1924).

(181) van Alphen, Rec. trav. chim. 46, 287-292 (1927). (182) Busch, Knoll, Ber. 60, 2253-2254 (1927). (183) Schorigin, Ber. 59, 2502-2508 (1926). (184) Parsons, Porter, J. Am. Chem. Soc. 54, 363-365 (1932). (185) Schorigin, Ber. 60, 2369-2372 (1927). (186) Boyd, Hardy, J. Chem. Soc. 1928, 636-637. (187) Iddles, French, Mellon, J. Am. Chem. Soc. 61, 3192-3193 (1939). (188) Iddles, Miller, Powers, J. Am. Chem. Soc. 62, 71-73 (1940). (189) Iddles, Hussey, J. Am. Chem. Soc. 63, 2768-2770 (1941). (190) Schorigin, Ber. 60, 2373-2378 (1927).

(191) Schorigin, Makaroff-Semljanski, Ber. **61**, 2519–2521 (1928). (192) von Alphen, Ber. **63**, 95, Note 13 (1930). (193) van Alphen, Ber. **61**, 276-277 (1928). (194) van Alphen, Ber. **71**, 491 (1938). (185) Iddles, Minckler, J. Am. Chem. Soc. 62, 2757-2759; (1940). (196) Funakubo, Hirotani, Ber. 69, 2123-2130 (1936). (197) Fieser, J. Am. Chem. Soc. 48, 3213 (1926). (198) Schmidlin, Wohl, Thomnen, Ber. 43, 1298-1303 (1910). (199) Knoll, J. prakt. Chem. (2) 113, 44 (1926). (200) Lecher, Ber. 48, 535 (1915).

(201) Finzi, Bellavita, Gazz. chim. ital. 62, 705-708 (1932). (202) Schlenk, Hillemann, Rodloff, Ann. 487, 145, 148 (1931). (203) Gomberg, Bachmann, J. Am. Chem. Soc. 49, 2590-2591 (1927). (204) Unger, Ann. 504, 284 (1933).
(205) Schoepfle, J. Am. Chem. Soc. 47, 1469-1471 (1925).
(206) Rupe, Gisiger, Helv. Chim. Acta 8, 343 (1925).
(207) Lifschitz, Ber. 58, 2438 (1925).
(208) Wieland, Rosenfeld, Ann. 484, 239-241 (1931).
(209) Lecher, Simon, Ber. 54, 637-638

(1921). (210) Bayer, Villiger, Ber. 36, 2789 (1903).

(211) Marvel, Hager, Coffmann, J. Am. Chem. Soc. 49, 2327 (1927). (212) Wittig, Witt, Ber. 74, 1477 (1941). (213) Schlenk, Mark, Ber. 55, 2297-2298 (1922). (214) Spath, Monatsh, 34, 2012-2013 (1913). (215) Gomberg, Cone, Ber. 39, 1463-1469, 2961-2964 (1906). (216) Kuhn, Brann, Seyffert, Furter, Ber. 60, 1154-1155 (1927). (217) Fischer, Postowsky, Z. physiol. Chem. 152, 308-309 (1926). (218) Fischer, Walter, Ber. 60, 1988-1989 (1927). (219) Fieser, Heymann, J. Am. Chem. Soc. 64, 381-382 (1942). (220) Wooster, Mitchell, J. Am. Chem. Soc. **52**, 691-692 (1930).

(221) Gilman, Peterson, Rec. trav. chim. 48, 249 (1929). (222) Schoepfle, Trepp, J. Am. Chem. Soc. 58, 791-794 (1936). (223) Freund, Ber. 39, 2237-2238 (1906). (224) Wieland, Popper, Seefried, Ber. 55, 1825 (1922). (225) Ullmann, Munzhuber, Ber. 36, 407-409 (1903). (226) Gilman, Jones, J. Am. Chem. Soc. 51, 2840-2843 (1929). (227) Schmidlin, Ber. 43, 1141-1142 (1910). (228) van Alphen, Rec. trav. chim. 46, 501-505 (1927). (229) Bachmann, J. Am. Chem. Soc. 55, 2135-2138 (1933). (230) Schmidlin, Ber. 40, 2325-2327 (1907).

(231) Wieland, Kloss, Ann. 470, 211–215 (1929). (232) Wieland, Ber. 42, 3021–3026 (1909). (233) Senior, J. Am. Chem. Soc. 38, 2720-2721 (1916). (234) Pinck, J. Am. Chem. Soc. 55, 1713 (1933). (235) Stieglitz, Brown, J. Am. Chem. Soc. 44, 1276-1277 (1922). (236) Hemilian, Silberstein, Ber. 17, 745-746 (1884). (237) Goldschmidt, Wurzschmidt, Ber. 55, 3218-3219 (1922). (238) Elbs, Wittich, Ber. 17, 705-706 (1884). (239) Schoepfle, Trepp, J. Am. Chem. Soc. 54, 4065 (1932). (240) Jones, Seymour, J. Am. Chem. Soc. 50, 1153-1154 (1928).

(241) Wieland, Ann. 381, 214–216 (1911). (242) Lewis, Bigeleisen, J. Am. Chem. Soc. 64, 2808 (1942). (243) Wieland, Dolgow, Albert, Ber. 52, 895–898 (1919). (244) Campbell (to B. F. Goodrich Co.), U.S. 1,902,115, March 21, 1933; Cent. 1933, I 3637; [C.A. 27, 3358 (1933)]; U.S. 1,950,079, March 6, 1934; Cent. 1934, II 1201; C.A. 28, 3079 (1934). (245) Sloan (to B. F. Goodrich Co.), U.S. 1,975,980, Oct. 9, 1934; Cent. 1935 II 609; [C.A. 28, 7593 (1934)]. (246) Dilthey, Escherich, Ber. 66, 782-783 (1933). (247) Dilthey, Schommer, Escherich, Ber. 65, 95-97 (1932). (248) Dilthey, Ber. 64, 1284-1285 (1931). (249) Hughes, J. Chem. Soc. 1933. 75-77. (250) Hickinbottom, J. Chem. Soc. 1934, 1703.

(251) Fischer, Luckmann, Z. physiol. Chem. 115, 93 (1921). (252) Rebek, Ber. 62, 2508-2509 (1929). (253) Helferich, Dehe, Ber. 58, 1605 (1925). (254) Gomberg, Berger, Ber. 36, 1089-1090 (1903). (255) Schlenk, Mair, Bornhardt, Ber. 44, 1175-1176 (1911). (256) Gomberg, J. Am. Chem. Soc. 20, 775-776, 785 (1898). (257) Wieland, Popper, Seefried, Ber. 55, 1822-1823, 1829 (1922). (258) Wieland, Heymann, Am. 514, 154-157 (1934). (259) Goldschmidt, Nathan, Ann. 437, 224-225 (1924). (260) Wieland, Hintermaier, Dennsted, Ann. 452, 1-34 (1927).

(261) Wieland, von Hore, Borner, Ann. 446, 31-48 (1926).

3:3415 3.4'-DICHLOROBENZOPHENONE C₁₃H₈OCl₂ Beil. S.N. 652 (m-Chlorophenyl p-chlorophenyl ketone)

M.P. 112.6-113.4° (1)

For prepn. of C from 1,1-dichloro-2-(m-chlorophenyl)-2-(p-chlorophenyl)ethylene (3:9863) by oxidn. with CrO_3 (41% yield) see (1).]

① 3.4'-Dichlorobenzophenone 2,4-dinitrophenylhydrazone: m.p. 258-260° (1).

3:3415 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., J. Am. Chem. Soc. 67, 1601-1602 (1945).

3:3420 5,8-DICHLORONAPHTHOL-1



C₁₀H₆OCl₂

Beil. VI - 613 VI₁---VI₂---

M.P. 114-115° (1)

Cryst. (from CS₂) (1). — Spar. sol. hot aq. (1).

[For prepn. (in very poor yield) from γ -(2,5-dichlorophenyl)paraconic ac. [Beil. XVIII-422] by distn. see {1}.]

Č with FeCl₃ gives a white turbidity, changing on warming to flocculent violet ppt. (1). Č in alk. soln. coupled with diazotized naphthionic acid (1-naphthylaminesulfonic acid-4) gives dark violet color (1).

[For use in dyestuff industry see (2) (3) (4).]

 \oplus 5,8-Dichloro-1-naphthyl acetate: yellowish pr. from CS₂ + lgr., m.p. 144-145° (1).

3:3420 (1) Erdmann, Schwechten, Ann. 275, 285 (1893).
 (2) Aktien Ges. für Anilin Fabrikation, French 517,558, May 7, 1921; Cent. 1921, IV 194.
 (3) Soc. Chem. Ind. Basel, French 593,751, Aug. 31, 1925; Cent. 1926, I 1048.
 (4) Soc. Chem. Ind. Basel, Swiss 185,148, Sept. 16, 1936; Cent. 1937, I 1561.

3:3432 CHLOROMALEIC ACID CI—C—COOH $C_4H_3O_4Cl$ Beil. II - 752 Π_1 — Π_2 -(646)

M.P. 115° (1) (2) 114-115° (3) (4) [108° after sintering at 95° (5) (6)]

[See also chlorofumaric acid (3:4853).]

Cryst. from AcOH/CHCl₃, ether/CHCl₃, ether/pet. ether, or ether alone. — Eas. sol. alc., ether, AcOH; spar. sol. CHCl₃ or C₆H₆; insol. pet. ether.

[For prepn. of \bar{C} from $meso-\alpha,\alpha'$ -dichlorosuccinic acid (3:4930) with NaOAc/dil. AcOH on boilg. (5) (1), or from its neutral sodium salt in aq soln. on boilg. ½ hr. (4), see indic. refs.; from chloromaleic anhydride (3:0280) by hydrolysis with aq. and subsequent evapn. see (4) (5) (6) (7); from 3,5,5,5-tetrachloro-4-ketopenten-2-oic acid-1 (" β -(trichloroacetyl)- β -chloroacrylic acid") [Beil. III-733] on 24 hr. stdg. at room temp. of its soln. in excess 10% aq. Na₂CO₃ see (6); from chloromaleonitrile (b.p. 185° at 753 mm., 71.0-71.5° at 10 mm., $D_4^{20} = 1.2293$, $n_D^{20} = 1.48944$ (9)) by. hydrol. see (9).]

C on htg. at 180° loses H₂O yielding (6) chloromaleic anhydride (3:0280).

Č although unchanged by conc. HCl at ord. temp. for as long as 10 days (4) is by repeated evapn, with conc. HCl (7) isomerized to chlorofumaric acid (3:4853).

 \bar{C} in aq. soln. with Zn filings is dehalogenated yielding (4) fumaric acid (1:0895); \bar{C} (as Na₂ \bar{A}) in aq. soln. with 1% Na/Hg gives (4) mainly succinic acid (1:0530) accompanied by some fumaric acid (1:0895).

C readily reduces aq. KMnO₄.

[C readily combines with Br₂ if heated in s.t. to 100° (7).]

Č behaves normally as a dibasic acid: cg, titration with standard dil. aq. alk. gives Neut. Eq. 75.3; for study of electrometric titration see (1).

[Salts: KHĀ, eas. sol. aq. (dif. from corresp. salt of chlorofumaric acid (3:4853)), e.g., 100 g. of its satd. aq. soln. at 15° cont. 29.2 g. of KHA (7); for crystallographic data see (7).

332

— NaH \bar{A} .3H₂O, eas. sol. aq. (7). — Ag₂ \bar{A} , insol. aq. (7). — Ba \bar{A} .2H₂O (4) (5) (6), spar. sol. aq. — Ca \bar{A} .4H₂O (4). — Sr \bar{A} .4½H₂O, spar. sol. cold aq. (5). — Pb \bar{A} , insol. aq. (4).]

[\bar{C} on stdg. at ord. temp. with slight excess 0.76 N aq. KOH gives chlorine ion only $\frac{1}{2}$ as rapidly (4) as the isomeric chlorofumaric acid (3:4853).]

The acid chloride corresp. to \bar{C} , viz., chloromaleyl (di)chloride (3:6158) q.v., has been reported only by indirect means.

- Dimethyl chloromaleate: oil (see 3:9351).
- —— Diethyl chloromaleate: oil (see 3:6697).
- Chloromaleanii [N-phenyl-chloromaleimide]: ndls. from boilg. alc., m.p. 170° (8). [From aniline salt of C̄ (or of chlorofumaric acid) on htg. for a few minutes at 170–180° (8); note that this prod. on htg. with aniline yields (8) α-anilinosuccinanil [Beil. XXI-554, XXI₁-(432)], yel. cryst. from acetone + C₆H₆, m.p. 232° (8), and that a little of this latter cpd. which may accompany the former is readily removed from it by washing with warm C₆H₆ (8).]
- © Chloromaleic p-chloroanil [N-(p-chlorophenyl)chloromaleinimide]: pl. from hot alc., m.p. 175° (8). [From p-chloroaniline salt of \(\tilde{\C}\) on htg. for a few minutes at 170-180° (8).]
- © Chloromaleic p-bromoanil [N-(p-bromophenyl)chloromaleinimide]: microcrystn. powder from boilg. alc., m.p. 190° (8). [From p-bromoaniline salt of C on htg. for a few minutes at 170–180° (8).]

3:3432 (1) Ashton, Partington, Trans. Faraday Soc. 30, 602, 605 (1934). (2) Stelling, Z. physik. Chem. B-24, 410, 424 (1934). (3) Langseth, Z. physik. Chem. 118, 54 (1925). (4) Michael, Tissot, J. prakt. Chem. (2) 52, 306-308, 321, 331-334 (1895). (5) van der Riet, Ann. 280, 224-230 (1894). (6) Zincke, Fuchs, Ber. 26, 506-509 (1893). (7) Perkin, J. Chem. Soc. 53, 706-708 (1888). (8) Chattaway, Parkes, J. Chem. Soc. 125, 466 (1924). (9) Mommaerts, Bull. classe sci., Acad. roy Belg. (5) 27, 579-597 (1944); Cent. 1943, I 615-616; C.A. 38, 3621 (1944).

3:3445 2.7-DICHLORONAPHTHALENE

Cryst. from alc or C6H6; sublimes under reduced press. — Eas. sol. boilg. alc.

[For prepn. of \bar{C} from naphthalene-2,7-bis-(sulfonyl chloride) [Beil. XI-217] (4) (1), from 7-chloronaphthalene-2-sulfonyl chloride [Beil. XI-181] (4) (5), from 7-bromonaphthalene-2-sulfonyl chloride [Beil. XI-184] (7), from sodium 7-hydroxynaphthalenesulfonate-2 [Beil. XI-285, XI₁-(67)] (3) by htg. with PCl₅ as directed, see indic. refs.; from 7-sulfonaphthylamine-2 [Beil. XIV-763, XIV₁-(736)] by treatment of the corresp. diazonium chloride with PCl₅ in POCl₃ see (8); from 3,6-dichloronaphthalimide or 3,6-dichloronaphthalic acid (3:4870) with HgO + aq. in s.t. 6 hrs. at 200-210° see (10).]

 $\ddot{\mathbf{C}}$ on oxidn. with dil. HNO₃ (D=1.21) in s.t. at 140° yields (9) 4-chlorophthalic acid (3:4390), m.p. 157°.

[C on mononitration yields (9) a prod., m.p. 141.5-142°.]

[C on treatment with chlorosulfonic acid in CS₂, followed by conversion as directed (11), yields mixt. of two sulfonic acids; the major prod is 2,7-dichloronaphthalenesulfonic acid-3 (corresp. sulfonyl chloride, m.p. 166°, corresp. sulfonamide, m.p. 218° (12)), the minor prod. (10% of total) is 2,7-dichloronaphthalenesulfonic acid-4 (corresp. sulfonyl chloride, m.p. 152°) (11).]

3:3445 (1) Weissberger, Sängewald, Hampson, Trans. Faraday Soc. 30, 890 (1934). (2) Krollpfeiffer, Ann. 430, 198 (1923). (3) Bayer, Duisberg, Ber. 20, 1432 (1887). (4) Cleve, Bull. soc. chim. (2) 26, 244-245 (1876). (5) Armstrong, Chem. News 58, 295 (1888). (6) Armstrong, Wynne, Chem. News 59, 189 (1889). (7) Sindall, Chem. News 60, 58 (1889). (8) Erdmann, Ann. 275, 280 (1893). (9) Alén, Bull. soc. chim. (2) 36, 433 (1881). (10) Dziewonski, Majewicz, Schimmer, Bull. intern. acad. polon. sci., Classe scr. math. nat. 1936-A, 43-45; Cent. 1936, II 4214; C.A. 31, 3906 (1937).

(11) Turner, Wynne, J. Chem. Soc. 1941, 256. (12) Armstrong, Wynne, Chem. News 61, 274 (1890).

3:3448 3,4,5-TRICHLOROCATECHOL OH
$$C_0H_3O_2Cl_3$$
 Beil. VI - 783 (3,4,5-Trichloropyrocatechol) OH VI_1 -(389) VI_2 —

M.P. 115° (1) Abt. 106-109° (2) 104-105° (3)

Note that the prod. for which the above m.p.'s are recorded is actually a monohydrate, viz., $\bar{C}.H_2O$, which in vac. over H_2SO_4 (3) or at 70° (1) loses $\frac{1}{2}$ H_2O giving a hemihydrate, pr. from C_6H_6 , m.p. $134-135^\circ$ (3) (1).

C (as monohydrate) cryst. from AcOH in colorless pr.; insol. cold aq. but sol. in alc., ether, or AcOH.

[For prepn. of \tilde{C} (as monohydrate) from catechol (1,2-dihydroxybenzene) (1:1520) in AcOH soln. with Cl₂ (3) or ICl (1) see indic. refs.; from 4,5-dichlorocatechol (3:3525) in AcOH soln. with Cl₂ see (2).]

[C with excess Cl₂ gives (3) 3,4,5,6-tetrachlorocatechol [Beil. VI-784, VI₁-(389)], anhydrous cryst. from hot dil. alc. or lgr., m.p. 194-195° (4), 193-194° (1); trihydrate, m.p. 94° (2); 1:1 mol. cpd. with AcOH, m.p. 123-124° (2).

C with FeCl₃ gives (3) green coloration.

- 3,4,5-Trichlorocatechol dimethyl ether (3,4,5-trichloroveratrole): m.p. 68-69° (5). [From Č by methylation (no details) (5)] [Note that two mono methyl ethers of Č are known, one m.p. 114-115° (5), the other, m.p. 107-108° (6), both obtained indirectly.]
- --- 3,4,5-Trichlorocatechol diethyl ether: unreported.
- --- 3,4,5-Trichlorocatechol diacetate: unreported.
- --- 3.4.5-Trichlorocatechol dibenzoate: unreported.

3:3448 (1) Jackson, Boswell, Am. Chem. J. 35, 526-529 (1906). (2) Willstatter, Müller, Ber. 44, 2185-2186 (1911). (3) Cousin, Bull. soc. chm. (3) 13, 719-720 (1895); Ann. chim. (7) 13, 483-486 (1898). (4) Zincke, Küster, Ber. 21, 2729 (1888). (5) Cousin, Ann. chim. (7) 29, 60-62 (1903). (6) Peratoner, Ortoleva, Gazz. chim. ital. 28, I 230-231 (1898).

3:3460 2,3,5,6-TETRACHLOROPHENOL OH
$$C_6H_2OCl_4$$
 Beil. VI — VI_1 — VI_2 -(182)

M.P. 115° (1) (2) (3)

Cryst. from pet. eth.

[For prepn. of C from 2,3,5,6-tetrachloroaniline (1) (4) via diazotization and reaction with aq. in pres. of H₂SO₄ (1) or CuSO₄ (18% yield (3)) see indic. refs.; for formn. of C

from pentachlorobenzene (3:2290) with N/2 MeOH/NaOMe at 180° in s.t. for $7\frac{1}{2}$ hrs. (note that some of the iosmeric 2,3,4,5-tetrachlorophenol (3:3523) is also formed) see (1).]

 \overline{C} in aq. behaves as a fairly strong acid, K at $25^{\circ} = 3.3 \times 10^{-6}$ (2), and can be directly titrated with N/10 aq. NaOH (3) (1), Neut. Eq = 232.

- \bar{C} (1 wt. pt.) added to HNO₃ (D=1.5, 6 wt. pts.) in 20 pts. AcOH at 10°, and after 1 hr. poured onto ice, gives (65% yield (4)), 2,3,5,6-tetrachloro-4-nitrophenol, ndls. from AcOH, m.p. 148-149° dec. (4) (corresp. acetate, ndls. from dil. alc., m.p. 113-114° (4)).
 - 2,3,5,6-Tetrachlorophenol methyl ether (2,3,5,6-tetrachloroanisole): ndls. from alc., m.p. 88° (1). [From C with alk. + Me₂SO₄ (1).] [Note that this prod. on nitration with 4-5 wt. pts. HNO₃ (D = 1.5) at 0° gives (95% yield (4)) 2,3,5,6-tetrachloro-4-nitroanisole, ndls. from dil. alc., m.p. 112-113° (4)]

 - ---- 2,3,5,6-Tetrachlorophenyl acetate: unreported
 - **② 2,3,5,6-Tetrachlorophenyl benzoate:** m p. 136° (5). [From \bar{C} + large excess BzCl in aq. alk. (5).]
 - **2.3.5.6-Tetrachlorophenyl** N-phenyl carbamate: unreported.
- 3:3460 (1) Holleman, van der Hoeven, Rec. trav. chim. 39, 746-748 (1920). (2) Tiessens, Rec. trav. chim. 48, 1068 (1929). (3) Tiessens, Rec. trav. chim. 50, 116, 119 (1931). (4) Peters, Rowe, Stead, J. Chem. Soc. 1943, 233-235. (5) Bures, Kovarovicova, Časopis Českoslov. Lékárnictva 10, 197-202, 233-239 (1930); Cent. 1930, II 2775; C.A. 25, 1816-1817 (1931).

3:3470 1,2,4,4,6,6-HEXACHLORO-CYCLOHEXEN-1-DIONE-3,5 ("Hexachlororesorcinol")

 $\begin{array}{cccc} O & & C_6O_2Cl_6 & & Beil.\,VII - 572 \\ & & & & VII_1 - \\ Cl & & & & & \\ Cl & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ &$

M.P. 115° (1) B.P. 159-160° at 13-15 mm. (1)

Colorless tbls. or thick pr. (from AcOH or ether/pet. ether). — Penetrating lachrymatory odor. — \bar{C} can be distd at atm. press. without decompn. — Eas. sol. ether, CHCl₃, C₆H₆, spar. sol. pet. ether. — Readily forms supersatd solns.

[For prepn. from 3,5-dihydroxybenzoic acid [Beil. VI-404] by actn. of Cl₂ in AcOH see (1)] \bar{C} with KI in AcOH liberates I₂ (1). — \bar{C} with SnCl₂ in AcOH reduces smoothly (1) to tetrachlororesorcinol (3:4135), m.p. 141° (1).

[For use as seed disinfectant see (2); for other reactions see (1).]

3:3470 (1) Zincke, Fuchs, *Ber.* **24**, 2689-2690 (1892). (2) Bonrath, Urbschat (to I.G.), Ger 534,597, Sept. 29, 1931; *Cent.* **1931**, II 3143.

CHAPTER IX

DIVISION A. SOLIDS

(3:3500-3:3999)

3:3500 6-CHLORONAPHTHOL-2

M.P. 115° (1) (2) (3) (4)

Ndls. from hot aq (1) (2); sol. alc., ether, AcOH, C₆H₆, CHCl₃, CS₂. — Sublimes in prisms. — \bar{C} depresses m.p. of 8-chloronaphthol-2 (3:2965), m.p. 101° to 79-88° (2).

[For prepn. of \bar{C} from 1,6-dichloronaphthol-2 (3:3600) with FeSO₄ + NaOH see (4); from 6-chloronaphthol-2-sulfonic acid-4 (2) (3) with Na/Hg in dil. HCl see (2) (3); from K salt of 2-naphtholsulfonic acid-6 [Beil. XI-282, XI₁-(66)] with 3 moles PCl₅ at 165° as directed see (1) (2)]

 $[\bar{C}$ (as dry sodium salt) with CO₂ under press and at elevated temp. yields (5) 6-chloro-2-hydroxynaphthoic acid-3, yel. lfts. from AcOH, m.p. 260° (5).]

 \bar{C} on oxidn, with dil HNO₃ ($D=1\,13$) in s.t. at 190–200° gives (6) 4-chlorophthalic acid (3:4390).

- © 6-Chloro-2-naphthyl benzoate: mp. 124-125° (3).
- **©** 6-Chloro-2-naphthyl m-nitrobenzoate: ndls. from much alc., m.p. 146-147° (2). [From \tilde{C} dislyd in 10% NaOH at 50-60° and shaken with m-nitrobenzoyl chloride (2).]

3:3500 (1) Claus, Zimmermann, Bcr 14, 1483-1485 (1881). (2) Ruggli, Knapp, Merz, Zimmermann, Helv. Chim. Acta 12, 1048-1050 (1929). (3) Battegay, Silbermann, Kienzle, Bull. soc. chim. (4) 49, 721 (1931). (4) Herzberg, Spengler, Schmid (to I.G.), Ger. 431,165, June 30, 1926; Cent 1926, II 1196. (5) Lange, Luce, Jacobs (to I.G.), Ger. 564,128, Nov. 14, 1932, Cent. 1933, II 446. (6) Claus, Dehne, Bcr 15, 321 (1882).

3:3505 4-CHLORO-3,5- OH C_8H_9OCl Beil. VI — VI₁— VI₂—(463)

Cryst. from benzene.

[For prepn of \tilde{C} from 3,5-dimethylphenol (m-5-xylenol = sym.-m-xylenol) (1:1455) with SO_2Cl_2 (1 mole) in CHCl₃ (1) or with Cl_2 in AcOH (66% yield (2)) or from crude coaltar fraction consisting mainly of 3,5-dimethylphenol with Cl_2 or SO_2Cl_2 (5) see indic. refs. (note that some 2-chloro-3,5-dimethylphenol (6-chloro-m-5-xylenol) (3:0844) is formed as a by-product (1) (5); also that 3,5-dimethylphenol in AcOH on complete saturation

with Cl₂ gives (2) 2,4,4,6-tetrachloro-3,5-dimethylcyclohexadien-2,5-one-1, m.p. 106-107°

(2)).]

C and its derivatives have attracted much attention as antiseptics, disinfectants, preservatives, bactericides, fungicides, etc. [e.g., for studies from various aspects of bactericidal properties of C see (4) (6) (7) (8) (9) (10) (11) (12) (13) (14) (15) (16); for studies on use as fungicide in leather (17) (18) including toxicity (19) see indic. refs.].

[For patents on use of C for improving wettability of materials (20), or for use with soaps, etc., as disinfectant (21), as component of mixtures for insecticides (22) see indic. refs.

[For study of fate of C in animal and human metabolism see (23).]

[For study of tests for detection of \bar{C} see (24); for studies of quant. detn. of \bar{C} (3) (25) in urine, blood, or tissue (26) see indic. refs.]

CHEMICAL BEHAVIOR OF C

NUCLEAR SUBSTITUTION

Halogenation. [C̄ with Cl₂ (1 mole) (used in form of N-chloroacetamide (27)) gives 2,4-dichloro-3,5-dimethylphenol (2,4-dichloro-m-5-xylenol) (3:2182), m.p. 83°; C̄ with Cl₂ (2 moles) should give 2,4,6-trichloro-3,5-dimethylphenol (trichloro-m-5-xylenol) (3:4713), m.p. 177°, although such prepr. of the latter is not actually reported; for action of excess Cl₂ in AcOH see note above under prepr. of C̄.]

C with Br₂ (2 moles) in AcOH gives (1) 2,6-dibromo-4-chloro-3,5-dimethylphenol, ndls., m.p. 158° (1).

Nitration. \bar{C} on mononitration with conc. HNO₃ in AcOH gives (28) (2) 4-chloro-2-nitro-3,5-dimethylphenol, m.p. 90° (28), 87-89° (2) (corresp. methyl ether, m.p. 166°; corresp. ethyl ether, m.p. 107° (28)). — Note that the dinitro deriv. of \bar{C} , viz., 4-chloro-2,6-dinitro-3,5-dimethylphenol, appears to be unreported.

Mercuration. [For study of mercuration of C see (29); for patents see (30).]

Alkylation. \bar{C} with alcs. in pres. of ZnCl₂ at 80° undergoes nuclear alkylation (perhaps by rearr. of intermediate ethers). [E.g., \bar{C} with isopropyl alc. (1:6135) gives (9) (32) 4-chloro-3,5-dimethyl-2-isopropylphenol, b.p. 125° at 3 mm., \bar{C} with diethylcarbinol (1:6175) gives (9) (32) 4-chloro-3,5-dimethyl-2-(diethylmethyl)phenol, b.p. 141–142° at 3 mm.; etc. — \bar{C} (as Na \bar{A}) with benzyl chloride (3:8535) in toluene gives (33) 4-chloro-3,5-dimethyl-2-benzylphenol (5-chloro-4,6-dimethyl-2-hydroxydiphenylmethane), m.p. 68.7°, b.p. 182–185° at 4 mm., etc.]

Other nuclear substitutions. [For behavior of \bar{C} with o-nitrophenylsulfenyl chloride see (34) (35) (36).]

[$\tilde{\mathbf{C}}$ with hexamethylenetetramine htd. with glycerol + boric acid, then hydrolyzed with conc. H₂SO₄, all as directed (38), gives (27% yield) 4-chloro-3,5-dimethyl-2-aldehydophenol (5-chloro-4,6-dimethylsalicylaldehyde), m.p. 96° (corresp. oxime, m.p. 197°); note that $\tilde{\mathbf{C}}$ with CHCl₃ + aq. NaOH (Reimer-Tiemann process) gives only 10% yield and prod. is dif. separable (38).]

OTHER REACTIONS OF C

[Č (1 mole) with ethyl acetoacetate (1 mole) + conc. H₂SO₄ gives (35% yield (37)) 6-chloro-2,5,7-trimethylchromone, m.p. 145-146° cor.; note that the isomeric 6-chloro-4,5,7-trimethylcoumarin, m.p. 194-195.5° cor., which might be expected in the above condensation has been obtd. indirectly (37).]

^{—— 4-}Chloro-3,5-dimethylphenol methyl ether: m.p. 22.5-23.5°, b.p. 117° at 14 mm. (2).

- ---- 4-Chloro-3,5-dimethylphenol ethyl ether: unreported.
- ① 4-Chloro-3,5-dimethylphenol benzyl ether: m.p. 57° (28). [Note that nitration of this ether gives 4-chloro-2-nitro-3,5-dimethylphenol benzyl ether, m.p. 105° (28).]
- 4-Chloro-\$\overline{3}\$,5-dimethylphenyl acetate: m.p. 48.7° (9), 48° cor. (37), b.p. 102° at 2.5 mm. (9). [From \$\overline{C}\$ + Ac₂O + trace H₂SO₄ (93% yield (37)); for study of Fries rearr. of this ester with AlCl₃ to 4-chloro-3,5-dimethyl-2-acetylphenol methyl ether see (37).]
- ---- 4-Chloro-3,5-dimethylphenyl benzoate: unreported.
- 3:3505 (1) Lesser, Gad, Ber. 56, 974, 976 (1923). (2) von Auwers, Mürbe, Saurwein, Fortschr. Chem. Physik. u. physik. Chem. 18, No. 2, 1-45 (1924); Cent. 1924, II 2267; C.A. 19, 2339 (1925). (3) McNicoll, Merritt, West, Analyst 64, 261-262 (1939); C.A. 33, 4160 (1939). (4) Heicken, Angew. Chem. 52, 263-265 (1939). (5) Gladden, Cocker, U.S. 2,350,677, June 6, 1944; C.A. 38, 4964 (1944), Brit. 529,070, Nov. 13, 1940; C.A. 35, 7982 (1941). (6) Lebduska, Pidra, Zentr. Bakt. Parasitenk. I Abt., Orig. 145, 425-438 (1940); C.A. 25, 8008 (1941). (7) Lockemann, Heicken, Zentr. Bakt. Parasitenk. I Abt., Orig. 145, 61-71 (1939); C.A. 34, 2534 (1940). (8) Heading, Pharm. J. 138, 321-322 (1937); Chemist and Druggist 126, 392-393 (1937); Cent. 1937, II 2208; C.A. 31, 8119 (1937). (9) Klarmann, Shternov, Gates, J. Am. Chem. Soc. 55, 2576-2589 (1933). (10) Lockemann, Kunzmann, Angew. Chem. 46, 296-301 (1933).
- (11) Rapps, J. Soc. Chem. Ind., 52-T 175-176 (1933); Cent. 1933, İI 1047, C.A. 27, 3967 (1933). (12) Lockemann, Ulrich, Z. Hyg. Infektionskrankh. 113, 475-481 (1932); Cent. 1932, II 99. (13) Etinger-Tulezynska, Ulrich, Z. Hyg. Infektionskrankh. 113, 437-444 (1932); Cent. 1932, II 77; C.A. 26, 2551 (1932). (14) Kliewe, Rabenau, Prakt. Desinfektor 31, 67-71 (1939); Cent. 1939, II 1532; C.A. 35, 3766-3767 (1941). (15) Alchin, Chem. Products 2, 93-95 (1939); C.A. 33, 7961 (1939). (16) Lum. Pharm. J. 138, 76 (1937). Cent. 1937, II 2208; C.A. 31, 8118 (1937). (17) Greene, Lollar, J. Am. Leather Chem. Assoc. 39, 209-218 (1944); C.A. 38, 6595 (1944). (18) Seldowitz, Arch. Dermatol. Syphiol. 42, 576-586 (1940); C.A. 35, 1509 (1941). (19) Lollar, J. Am. Leather Chem. Assoc. 39, 203-209 (1944); C.A. 38, 6594 (1944). (20) Chapman (to Monsanto Chem., Ltd.), U.S. 2,062,504, Dec. 1, 1936; Cent. 1937, I 2302; C.A. 31, 890 (1937); Brit. 431,645, Aug. 8, 1935, Cent. 1935, II 4001; [C.A. 28, 8258 (1935)].
- (21) Deutsche Hydriewerke, A.G., French 823,289, Jan. 18, 1938; Cent. 1938, I 2588; [C.A. 32, 5582 (1938)]. (22) Dispersoid Syndicate, Ltd., French 569,912, April 19, 1924; Cent. 1925, I 1125; not in C.A. (23) Zondek, Shapiro, Biochem. J. 37, 592-595 (1943), C.A. 38, 2393 (1944). (24) Rosenthaler, Pharm. Ztg. 78, 229-231 (1933); Cent. 1933, I 3990. (25) Merritt, West, Analyst 63, 257-261 (1938); C.A. 32, 4279 (1938). (26) Zondek, Shapiro, Hestrin, Biochem. J. 37, 589-591 (1943); C.A. 38, 2677 (1944). (27) Jones, J. Chem. Soc. 1941, 275. (28) Jones, J. Chem. Soc. 1943, 445. (29) Bordeianu, Ann. sci. univ. Jassy, Pt. I, 23, 240-264 (1937); Cent, 1938, I 61, C.A. 32, 5802 (1938). (30) Christiansen, Moness (to Squibb and Sons), U.S. 2,137,236. Nov. 22, 1938; Cent. 1939, I 5007; C.A. 33, 1886 (1939).
- (31) Christiansen (to Squibb and Sons), U.S. 2,252,705, Aug. 19, 1941; C A. 25, 7657 (1941). (32) Klarmann, Gates (to Lehn and Fink, Inc.), U.S. 1,938,912, Dec. 12, 1933; Cent. 1934, I 2006 [C.A. 28, 1472 (1934)]. Brit. 432,955, Sept. 5, 1935; Cent. 1936, I 809; [C.A. 30, 575 (1936)]. (33) Klarmann, Gates (to Lehn and Fink, Inc.), U.S. 1,926,874, Sept. 12, 1933; Cent. 1934, I 83; [C.A. 27, 5896 (1933)]. (34) Kent, Smiles, J. Chem. Soc. 1934, 424, 428. (35) Learmonth, Smiles, J. Chem. Soc. 1936, 327-328. (36) McClement, Smiles, J. Chem. Soc. 1937, 1016-1021. (37) Adams, Mecorney, J. Am. Chem. Soc. 66, 802-804 (1944). (38) Duff, J. Chem. Soc. 1941, 548-549.

[Note that, in addition to its ordinary use to designate \bar{C} specifically, the term "chloralide" is also used generically to denote a class of compounds formed by condensation of chloral (3:5210) with α -hydroxy acids]

Cryst. from alc. or ether; eas. sublimable; insol. aq; eas. sol. hot but spar. sol. cold alc.; eas. sol. ether; eas. sol. in 80% AcOH (dif. and sepn. from metachloral (1)). — For crystallographic studies see (10).

Note that m.p. of \bar{C} is almost identical with that of α -parachloral, m.p. 116°, but that mixed m.p. of the two is depressed as low as 85–90° (2); β -parachloral, however, has m.p. 152° (2).

[For prepn. of $\bar{\mathbb{C}}$ from chloral (3:5210) or chloral hydrate (3:1270) with cone. or fumg. H_2SO_4 (yields: 61% (11), 44–51% (4) both based on chloral hydrate) see (11) (4) (8) (12) (6); for form. of $\bar{\mathbb{C}}$ from chloral hydrate with H_2SO_4 as a by-product (abt. 2% (2)) in prepn. of α - and β -parachloral + metachloral, or from chloral by warming with AlCl₃ (1), see indic refs.; for formn. of $\bar{\mathbb{C}}$ from chloral with ClsO₃II as by-prod. of prepn. of octachlorodiethyl ether (3:0738) see (3); for formn. of $\bar{\mathbb{C}}$ from chloral (excess) with β,β,β -trichloro- α -hydroxypropionic acid (trichlorolactic acid) [Beil. III-286, III₁-(111), III₂-(210)] in s.t. at 150–160° see (4) (13) of (17).]

[$\bar{\mathbf{C}}$ on reduction with Zn + HCl in alc. soln. gives according to conditions very small amts. of β,β -dichloroacrylic acid (3:1875) (14) (15) (16), β -chloroacrylic acid (3:2240) (11), and acetaldehyde (1.0100) (15) (16).] — [$\bar{\mathbf{C}}$ is unaffected by boilg HNO₃ (8).]

[$\ddot{\mathbf{C}}$ with PCl₅ in s t. at 270–290° for several days gives (18) (9) 5-chloro-2,5-bis-(trichloromethyl)dioxolane-1,3-one-4 ("trichlorolactic acid-tetrachloroethylidene ether-ester") [Beil. XIX-105], oil, b p. 276° (18), $D_4^{20}=1.7426$ (18).]

Č with boilg. alkalies undergoes hydrolytic cleavage yielding (4) (12) (6) (7) chloroform (3:5050) and salts of formic acid (1:1005).

[\bar{C} with abs. EtOH in s.t. at 140–150° gives (16) (4) chloral ethylalcoholate (3:0860) and ethyl β,β,β -trichlorolactate [Beil. III-287, III₁-(111), III₂-(210)], m.p. 66–67°.]

3:3510 (1) Böeseken, Rec. trav. chim. 29, 108 (1910). (2) Chattaway, Kellett, J. Chem. Soc. 1928, 2709–2712. (3) Fuchs, Katscher, Ber. 62, 2384–2385 (1929). (4) Wallach, Ann. 193, 4, 8, 11-19 (1878). (5) Wallach, Ber. 6, 118, Note (1873). (6) Stadeler, Ann. 61, 104–114 (1847); 106, 253–255 (1858). (7) Personne, Bull. soc chim (2) 21, 529 (1874). (8) Grabowski, Ber. 8, 1433–1437 (1875). (9) Anschutz, Haslam, Ann. 239, 297–300 (1887). (10) Wallach, Bodewig, Ann. 193, 58–59 (1878), Z. Krist. 1, 594 (1877).

(11) Otto, Ann. 239, 262-266 (1887). (12) Kekulé, Ann. 105, 293-295 (1858) (13) Wallach, Heymer, Ber. 9, 545-547 (1876). (14) Wallach, Ann. 203, 83 84 (1880). (15) Wallach, Ann. 193, 6, 20, 27 (1878). (16) Wallach, Ber. 8, 1578-1583 (1875). (17) Routala, Neovius, Ber. 57, 252, Note 4 (1924). (18) Anschutz, Haslam, Ann. 253, 121-123 (1889).

3:3520 2,4,6-TRICHLORO-3-HYDROXYBENZALDEHYDE

M.P. 115.5-116.5° (1) 115-116° (6) 114° (2) 113° (3)

Colorless cryst. from 50% AcOH; \bar{C} seps. with AcOH of crystn. but this immediately effervesces in air. — \bar{C} has pronounced sternutatory props. and on moist skin produces painful blisters (2).

[For prepn. of \bar{C} from *m*-hydroxybenzaldehyde (1:0055) in AcOH with excess Cl_2 see (1) (2).]

[For condens. of \bar{C} with 2,4-dichlorophenol (3:0560) see (4); with 2,4-dihydroxybenzoic acid (1:0843) and use of prod as dye intermediate see (5).]

 \bar{C} in 50% aq. KOH warmed for 4 hrs at 60-70° gives (89.9% yield (3)) 2,4,6-trichlorophenol (3:1673).

NaA, pure yel. ndls., spar. sol. aq (2).

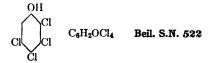
C in Na₂CO₃ soln. with Me₂SO₄ yields 2,4,6-trichloro-3-methoxybenzaldehyde, ndls. from alc, mp. 76° (2); on very slow oxidn. with alk. KMnO₄ this prod. yields 2,4,6-trichloro-3-methoxybenzoic acid, mp. 109° (2).

- 2,4,6-Trichloro-3-hydroxybenzaldoxime: ndls. from dil. alc., m.p. 174° (2), 170° (6).

 [This with boilg Ac₂O yields 2,4,6-trichloro-3-acctoxybenzonitrile, lfts. from dil. AcOH, m.p. 82-83° (6)]
- ① 2,4,6-Trichloro-3-hydroxybenzaldehyde p-nitrophenylhydrazone: yel.-or. ndls., m.p. 272-273° dec. (2) [From \bar{C} in alc. with p-nitrophenylhydrazine + 1 drop aq. (2).]

3:3520 (1) Bissell, Kranz (to Nat Aniline & Chem. Co.), U.S. 1,776,803, Sept. 30, 1930; Cent. 1931, I 150, C A 24, 5769 (1930). (2) Hodgson, Beard, J. Chem. Soc 1926, 148-149, 153. (3) Lock, Monatsh. 55, 312 (1930). (4) I.G., Swiss 137,923-137,929, incl., 138,180-138,183, incl., April 16, 1930; Cent. 1930, II 1453. (5) Weiler (to F. Bayer & Co.), U.S. 1,532,790, April 7, 1925; Cent. 1925, II 352. (6) Krause, Ber. 32, 123 (1899).

3:3523 2,3,4,5-TETRACHLOROPHENOL



M.P. 116-117° (1) 116° (2) (3)

[For prepn. of \bar{C} from 2,3,4,5-tetrachloroaniline [Beil. XII-630, XII₁-(313)] via diazotization and reaction with aq. (65% yield) see (1); from 2-amino-3,4,5,6-tetrachlorophenol [Beil. XIII-386] (3) via diazotization and elimination of diazo group with alc. see (3); for formn of \bar{C} from pentachlorobenzene (3:2290) with N/2 MeOH/NaOMe at 180° in s.t. for 7½ hrs. as by-prod. of the isomeric 2,3,5,6-tetrachlorophenol (3:3460) see (4).]

 \bar{C} in aq. behaves as an acid, K at $25^\circ = 1.1 \times 10^{-7}$, and can be titrated with N/10 aq. NaOH (1), Neut. Eq. = 232.

- 2,3,4,5-Tetrachlorophenol ethyl ether (2,3,4,5-tetrachlorophenetole): unreported.
 2,3,4,5-Tetrachlorophenyl acteate: unreported.
- © 2,3,4,5-Tetrachlorophenyl benzoate: m.p 110° (4) (5). [Note that this prod. depresses m.p. of corresp. benzoate from the isomeric 2,3,4,6-tetrachlorophenol (3:1687) (5).]
- 2.3.4.5-Tetrachlorophenyl N-phenylcarbamate: unreported.

3:3523 (1) Tiessens, Rec. trav. chim. 50, 115-116, 119 (1931). (2) Tiessens, Rec. trav. chim. 48, 1068 (1929). (3) Bures, Havlinova, Časopis Českoslov. Lékárnictva, 9, 101-107, 129-134, 153-157 (1929); Cent. 1929, II 1403; C.A. 24, 2998 (1930). (4) Holleman, van der Hoeven, Rec. trav. chim. 39, 748 (1920). (5) Holleman, Rec. trav. chim. 40, 318-319 (1921).

D1 151011

3:3525 4,5-DICHLOROCATECHOL (4,5-Dichloropyrocatechol)

Colorless pr. from CHCl₃ + CS₂ (1); ndls. from C_6H_6 + pet. ether (2). — \bar{C} is eas. sol. in cold aq. from which it crystallizes as a hemihydrate (1) (it is possible that the m.p. of $105-106^\circ$ observed by some workers may have been due to formn. of this prod.). — \bar{C} cryst. from AcOH with 1 mole of solvent, viz., \bar{C} .AcOH (1).

[For prepn. of \bar{C} from pyrocatechol (1:1520) with SO₂Cl₂ (2 moles) or from 4-chloropyrocatechol (3:2470) with SO₂Cl₂ (1 mole) see (2)

[C with silver oxide in dry ether gives (1) 4,5-dichlorobenzoquinone-1,2 [Beil. VII₁-(338)], m.p. 94°; note, however, that C with this prod. forms a corresp. quinhydrone, dec. abt. 85°.]

[C with Cl₂ in AcOH gives (1) 3,4,5-trichloropyrocatechol (3:3448) cryst. from aq. as monohydrate, m.p. abt. 106-109° (1), 104-105° (4), 115° (5).

[C with PCl₅ gives (2) 1,2,4,5-tetrachlorobenzene (3:4115).]

 \bar{C} with N/10 aq. KOH titrates (1) as a monobasic acid, i.e., Neut. Eq. = 89.5. — \bar{C} with aq. FeCl₃ gives blue-green coloration becoming red on addn. of aq. Na₂CO₃ (1).

C does not (6) condense with xanthydrol (1:5205) in AcOH (dif. from 4-chloropyrocatechol (3:2470)).

- ---- 4,5-Dichloropyrocatechol diacetate: unreported.
- 1. 4.5-Dichloropyrocatechol dibenzoate [Beil. IX₁-(72)]: m.p. 140.0-140.5° (1).

3:3525 (1) Willstatter, Müller, Ber. 44, 2184-2186 (1911). (2) Peratoner, Gazz. chim. ital. 28, I 222-224 (1898). (3) Frejka, Sefranek, Zika, Collection Czechslov. Chem. Commun. 9, 243-244 (1937). (4) Cousin, Bull. soc. chim. (3) 13, 719 (1895); Ann. chim. (7) 13, 483 (1898). (5) Jackson, Boswell, Am. Chem. J. 35, 526-527 (1906). (6) Fabre, Ann. chim. (9) 18, 115 (1922). (7) Peratoner, Ortoleva, Gazz. chim. ital. 28, I, 229-232 (1898).

3:3530 5-CHLORORESORCINOL

M.P. 117° (1)

 \bar{C} cryst. from C_6H_6 in colorless ndls. of monohydrate, m.p. 67° (1), which on sublimation in vac. yield anhydrous \bar{C} (1).

Č is readily sol. in all usual solvents except lt. pet.; it rapidly absorbs aq. regenerating above monohydrate, m.p. 67° (1).

Č with FeCl₃ gives bluish-purple color; Č reduces boilg. Fehling soln.

Č on bromination (no details (1)) yields 5-chloro-2,4-tribromoresorcinol, colorless ndls. from AcOH or dil. alc., m.p. 143° (1).

3:3530 (1) Hodgson, Wignall, J. Chem. Soc. 1926, 2827.

Colorless cryst. from alc. or pet. ether. — Insol. aq; sol. alc. or lt. pet.; freely sol. ether, acetone, benzene, or CHCl₃. — [For use of \bar{C} in stimulation of action of estrogenic hormones see (7); for aq. susp. of \bar{C} for medicinal use see (9).]

[For prepn. of C from 1,1,2-triphenylethanol-1 (benzyl-diphenyl-carbinol) [Beil. VI-721, VI₁-(354)] in AcOH by treatment with Cl₂ at 30-40°, then htg. to b.p. to remove AcOH and effect loss of HCl (87% yield), see (1); from 1,2-dichloro-1,1,2-triphenylethane (1) by htg. just above m.p. (115°) (100% yield (1)) or by refluxing 5 hrs. in pyridine (65% yield (1)) see (1); from triphenylethylene [Beil V-722, V₁-(355)] in AcOH with Cl₂ (1), in C₆H₆ with PCl₅ (4), or in CCl₄ with SO₂Cl₂ in pres. of dibenzoyl peroxide (2) see indic. refs.; from ω,ω-diphenylacetophenone (1,1,2-triphenylethanone) (triphenylvinyl alcohol) [Beil. VII-522, VII₁-(291)] (5) (3) or from triphenylacetaldehyde [Beil. VII₁-(292)] (6) with PCl₅ see indic. refs.]

3:3560 (1) van de Kamp, Sletzinger, J. Am. Chem. Soc. 63, 1879-1881 (1941). (2) Tadros, Nature 148, 53 (1941). (3) Schonberg, Robson, Tadros, Fahim, J. Chem. Soc. 1940, 1328.
 (4) Bergmann, Bondi, Ber. 64, 1467-1468 (1931). (5) Gardeur, Bull. acad. roy. Belg. 34, 67-100 (1897); Cent. 1897, II 662. (6) Danniov, J. Russ. Phys.-Chem. Soc. 51, 125 (1919); Cent. 1923, III 761. (7) Robson, Schonberg, Fahim, Nature 142, 292 (1938). (8) MacPherson, Robertson, Lancet (2) 237, 1362 (1939). (9) Collie & Imperial Chem. Ind., Ltd., Brit. 543,897, March 18, 1932; C.A. 36, 6313 (1942).

3:3580 2-CHLORONAPHTHO-QUINONE-1,4 (2-Chloro-α-naphthoquinone)

C₁₀H₅O₂Cl Beil. VII - 729 VII₁—

Yel. ndls. with pungent quinone odor from dil. alc. or dil. AcOH. — Volatile with steam. — Eas. sol. alc., C₆H₆; spar. sol. ether.

[For prepn. of \tilde{C} from naphthoquinone-1,4 (α -naphthoquinone) (1:9040) by conversion with Cl₂ in AcOH to 2,3-dichloro-1,4-diketo-1,2,3,4-tetrahydronaphthalene (" α -naphtho-

quinone dichloride") [Beil. VII-702] and subsequent elimination of 1 HCl with NaOAc/AcOH see (4) cf. (7); from α -naphthol (1:1500) by conversion with Cl₂ in AcOH to 2,2,4-trichloro-1-keto-1,2-dhydronaphthalene [Beil. VII-387] and subsequent hydrolysis (with rearr.?) in boilg. dil. alc. or dil. AcOH see (5).

[For prepn. of \bar{C} from 1,3-dichloronaphthalene (3:1310) by oxidn. with $CrO_3/AcOH$ see (8); from 2,4-dichloronaphthol-1 (3:3250) by oxidn. with $CrO_3/AcOH$ or $HNO_3/AcOH$ see (5) (9); from 2-chloro-1,2-diaminonaphthalene (2-chloronaphthylenediamine-1,2) by oxidn. with 2% alk $KMnO_4$ see (2); from 2-chloronaphthol-1-sulfonic acid-4 by oxidn. with MnO_2 in boilg. 50% H_2SO_4 see (1); from 2,4-dimitronaphthol [Beil. VI-617, VI₁-(308)] by oxidn. with NaOCl in HCl soln (3) or $HCl + KClO_3$ (10) see indic. refs; from sodium salt of 4-(p-sulfobenzeneazo)naphthol-1 ("Orange I") [Beil. XVI-275, XVI_1 -(296)] by oxidn. with NaOCl in HCl soln see (3)]

[$\bar{\mathbf{C}}$ on reduction might be expected to give 2-chloro-1,4-dihydroxynaphthalene [Beil. VI-975], m.p. 116-117°; note, however, that this reaction has not actually been reported and that this prod. is also obtained by SO₂ reduction of 3-chloronaphthoquinone-1,2 (3:4704). — For study of oxidn.-reductn. potential of $\bar{\mathbf{C}}$ see {7}.]

[C with Cl2 in AcOH gives (4) (5) 2,3-dichloronaphthoqumone-1,4 (3:4857).]

[C in boilg. alc. with aq. NaN₃ splits out NaCl giving (90% yield (11)) 2-azidonaphtho-quinone-1,4, long yel. pr. from alc, mp. 118° dec]

Č with aniline on htg. (5) (6) in alc. soln. (8) (9) gives 3-chloro-2-anilino-naphthoquinone-1,4 [Beil. XIV-168, XIV₁-(434)], red ndls, m.p. 207-208° (10), 207° (8), 202-203° (9) (6).

 \bar{C} like many other quinones is able to form Diels-Alder type adducts with many conjugated dienes [e.g., \bar{C} with 2,3-dimethylbutadiene-1,3 (1:8050) gives an adduct which with aq. 5% NaOH and a little Na₂S₂O₄ at 70° reduces (with loss of halogen) to 2,3-dimethyl-1,4-dihydroanthrahydroquinone which in turn upon oxidn. with air at 0° gives (12) 2,3-dimethylanthraquinone [Beil. VII-815, VII₁-(425)], yel. ndls from alc or AcOH, m.p. 210° (13), 209° (14), 208-209° (15), 208° (16), 205-206° (17); note also that this 2,3-dimethylanthraquinone is also obtd. (18) from the initial adduct with pyridine in absence of air, or (18) from \bar{C} + 2,3-dimethylbutadiene-1,3 (1:8050) at 100-105° under press. — For behavior of \bar{C} with 2-methylbutadiene-1,3 (isoprene) (1:8020) and with butadiene-1,3 see (18).]

- 2-Chloronaphthoquinone-1,4-(p-nitrophenylhydrazone-4) = 4-(p-nitrobenzeneazo)-2-chloronaphthol-1: m.p. 274° dec. (1). [From $\bar{\mathbb{C}}$ with p-nitrophenylhydrazine (1); also from 2-chloronaphthol-1 (3:1490) in alk. soln. on coupling with diazotized p-nitroaniline (1).]
- 3:3580 (1) Hodgson, Rosenberg, J. Soc. Chem. Ind. 48-T, 287-289 (1929). (2) Hodgson, Elliott, J. Chem. Soc. 1935, 1852. (3) Seyewetz, Chaix, Bull. soc. chim. (4) 41, 201, 338 (1927). (4) Zincke, Schmidt, Ber. 27, 2757 (1894). (5) Zincke, Kegel, Ber. 21, 1036-1039 (1888). (6) Russig, J. prakt. Chem. (2) 62, 41-42 (1900). (7) Conant, Fieser, J. Am. Chem. Soc. 46, 1872, 1875 (1924). (8) Cleve, Ber. 23, 955 (1890). (9) Cleve, Ber. 21, 892-893 (1888). (10) Plagemann, Ber. 15, 485, Note 1 (1882).
- Fieser, Hartwell, J. Am. Chem. Soc. 57, 1484 (1935).
 I.G., French Addition 37,684, Jan 14, 1931; Cent. 1931, II 124; C.A. 25, 4559 (1931).
 Barnett, Marrison, Ber. 64, 537 (1931).
 L. Fieser, M. Fieser, J. Am. Chem. Soc. 57, 1681 (1935).
 Fieser, Seligman, Ber. 68, 1751 (1935).
 Fairbourne, J. Chem. Soc. 119, 1578 (1921).
 Fieser, Seligman, J. Am. Chem. Soc. 56, 2695 (1934).
 Italian Chem. Soc. 56, 2695 (1934).
 Fieser, Seligman, J. Am. Chem. Soc. 57, 1681 (1935).

3:3585 α-CHLORO-DIPHENYL-ACETIC ACID

(Diphenylchloroacetic acid)

M.P. 120° dec. (1) 118-119° dec. (2) (3)

[See also \alpha-chlorodiphenylacetyl chloride (3:0885).]

Tbls. from C₆H₆/lgr.; very eas. sol lgr.

[For prepn of \bar{C} from benzilic acid (α -hydroxydiphenylacetic acid) (1:0770) with POCl₃ on warming (not boilg.) until red color begins to appear (65% yield (3)) (4); with PCl₅ (62.5% yield (1)) or PCl₃ (68% yield (1)) both at room temp.; with SOCl₂ directly at room temp. (92% yield (1)) or with SOCl₂ (3 moles) in CCl₄ at ord. temp. (5) (2) see indic. refs.; note, however, that benzilic acid (1:0770) with PCl₅ (2 moles) at 120–130° (6) or 100° (7) or excess PCl₅ (5 moles) in C₆H₆ at room temp. (1) gives instead α -chlorodiphenylacetylehloride (3:0885), m p 50°; note also that benzilic acid (1:0770) with large excess (6 moles) SOCl₂ refluxed for several days gives (5) α -chlorodiphenylacetic acid anhydride [Beil. IX₁-(228)], m.p. 129° (5)].

[For prepn. of \bar{C} from O-carbomethoxybenzilic acid (2) with SOCl₂ see (2); for prepn. of \bar{C} from α -chlorodiphenylacetyl chloride (3:0885) by hydrolysis (even in moist air) see (8)]

Č on reduction with T₁Cl₃ in boilg. AcOH gives (8) diphenylacetic acid (1:0765), m.p. 148°.

Č (or its sodium salt) htd. under reduced press. at 125° for 10 hrs gives (80-90% yield (9)) benzilide [Beil. XIX-187, XIX₁-(700)], ndls. from alc., m p 196° (10), 194° (11) (5), 193° (12), 192-193.5° (9) [the structure of this prod. is disputed, but it is either 2,2,5,5-tetraphenyl-3,6-diketodioxane-1,4 or tetraphenyldiglycolic acid anhydride].

 \bar{C} with aq. KSH (or NaSH) does not (21) give the expected α -mercaptodiphenylacetic acid (diphenylthioglycolic acid) (thiobenzilic acid) [Beil. X_{1} -(154)], but rather (apparently because of alkalinity of the soln.) benzilic acid (1:0770).

[\bar{C} with NaOMe (?) gives (13) α -methoxydiphenylacetic acid (benzilic acid O-methyl ether) [Beil. X₁-(152)], m.p. 100° (13); note that various compounds prepd. by a wide variety of methods but all supposed to have this structure have been reported with m.p.'s as follows: 99-100° (14), 102° (15), 106° (16), 107° (17), 111-112° (18), 120-121° (9); note also that the corresp. methyl ester, viz., methyl α -methoxydiphenylacetate, oil, b.p. 199-200° at 27 mm., has been prepd. (19) from α -bromodiphenylacetyl bromide with MeOH.]

[C with EtOH/NaOEt gives (8) cf. (13) α -ethoxydiphenylacetic acid [Beil X₁-(152)], tbls. from ether, m.p. 114-115° (20) (8), 114° (13), 113-114° (14); the corresp. ethyl ester, viz., ethyl α -ethoxydiphenylacetate, appears to be unreported]

 \tilde{C} with Na phenolate might be expected to give α -phenoxydiphenylacetic acid, but neither this reaction nor the expected prod. is reported. — However, \tilde{C} with thiophenol in C_6H_6 refluxed 2 hrs. evolves HCl and gives (22) α -thiophenoxy-diphenylacetic acid, cryst. from 50% AcOH, m.p. 126-128° (22).

[\bar{C} with C_6H_6 + AlCl₃ gives normal Friedel-Crafts type reaction giving (25% yield (3)) triphenylacetic acid [Beil. IX-712, IX₁-(309)], m.p. 265°.]

 \tilde{C} with various amines or amino compds. splits out HCl giving the corresp. α -aminodiphenylacetic acid derivatives [e.g., \tilde{C} with NH₃ gives (13) α -aminodiphenylacetic acid (diphenylglycine), m.p. 245° (13); \tilde{C} with piperidine gives (13) α -piperidinodiphenylacetic acid, m.p. 180° (13); for other cases see (13)].

C with benzhydrazide in C₆H₆ splits out HCl and yields (8) α-benzhydrazido-diphenylacetic acid, m.p. 167-168° (8).

 \bar{C} with excess SOCl₂ on warming does not give the expected α -chlorodiphenylacetyl chloride (3:0885), m.p. 50°, but rather (5) α-chlorodiphenylacetic acid anhydride, m.p. 129° (5).

C in pyridine on htg. at 100° (23) evolves CO2 presumably yielding benzohydryl chloride (a-chlorodiphenylmethane) (3:0060) as its quaternary salt with pyridine.

- Methyl α -chlorodiphenylacetate: oil, b.p. 196° at 16 mm. (4). [From \bar{C} in dioxane soln. with diazomethane (100% yield) (4); note also that this ester with Cu bronze refluxed in C₆H₆ for 5 hrs. then evaporated in air gives (4) the peroxide, m.p. 151-152°, of dimethyl tetraphenylsuccinate.]
- Ethyl α -chlorodiphenylacetate: cryst. from alc., m.p. 43-44° (24) (6), b.p. 185° at 14 mm. (24). [From C with EtOH + dry HCl (10) best in pres. of C₆H₆ as directed (90% yield (25)), or from α-chlorodiphenylacetyl chloride (3:0885) with EtOH (6), or from ethyl benzilate (1:2086) with PCl₅ (6)]
- α -Chlorodiphenylacetamide: m.p. 115° (6), 111–113° (26). [From α -chlorodiphenylacetyl chloride (3:0885) in ether with NH₃ gas (6) (13).]
- α -Chlorodiphenylacetanilide: m.p. 88°. [See text of α -chlorodiphenylacetyl chloride (3:0885).]
- 3:3585 (1) Setlur, Nadkarny, Proc. Indian Acad. Sci. 12-A, 268 (1940); C.A. 35, 1398 (1941). (2) McKenzie, Lesslie, Ber. 61, 160-161 (1928). (3) Bistrzycki, Herbst, Ber. 36, 145-147 (1903).
- (4) Schlenk, Hillemann, Rodloff, Ann. 487, 138, 154 (1931). (5) Stollé, Ber. 43, 2471-2473 (1910).
- (6) Bickel, Ber. 22, 1537-1539 (1889). (7) Staudinger, Ann. 356, 72-73 (1907). (8) Aspelund, Acta Acad. Aboensis Math. et Phys. 6, No. 17, 17 pp. (1932); Cent. 1933, I 782-783; C.A. 28, 5441-5442 (1934). (9) Staudinger, Dyckerhoff, Klever, Ruzicka, Ber. 58, 1087 (1925). (10)

Klinger, Standke, Ber. 22, 1213-1214 (1889).

(11) Einhorn, Mettler, Ber. 35, 3642 (1902). (12) Staudinger, Ber. 44, 545-547 (1911). (13) Setlur, Kothare, Nadkarny, J. Univ. Bombay 12-A, Pt. 3, 68-70 (1943); C.A. 38, 3250, 1739 (1944). (14) Klinger, Ann. 390, 371-372 (1912). (15) Schlenk, Bergmann, Ann. 464, 38 (1928). (16) Kohler, Larsen, J. Am. Chem. Soc. 58, 1521 (1936). (17) Ziegler, Thielmann, Ber. 56, 1741, Note 8 (1923). (18) Staudinger, Bereza, Ann. 380, 271 (1911). (19) Bergmann, Fujise, Ann. 483, 76-77 (1930). (20) Salkind, Peschekerowa, J. Russ. Phys.-Chem. Soc. 46, 488 (1914); Cent. 1914, II 1269.

(21) Bistrzycki, Brenken, Helv. Chim. Acta 3, 465-466 (1920). (22) Bistrzycki, Risi, Helv. Chim. Acta 8, 585 (1925). (23) Bezzi, Atti ist. Veneto sci., Ser. II, 94, 167-182 (1935). Cent. 1937, II 3605; not in C.A. (24) Kl.nger, Ann. 389, 262-263 (1912). (25) Adickes, J. prakt. Chem. (2) 150, 91 (1938). (26) Steinkopf, Ber. 41, 3593 (1908).

3:3590 PENTACHLOROBENZAL (DI)CHLORIDE

C7HCl7 Beil. V - 304 V_{1} -(153)

Colorless lfts. from alc.; eas. sol. hot, spar. sol. cold, alc.

[For prepn. of C from 2,3,4,5,6-pentachlorotoluene (3:4937) with Cl₂ at 210-230° as directed (70-80% yield) see (3); for formn. of C from benzal (d1)chloride (3:6327) with Cl₂ in pres. of I₂ + SbCl₅ see (2); from "pentachloro-orcinol" [Beil. VII-576, VII₁-(323)] with PCl₅ (2 moles) at 230° for 12-16 hrs. (together with hexachlorobenzene (3:4939)) see (1).]

C is unaffected by aq. even in s.t. at 300°; however, C on hydrolysis with conc. HoSO4

at $60-100^{\circ}$ or with fumg. H_2SO_4 at $40-50^{\circ}$ gives (90% yield (3)) (4) pentachlorobenzaldehyde (3:4892), m.p. 202.5° (3).

3:3590 (1) Zincke, von der Linde, Ber. **26**, 318 (1893). (2) Beilstein, Kuhlberg, Ann. **150**, 306–308 (1869). (3) Lock, Ber. **66**, 1533 (1933). (4) Bayer and Co., Ger. **243**, 416, Feb. 10, 1912; Cent. **1912**, I 618; [C.A. **6**, 2292 (1912)]: U.S. 998,140, July 18, 1911; [C.A. **5**, 2904–2905 (1911)].

3:3600 1,6-DICHLORONAPHTHOL-2 Cl
$$C_{10}H_6OCl_2$$
 Beil. VI — VI₁— VI₂-(604)

M.P. 119.5° (1)

Ndls, from hot lgr.

[For prepn. from 1-chloronaphthol-2 (3:1700) by actn. of Cl₂ in sunlight see (1).] C on reduction with FeSO₄ + NaOH yields (2) 6-chloronaphthol-2 (3:3500), m.p. 115° (2).

3:3600 (1) Ruggli, Knapp, Merz, Zimmermann, Helv. Chim. Acta 12, 1050-1051 (1929). (2) Herzberg, Spengler, Schmidt (to I.G.), Ger. 431,165, June 30, 1926; Cent. 1926, II 1196.

M.P. 119-120° (1) 118.5-119° (2) 118-119° (3) 116° (4)

[See also dichloromalesc anhydride (3:3635) and dichloromaleyl (di)chloride (3:6197).]

Ndls. from lgr./ether. — Eas. sol. aq.; sol. alc., Λ cOH; insol. C_6H_6 , $CHCl_3$, CS_2 . — Note that \bar{C} on htg. very readily loses H_2O and is converted to dichloromaleic anhydride (3:3635); the m.p.'s observed for \bar{C} are probably actually those of its anhydride.

Note also that, although the structure corresp. to Č should be capable of existing also in the geometrically isomeric *trans* configuration, no such dichlorofumatic acid or its derivatives has ever been reported.

[For prepn. of \bar{C} from furfural (1:0185) in conc. HCl soln. with Cl₂ (30% yield) see (5); from dichloromaleinaldehyde-acid ("mucochloric acid") [Beil. III-727] by oxidn. with fumg. HNO₃ on stdg. at ord. temp. for several days (100% yield (4)) (2) see indic. refs.; from α,β -dichloro- β -(trichloroacetyl)acrylic acid ("perchloro- β -acetylacrylic acid") [Beil. III-733] by hydrolytic cleavage with aq. NaOH (chloroform is also formed) see (3); from hexachlorocyclohexen-1-dione-3,6 [Beil. VII-574] by hydrolytic cleavage with 10% aq. NaOH (trichloroethylene (3:5170) is also formed) see (1); from hexachlorocyclohexen-1-dione-3,5 ("hexachlororesorcinol") (3:3470) (6) or from 2,2,3,4,6,6-hepta-chlorohexen-3-one-5-acid-1 [Beil. III-735, III₁-(255)] (6) with large excess dil. aq. Ca(OCl)₂ see indic. refs.]

[For formn. of \bar{C} from 3,4-dichlorofuroic acid [Beil. XVIII-282] by oxidn. with boilg dil. HNO₃ (7) or from 3,4,5-trichlorofuroic acid [Beil. XVIII-283] by oxidn. with hot dil. HNO₃ or cold Br₂/aq. (7) see indic. refs.; from pyrrole with aq. NaOCl (other prods. are also formed) see (8).]

 $\bar{\mathbf{C}}$ behaves normally as a dibasic acid: e.g., $\bar{\mathbf{C}}$ on titration with standard dil. aq. alk. gives Neut. Eq. 92 5 (2).

[Salts: for Li₂ \bar{A} , Na₂ \bar{A} .H₂O, NaH \bar{A} .H₂O, K₂ \bar{A} .2H₂O, K₂ \bar{A} .H₂O, Cu \bar{A} .H₂O, Pb \bar{A} .H₂O, Ni \bar{A} .2H₂O see (4). — Ba \bar{A} .2½H₂O (3). — Ag₂ \bar{A} , white ndls. which explode on htg. (3) (8) (9).]

- Dimethyl dichloromaleate: oil, b.p. 225° (9). [From dichloromaleic anhydride (3:3635) in MeOH with HCl gas on boilg. (9). This prod. with aniline at 100° yields (4) dimethyl α,β -dianilinomaleate, cryst. from alc., m.p. 172° (4).]
- Diethyl dichloromaleate: unreported.
- Dichloromaleinimide [Beil XXI-401] ndls. from aq., m.p. 179° (10). [From dichloromaleic anhydride (3:3635) with urea on htg. at 110-115° (10)]
- --- N-Phenyldichloromaleinimide (dichloromaleanil) [Beil. XXI-402]: colorless lfts. from MeOH. m.p. 203°. [Reported only by indirect means.]
- Dichloromaleic dianilide: see under text of dichloromaleyl (di)chloride (3:6197).
- **3:3634** (1) Zincke, Fuchs, Ann. 267, 19-22 (1892). (2) Stelling, Z physik Chem. B-24, 424 (1934). (3) Zincke, von Lohr, Ber. 25, 2230 (1892) (4) Salmony, Simonis, Ber. 38, 2588-2590, 2594-2595, 2598-2599 (1905) (5) Leder, Russ 48,297, Aug. 31, 1936; Cent. 1937, II 288. (6) Zincke, Fuchs, Ber. 26, 509 510 (1893). (7) Hill, Jackson, Am. Chem. J. 12, 43-44, 124-125 (1890). (8) Ciamician, Silber, Ber. 17, 1743-1744 (1884). (9) Kauder, J. prakt. Chem. (2) 31, 5-6 (1885). (10) Dunlap, Am. Chem. J. 18, 333-334 (1896).

M.P. 119-120° (1) (2) 119.5° (3) 119° (4) (8)

119' (4) (8) 117-118° (5)

[See also dichloromaleic acid (3:3634).]

Colorless lfts. very eas. sol. alc., ether, C6H6, or CS2; sublimable.

[For prepn. of \bar{C} from dichloromaleic acid (3:3634) by htg. see (1) (2) (10); for prepn. of \bar{C} from maleic anhydride (1:0625) with Cl_2 at 130° in pres. of Fe (80% yield (7)) or from chlorofumaryl dichloride with Cl_2 in pres. of Fe (8) see indic. refs.; for prepn. of \bar{C} from furoic acid (1:0475) by conv with $MnO_2 + HCl$ to mucochloric acid, OCH.CCl= CCI.COOH [Beil. III-727] (9), and subsequent treatment with fung. HNO_3 (4) (9) or from 3,4-dichlorofuran (9) by oxidin with fung. HNO_3 (9) see indic. refs; for formin. \bar{C} (together with other products) from diethyl tartrate (1:4256) with PCl_5 for 7-8 hrs. at 100° see (6); from either dichloromaleo(di)nitrile (m.p. 58-59°, $D_4^{62} = 1.32501$, $n_D^{62} = 1.48824$ (12)) or from dichlorofumaro(di)nitrile (m.p. 60.0-60.5°, $D_4^{62} = 1.32543$, $n_D^{62} = 1.48845$ (12)) by hydrol. see (12).]

 \tilde{C} is itself spar. sol. aq. but slowly dissolves (1) (6) yielding a soln. of dichloromaleic acid (3:3634).

C with PCl₅ yields (8) dichloromaleyl dichloride (3:6197).

 \bar{C} with 1 mole anthracene (1:7285) htd. for 10 min. at 170° gives 100% yield (4) of anthracene-9,10-endo-dichloromaleic anhydride, ndls. from acetonitrile, m.p. 235° (4).

Č with 1 mole urea htd. to 90-95° for 20 min. yields (11) dichloromaleic acid monoureide [Beil. III-68], m.p. 158° dec. (11); this prod. on fusion or the original system htd. at 110-115° yields (11) dichloromaleinimide [Beil. XXI-401], m.p. 179° (11).

 \bar{C} on htg. with aniline (9) yields α -chloro- α -anilinomalein- α' -isoanil [Beil. XVII-555], greenish yel. cryst. from alc., m.p. 188.7-190 2° cor. (9), 187° (10).

3:3635 (1) Ciamician, Silber, Ber. 16, 2396 (1883). (2) Zincke, Fuchs, Ann. 267, 20-22 (1892).
(3) Kauder, J. prakt. Chem. (2) 31, 4 (1885). (4) Diels, Thiele, Ber. 71, 1173-1178 (1938).
(5) Leder, J. prakt. Chem. (2) 130, 271 (1931). (6) Patterson, Todd, J. Chem. Soc. 1929, 1768-1771. (7) Leder, Russ. 43,419, June 30, 1935, Cent. 1936, I 1310, C.A. 31, 7447 (1937). (8) Vandevelde, Bull. acad. roy. Belg. (3) 37, 680-700 (1900); Cent. 1900, I 404. (9) Shepard, Winslow, Johnson, J. Am. Chem. Soc. 52, 2088-2089 (1930). (10) Salmony, Simonis, Ber. 38, 2588 (1905).

(11) Dunlap, Am. Chem. J. 18, 333-334 (1896). (12) Mommaerts, Bull. classe sci., Acad. roy. Belg. (5) 27, 579-597 (1944), Cent. 1943, I 615-616, CA. 38, 3621 (1944).

3:3665 2,3-DICHLORONAPHTHALENE

Spar. sol. cold, eas. sol hot alc or ether

[For prepn. of \bar{C} from naphthalenetetrachloride-1,2,3,4 (3:4750) by htg. with Ag₂O in s.t. at 200° (1) or (in small yield together with other prods.) by boilg, with alc. KOH (3) (4) see indic. refs.; from 1,2,3-trichloronaphthalene (3:2125) with Na/Hg in alc. see (4).]

[$\ddot{\mathbf{C}}$ on monosulfonation in CS₂ with ClSO₃H yields (4) mainly 2,3-dichloronaphthalene-sulfonic acid-8 [Beil. XI-164] (corresp. sulfonyl chloride, m.p. 142°, corresp. sulfonamide m.p. 268°) accompanied by 2,3-dichloronaphthalenesulfonic acid-6 (?) [Beil. XI-183] (corresp. sulfonyl chloride, m.p. 178°)]

3:3665 (1) Leeds, Everhart, J. Am. Chem. Soc. 2, 210-212 (1880). (2) Hampson, Weissberger, J. Chem. Soc. 1936, 394 (3) Widman, Ber. 15, 2162 (1882) (4) Armstrong, Wynne, Chem. News 61, 273-275, 284 (1890).

3:3695 3,4-DICHLOROPHTHALIC ANHYDRIDE

[See also 3,4-dichlorophthalic acid (3:4880).]

Tbls. from CCl₄; sol. in C₆H₆, toluene, CHCl₃.

[For prepn. of \bar{C} from 3,4-dichlorophthalic acid (3:4880) by protracted htg. at 220° see (2); for formn. of \bar{C} (together with other isomers) from phthalic anhydride (1:0725) with Cl_2 at 240° in pres. of Fe or Fe salts (3), from phthalic anhydride or 3-chlorophthalic

anhydride (3:3900) with Cl_2 in fumg. H_2SO_4 in pres. of I_2 (4) (1), see indic. refs.] [For sepn. of $\tilde{\text{C}}$ from isomeric dichlorophthalic anhydrides by means of salts of corresp. acids see (4) (1) (18); by means of differential hydrolysis with H_2SO_4 (prods. with no α -chlorine such as 4,5-dichlorophthalic anhydride require H_2SO_4 of 98-100% conen.; those with one α -chlorine such as $\tilde{\text{C}}$ hydrolyze with 56-95% H_2SO_4 ; those with two α -chlorines such as 3,6-dichloro- or 3,4,5,6-tetrachlorophthalic anhydrides hydrolyze at H_2SO_4 conens. of less than 50%) see (5).]

Č dislvd. in abs. alc. yields one of the two known acid esters, viz., 3,4-dichloro-2-car-bethoxybenzoic acid, pr. from dil. alc., m.p. 164° (6); see also under 3,4-dichlorophthalic acid (3:4880).

[\bar{C} with PCl₅ htd. in s.t. at 200° for 6 hrs. gives exclusively (6) pseudo-3,4-dichlorophthaloyl dichloride (3,3,6,7-tetrachlorophthalide), ndls. from C₆H₆, m.p. 133° (6) (this prod. shaken with abs. alc. susp. of CaCO₃ for 10 hrs. yields (6) 6,7-dichloro-3,3-diethoxyphthalide, pr. from pet. ether., m.p. 79° (6), which depresses m.p. of normal diethyl 3,4-dichlorophthalate, m.p. 80° (6) to 60°).]

Č with 1 mole NH₂OH.HCl + Na₂CO₃ in aq. as directed (2) yields 3,4-dichlorophthalylhydroxylamine (N-hydroxy-3,4-dichlorophthalimide) [Beil. XXI-504], ndls. from MeOH, m.p. 218-219° (2), 216-219° (7) (this prod. with boilg. aq. Na₂CO₃ yields (2) (7) a mixt. of 3,4-dichloro-2-aminobenzoic acid (3,4-dichloroanthranilic acid) [Beil. XIV-367, XIV₁-(549)] and 5,6-dichloro-2-aminobenzoic acid (5,6-dichloroanthranilic acid [Beil. XIV-368]).

[Č with steam passed over cat. at 380-420° loses CO₂ presumably yielding (8) 2,3-di-chlorobenzoic acid (3:4650) and/or 3,4-dichlorobenzoic acid (3:4925).]

[\bar{C} with hydroquinone (1:1590) + H_3BO_3 htd. at 190° and afterward treated with hot cone. H_2SO_4 (9), or \bar{C} with AlCl₃ + NaCl htd. at 200–220° for 45 min. (10), or \bar{C} with p-chlorophenol (3:0475) htd. with fumg. H_2SO_4 + H_3BO_3 (11), gives 5,6-dichloro-1,4-dihydroxyanthraquinone (5,6-dichloroquinizarin) [Beil. VIII₁-(715)], red. ndls. from AcOH, m.p. 239° (10), 208° (9) (diacetate, m.p. 170° (10), 140° (9)).]

[For study of behavior of \bar{C} with o-chlorotoluene + AlCl₃ see (12); for use of \bar{C} with dibenzanthrone derivs. in prepn. of vat dyes see (13); for reactn. with p-cresol see (16).]

C on fusion with urea yields (14) 3,4-dichlorophthalimide, m.p. 348-351° (14) (for use in prepn. of pigments of phthalocyanine type see (14) (15)).

Č (1 pt.) dislvd. in 5 pts. boilg. AcOH and treated with 1 pt. aniline gives on cooling 97% yield 3,4-dichlorophthalanil [Beil. XXI₁-(391)], cryst. from AcOH, m.p. 181-181.5° cor. (1), ndls. from alc., m.p. 179-180° (17) [note, however, that on protracted htg. with excess aniline one of the two nuclear halogens also reacts, e.g., Č (1 pt.) boiled with 3 pts. aniline for 10 hrs. gives 4-chloro-3-anilinophthalanil, cryst. from alc., m.p. 159.5-160° cor. (1); note also that under certain conditions both halogens can be removed, e.g., 3,4-dichlorophthalanil (above) on refluxing 6 hrs. with aniline + anhydrous Na₂CO₃ + Cu gives (10% yield (17)) 3-anilinophthalanil, or.-yel. pr., m.p. 144.5-145° (17).]

 \bar{C} on saponification with standard alk. (Sap. Eq. = 108.5), followed by acidification, yields 3,4-dichlorophthalic acid (3:4880) q.v.

3:3695 (1) Pratt, Perkins, J. Am. Chem. Soc. 40, 215-217 (1918). (2) Villiger, Ber. 42, 3542-3544 (1909). (3) Dvornikoff (to Monsanto Chem. Co.), U.S. 2,028,383, June 12, 1933; Cent. 1936, I 2830; C.A. 30, 1394 (1936). (4) Ref. 2, pp. 3538-3541. (5) Imperial Chem. Ind., Ltd., French 749,954, Aug. 2, 1933; Cent. 1933, II 2748-2749. (6) Kirpal, Jaluschka, Lassak, Ber. 68, 1333-1334 (1935). (7) B.A.S.F., Ger. 216,749, Dec. 6, 1909; Cent. 1910, I 310. (8) Jaeger (to Selden Co.), U.S. 1,964,516, June 26, 1934; Cent. 1934, II 3047. (9) Frey, Ber. 45, 1362-1363 (1912). (10) Waldmann, J. prakt. Chem. (2) 130, 99 (1931).

(11) Scottish Dyes, Ltd., Bangham, Hooley, Thomas, Brit. 339,589, Jan. 8, 1931; Cent. 1932,
 I 2095. (12) Keimatsu, Hirano, J. Pharm. Soc. Japan, 49, 20-26, 158-163 (1929); Cent. 1929.

I 2533; 1939, I 1303. (13) Imperial Chem. Ind., Ltd., Shaw, Thomson, Brit. 383,624, Dec. 15, 1931; Cent. 1933, I 1358. (14) Imperial Chem. Ind., Ltd., Thorpe, Linstead, Brit. 390,149, Apr. 27, 1933; French 737,392, Dec. 10, 1932; Cent. 1933, II 794. (15) Thorpe, Linstead, Thomas (to Scottish Dyes, Ltd.), Brit. 389,842, Apr. 20, 1933; Cent. 1933, II 3769. (16) Knescheck, Ullmann, Ber. 55, 306, 315 (1922). (17) Mariott, Robinson, J. Chem. Soc. 1939, 137. (18) Hodgson, J. Soc. Dyers Colourists 49, 215 (1933).

3:3720 4-CHLORONAPHTHOL-1 OH C₁₀H₇OCl Beil. VI - 611 VI₁-(308) VI₂-(582) M.P. 120-121° (1)

M.P. 120-121° (1) 120-120.5° (2) 120° (3) 116-117° (4) (26) 116° (5)

Ndls. from dil. alc. or from CHCl₃. — Very eas. sol. org. solv. — Sublimes in ndls. — Volatile with steam but less so than 2-chloronaphthol-1 (3:1490) (use in sepn from latter (6)).

[For prepn. of \tilde{C} from bis-(4-chloronaphthyl-1) carbonate (itself obtd. from bis-(α -naphthyl) carbonate in AcOH with Cl₂ in pres. of SbCl₃ (5)) by hydrolysis with alc. KOH see (5); from 4-chloronaphthyl-1 p-toluenesulfonate (itself obtd. from α -naphthyl p-toluenesulfonate in CCl₄ with Cl₂ + cat. (7)) by hydrolysis see (7); from α -naphthol (1:1500) with SO₂Cl₂ in CHCl₃ as directed (yields: 20–60% (1), 42% (6), 27–33% (8)) (26) (the isomeric 2-chloronaphthol-1 (3:1490) is also formed) see indic. refs.; from 1,4-dichloronaphthalene (3:1655) by htg. with MeOH/KOH in copper-lined autoclave 20 hrs. at 190–200° see (9); from 4-chloronaphthol-1-sulfonic acid-8 (10) (3) by hydrolysis (10) or reductive cleavage with Na/Hg (3) of the —SO₃H group see indic. refs.; from 4-chloro-1-hydroxynaphthoic acid-2 [Beil. X₁-(146)] by htg. in naphthalene or nitrobenzene in pres. of aniline (yield: 81–89%) see (2); from 4-chloronaphthyl-1 MgBr in ether by oxidn, with dry O₂ see (4).

 \bar{C} with Cl_2 in AcOH yields (4) 2,4-dichloronaphthol-1 (3:3250), m.p. 106° (4); \bar{C} with 1 mole Br_2 in AcOH gives alm. quant. yield (11) 2-bromo-4-chloronaphthol-1; ndls., m.p. 96° (11).

[\tilde{C} with 0.5 mole SCl₂ in CHCl₃ gives (79% yield (12)) bis-(4-chloro-1-hydroxynaphthyl-2) sulfide, colorless ndls. from hot alc., m.p. 172° dec. (12); for reactn. of \tilde{C} with 2-hydroxynaphthalene-1-sulfenyl bromide (13) (14), or with SCl₂ + β -naphthol (15), see indic. refs.]

[\bar{C} undergoes many condensations with various types of cpds.: e.g., for condensation of \bar{C} with formaldehyde (16) (17), with 2,6-bis-(hydroxymethyl)-4-methylphenol (18), and use of prods. as mothproofing cpds. see indic. refs.; for condensation of \bar{C} with naphthalene-2,3-dicarboxylic acid anhydride [Beil. XVII₁-(266)] see (19); for condensation of \bar{C} with malic acid (1:0450) or with ethyl acetoacetate (1:1710) or with ethyl methylacetoacetate (1:1712) using H_2SO_4 or P_2O_5 yielding naphthapyrone derivs. see (8); for condens. of \bar{C} with 2,3-dichloronaphthoquinone-1,4 (3:4857) for use in prepn. of vat dyes see (21).]

[Č with maleic anhydride (1:0625) + AlCl₃ + NaCl htd. ½ hr. at 210-220° gives (12% yield (20)) 10-chloro-1-hydroxyanthraquinone-4,9, dark red ndls. from C₆H₆, m.p. 205-206°; similarly Č with citraconic anhydride (1:1135) yields (20) both 10-chloro-1-hydroxy-2-methyl- and 10-chloro-1-hydroxy-3-methylanthraquinone-4,9]

[\bar{C} with 2,4-dinitrotoluene forms a mol. cpd., m.p. 65° (22); \bar{C} with 2,4-dinitroanisole forms a mol. cpd. (22); for use of these as fungicides see (22); for use of \bar{C} as disinfectant see (23).]

C with PkOH in CHCl₃ (5) forms an unstable mol. cpd., C.PkOH, or. ndls., m.p. 171° (5), 170-171° (4) (1).

Č with FeCl₃ or Ca(OCl)₂ in neutral soln. gives blue ppt. (5) (4)

- Č in alc. (10 pts.) treated with conc. HCl (5 pts.) and then with NaNO₂ (0.4 pt.) yields (2) 4-chloronaphthoquinone-1,2-oxime-2 [Beil. VII₁-(385)], purified via the beautifully crystg. dif. sol. red sodium salt, from which HCl ppts. the free oxime, pale yel. ndls., m.p. 157° (2).
 - ① 4-Chloro-1-naphthyl acetate: cryst. from lgr., m.p. 44° (4) (26). [From C with AcCl (2)] [For Fries rearr. of this acetate to 4-chloro-1-hydroxy-2-naphthyl methyl ketone see (24).]
 - —— 4-Chloro-1-naphthyl benzoate: ndls. from alc., m.p. 100-101° (25). [Reported only by indirect means (25).]

3:3720 (1) Kast, Ber. 44, 1337 (1911). (2) Reissert, Ber. 44, 867-869 (1911). (3) Friedlander, Karamessinis, Schenk, Ber. 55, 50 (1922). (4) Bodroux, Bull. soc. chrm. (3) 31, 35-36 (1904). (5) Réverdin, Kauffmann, Ber. 28, 3051 3053 (1805). (6) Lesser, Gad, Ber. 56, 972-973 (1923) (7) Akt.-Ges. fur Anihn Fabrikation, Ger. 240,038, Oct. 26, 1911; Cent. 1911, II 1565. (8) Chakravart, Bagchi, J. Indian Chem. Soc. 13, 651-653 (1936). (9) Soc. d'exploitation des brevets O. Matter, French 807,536, Jan. 14, 1937, Cent. 1937, I 4560, C.A. 31, 5382 (1937). (10) Kalle and Co., Ger. 343,147, Oct. 28, 1921; Cent. 1922, II 114.

Willstatter, Schuler, Bcr. 61, 367 (1928).
 Christopher, Smiles, J. Chem. Soc. 101, 717 (1912).
 Italy Evenson, Smiles, J. Chem. Soc. 1930, 1744.
 Child, Smiles, J. Chem. Soc. 1926, 957.
 Lesser, Giad, Bcr. 58, 2558 (1925).
 Weller, Wenk, Stotter (to I G), U.S. 1,707,181, March 26, 1929; French 651,646, Feb. 21, 1929, Cent. 1929, II 499.
 Lustian, 124,284, Aug. 25, 1931, Cent. 1931, II 3176.
 Weller, Wenk, Stotter (to I G), Ger. 542,068, Jan. 20, 1929, Cent. 1932, I 3014.
 Kranzlein, Vollmann (to I.G.), Ger. 518,925, March 10, 1931; Cent. 1931, II 2786.
 Maennchen (to I.G.), Ger. 461,650, June 25, 1938, Cent. 1928, II 715.
 Ley I.G., Ger. 1931, Ger. 461,650, June 25, 1938, Cent. 1928, II 715.

(21) Maennchen (to I.G.), Ger. 461,650, June 25, 1938, Cent. 1928, II 715. (22) I.G., Ger. 462,151, July 6, 1928, Cent. 1929, I 2686. (23) Heading, Pharm. J. 138, 321-322 (1937); Chemist and Druggist 126, 392-393; Cent. 1937, II 2208. (24) Chakravarti, Bagchi, J. Indian Chem. Soc. 13, 692 (1936). (25) Autenrieth, Muhlinghaus, Ber. 40, 748 (1907). (26) Airan, Shah, J. Univ. Bombay 10, Pt. 5, 131-134 (1942); C.A. 37, 633 (1943).

3:3750 2,6-DICHLOROBENZO-QUINONE-1,4

(m-Dichlorobenzoquinone)

[See also 2,6-dichlorohydroquinone (3:4600).]

Yellow cryst. from C_6H_6 or lgr.; yellow pr. from alc. or AcOH. — \bar{C} is somewhat solboilg, aq. or cold alc.; eas. sol. hot alc.; sol. CHCl₃. — Sublimes far below m.p.; volatile

with steam. — Č turns skin reddish brown. [For study of photochem. decompn. of alc. soln. see (43).]

[For prepn. of C from 2,6-dichlorohydroquinone (3:4600) with CrO₃ (7) or with excess aq. FeCl₃ soln. on warming (9) see indic. refs.; from 2,4,6-trichlorophenol (3:1673) on oxidn. with CrO₃ in AcOH at 30-40° (yields: 69% (3), 27% (10)) (2), with cold fumg. HNO_3 (25% yield (11)) (6), with mixt. of fumg. $HNO_3 + conc.$ H_2SO_4 (12), with PbO_2 in AcOH or in C₆H₆ (10) or in alc. with HNO₂ (13) (14) cf. (10), see indic. refs. (note that in addn. to C the crude oxidn. prod. contains also 2-chloro-6-(2',4',6'-trichlorophenoxy)benzoquinone-1,4, m.p. 134-135° (10), and 2,6-bis-(2',4',6'-trichlorophenoxy)benzoquinone-1,4, m.p. 245° (10), which resemble C in appearance, composition, and behavior); from 2.6-dichloro-4-fluorophenol (8) or its dimethyl ether (8) or from 2.6-dichloro-4-bromophenol (11) with ice-cold HNO₃ (D = 1.5) see indic. refs.; from 2,6-dichloro-4-nitrophenol [Beil. VI-241, VI₁-(122)] on htg. above its m.p. (125°) (15) or in small amt, with mixt, of fumg, HNO₃ + fumg. H₂SO₄ at ord. temp. (16); from 2,6-dichloro-4-aminophenol [Beil. XIII-512, XIII₁-(183)] by oxidn. with $K_2Cr_2O_7 + H_2SO_4$ (90% yield (1)) (17) see indic. refs.; from 3,5-dichloro-4-aminophenol [Beil. XIII-513] similarly see (18); from 2,6-dichloro-pphenylenediamine [Beil. XIII-118, XIII₁-(37)] by oxidn. with dichromate see (19) (10); from 2,6-dichloro-4-bromophenol bromide (4) or from "2,4,6-trichlorophenol bromide" (2,4,6-trichloro-6-bromocyclohexadiene-1,4-one-3) [Beil. VII-145] (5) with cold fumg. HNO₃ see indic. refs.; from 2,6-dichlorobenzoquinone-1,4-(2,4-dinitroanil)-4 [Beil. XII-754] on hydrolysis with dil. H₂SO₄ in s.t. at 200° see (20).]

[For study of bactericidal value of \bar{C} see (21); for use as vulcanization accelerator see (22); for condensation with β -naphthylamine and use of prods. as intermediates in prepn. of sulfur dyes see (23); for condensation with various amines to yield corresp. mono- and diarylaminoquinones see (24); for condensation with various aminophenols and use of prods. in prepn. of oxazine dyes see (25); for condensation of \bar{C} with ρ -aminoaryl mercaptans and use in prepn. of vat dyes see (26); for reactn. with Na₂S₂O₃ + AcOH in prepn. of sulfur dyes see (40).]

 \bar{C} on reductn. with aq. SO₂ gives (80% yield (3)) (27) (1) 2,6-dichlorohydroquinone (3:4600) (note, however, that \bar{C} in dil. aq. NaOH under N₂ with SO₂ is in part reduced to 2,6-dichlorohydroquinone (3:4600) and in part sulfonated to mono- and disulfonic acids of \bar{C} (28)). — [For studies of the oxidn.-reductn. potential of system \bar{C} + 2,6-dichlorohydroquinone see (3) (29) (30) (42)] — [\bar{C} forms with 2,6-dichlorohydroquinone the corresp. quinhydrone, brown prismatic ndls., m.p. 135° (31), but does so less readily than the benzoquinone-1,4/hydroquinone system (3); note that this same quinhydrone is obtd. (36) from \bar{C} + ord. hydroquinone (36).]

[Č in CHCl₃ at low temp. does not react with Cl₂ but at ord. temps. gives (22) tetrachlorobenzoquinone-1,4 (chloranil) (3:4978). — Č in AcOH at 15–20° gives (11) with 2 moles Br₂ 2,6-dichloro-3,5-dibromobenzoquinone-1,4 [Beil. VII-642], m.p. 291° (11), accompanied by a little 2,5-dichloro-3,6-dibromobenzoquinone-1,4 [Beil. VII-642], m.p. 292° (11); but Č in boilg. AcOH with 2 moles Br₂ gives exclusively the latter (11) cf. (19) (33).] [Č with conc. HCl gives on boilg. (34) both 2,3,5-trichlorobenzoquinone-1,4 (3:4672) and 2,3,5,6-tetrachlorobenzoquinone-1,4 (chloranil) (3:4978).]

[C in cold alc. treated dropwise with 10% alc. KOH gives first a green soln. turning to brownish red and pptg. in poor yield (2) a potassium salt of 2-chloro-3,6-dihydroxybenzo-quinone-1,4 [Beil. VIII-378]; C in satd. alc. soln. at 50-60° with conc. NH₄OH gives a purple soln. grad. turning brownish red and pptg. (20-25% yield (2)) 2-chloro-3,6-dihydroxybenzoquinone-1,4-diimide [Beil. VIII-379], bronze-colored lfts. from AcOH, subliming at 258-260° without melting.]

 $[\bar{C} \text{ (1 pt.) in alc. (15-20 pts.)} + \text{conc. HCl (0.3-0.4 pts.)} \text{ treated with aniline (0.25 pt.)}$

yields mainly (35) 2,6-dichloro-3-anilinobenzoquinone-1,4 [Beil. XIV-137], blue ndls. or lfts., m.p. 154° (35), and 2,6-dichlorohydroquinone (3:4600) accompanied by small amts. of 2-chloro-3,6-dianilinobenzoquinone-1,4 (see below); \bar{C} in either alc. or AcOH with excess aniline yields (35) 2-chloro-3,6-dianilinobenzoquinone-1,4 [Beil. XIV-143], brown lfts. from AcOH, m.p. 262° (35), and 2,6-dichlorohydroquinone (3:4600).] — [Note that \bar{C} with sulfanilic acid behaves similarly: e.g., \bar{C} with 2 moles sulfanilic acid in aq. (best in pres. of NaOAc) yields (37) 2-chloro-3,6-bis-(p-sulfoanilino)benzoquinone-1,4 together with 2,6-dichlorohydroquinone (3:4600); in aq. alc., however, 2,6-dichloro-3-(p-sulfoanilino)benzoquinone is also formed (37).]

[Č with NH₂OH.HCl in alc. yields (38) 2,6-dichlorobenzoquinone-1,4-monoxime-4, pale yel. Ifts. from dil. alc., m.p. 140° (38), which with cold conc. HNO₃ oxidizes to 2,6-dichloro-4-nitrophenol [Beil. VI-241], colorless ndls. from aq., Ifts. from AcOH, tbls. from ether, m.p. 125° dec.; note that no dioxime can be formed]

[Č with semicarbazide HCl in cold dil. alc. gives (39) 2,6-dichlorobenzoquinone-1,4-semicarbazone-4, in red or yel. forms acc. to conditions, but both of m.p. 218° dec. (39); note that no bis-semicarbazone can be formed.]

[C with 20% soln, of triphenylphosphine in CHCl₃ gives an orange-red, red, or brown color (41) (also shown by trichlorobenzoquinone and by chloranil); for other limitations and details see (41).

3:3750 (1) van Erp, Ber. 58, 664-665 (1925). (2) Kehrmann, Tiesler, J. prakt. Chem. (2) 40, 480-486 (1889). (3) Conant, Fieser, J. Am. Chem. Soc. 45, 2202-2204 (1923). (4) Kohn, Sussmann, Monatsh. 46, 586 (1925). (5) Kohn, Rabinowtsch, Monatsh. 48, 353 (1927). (6) Faust, Ann. 149, 153-155 (1869). (7) Den Hollander, Rec. trav. chem. 39, 481-482 (1920). (8) Hodgson, Nixon, J. Chem. Soc. 1930, 1868-1869. (9) Dakin, Am. Chem. J. 42, 491 (1909). (10) Hunter, Morse, J. Am. Chem. Soc. 48, 1615-1624 (1926).

(11) Ling, J. Chem. Soc. 61, 559-560, 566-567, 576-578, 580-581 (1892). (12) Guareschi, Daccomo, Ber. 18, 1170 (1885). (13) Weselsky, Ber. 3, 646-647 (1870). (14) Lampert, J. prakt. Chem. (2) 33, 381 (1886). (15) Armstrong, Ber. 7, 926 (1874). (16) Armstrong, J. Chem. Soc. 24, 1121 (1871). (17) Kollrepp, Ann. 234, 14-15 (1886). (18) Bargellini, Leone, Atti accad. Lincei 8, 399-404 (1928); Cent. 1929, I 1441. (19) Lovy, Ber. 16, 1445-1447 (1883).

(20) Reverdin, Crépieux, Bcr. 36, 3263 (1903).

(21) Morgan, Cooper, J. Soc. Chem. Ind. 43-T, 352-354 (1924). (22) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; Cent. 1933, I 3133. (23) Thiess, Maennehen (to I.G.), Ger. 507,833, Sept. 20, 1930; Cent. 1930, II 8239. (24) Becke, W. Suida, H. Suida, Ger. 300,706, Dec. 19, 1919; Cent. 1920, II 537. (25) I.G., French 758,247, Jan. 12, 1934, Cent. 1934, I 2661; French 43,096, Feb. 8, 1934; Cent. 1934, II 2662. (26) Herz (to Graselli Dyestuff Corp.), U.S. 1,588,384, June 8, 1926; Cent. 1927, I 1377; C.A. 20, 2587 (1926). (27) Kohn, Marberger, Monatsh. 45, 654 (1924). (28) Dodgson, J. Chem. Soc. 1930, 2498-2502. (29) Hunter, Kvalnes, J. Am. Chem. Soc. 54, 2874-2875, 2878 (1932). (30) Kvalnes, J. Am. Chem. Soc. 56, 667-670 (1934).

(31) Ling, Baker, J. Chem. Soc. 63, 1321-1322 (1893). (32) Oliveri-Tortorici, Gazz. chim. ital. 27, II 585-586 (1897). (33) Hantzsch, Schniter, Ber. 20, 2279-2282 (1887). (34) Levy, Schultz, Ann. 210, 153 (1881). (35) Niemeyer, Ann. 228, 334-337 (1885). (36) Siegmund, J. prakt. Chem. (2) 92, 361-362 (1915). (37) H. Suida, W. Suida, Ann. 416, 136-142 (1918). (38) Kehrmann, Ber. 21, 3318 (1888). (39) Heilbron, Henderson, J. Chem. Soc. 103, 1417 (1913). (40) B.A.S.F., Ger. 175,070, Sept. 19, 1906; Cent. 1906, II 1466-1468.

(41) Schönberg, Ismail, J. Chem. Soc. 1940, 1375-1377. (42) Conant, J. Am. Chem. Soc. 49,

293-297 (1927). (43) Leighton, Dresia, J. Am. Chem. Soc. 52, 3556-3562 (1930).

3:3780 4-CHLORO-3-HYDROXYBENZ- ClOHO C7H5O2Cl Beil. S.N. 748 ALDEHYDE

M.P. 121° (1) (2)

Colorless ndls. (1).

[For prepn. of Č from m-hydroxybenzaldehyde (1:0055) via 4-nitro-3-hydroxybenzaldehyde, reduction to amino cpd., and use of appropriate diazo reactn. see (1).]

Č in 50% AcOH mononitrated as specified (2) gives mainly 4-chloro-2-nitro-3-hydroxy-benzaldehyde, spar. sol. in hot CHCl₃, colorless pr. from AcOH, m.p. 175° (2) (3). [Note that this statement takes account of a very important correction (3).] [This 4-chloro-2 nitro-3-hydroxybenzaldehyde yields the following derivs.: p-nitrophenylhydrazone, deep maroon ndls. from hot AcOH, m.p. 275-276° dec.; semicarbazone, lt. or. ndls. from alc., m.p. 265-266° dec. (2).]

Č in aq. contg. NaHCO₃ treated with (CH₈)₂SO₄ yields (1) 4-chloro-3-methoxybenzaldehyde, m.p. 52° (1). [This prod. depresses m.p. of corresp. methyl ether of the isomeric 2-chloro-3-hydroxybenzaldehyde (3:4085), m.p. 56-57° (1); on keeping it acquires a beautiful silver-gray color (1); it yields an oxime, colorless ndls., m.p. 98-99°, and a p-nitrophenylhydrazone, old-gold ndls., m.p. 251° (1).]

- 4-Chloro-3-hydroxybenzaldoxime: colorless ndls. of hydrate, dec. 106-110° from dil. alc.; anhydrous oxime, m.p. 126° (1).
- ---- 4-Chloro-3-hydroxybenzaldehyde phenylhydrazone: unrecorded.
- 4-Chloro-3-hydroxybenzaldehyde p-nitrophenylhydrazone: violet-red ndls. from dil. alc., m.p. 226-227° (1).
- 4-Chloro-3-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.
- 4-Chloro-3-hydroxybenzaldehyde semicarbazone: pale yel. ndls., m.p. 238-239° (1).
 3:3780 (1) Hodgson, Beard, J. Chem. Soc. 1926, 150-154. (2) Hodgson, Beard, J. Chem. Soc. 1926, 2033-2034. (3) Hodgson, Beard, J. Chem. Soc. 1927, 2377-2378.

3:3810 7-CHLORONAPHTHOL-1

M.P. 123° (1)

Ndls. from aq. or CS_2 ; spar. sol. aq. — \bar{C} has odor suggesting that of iodoform.

[For prepn. of \tilde{C} from γ -(p-chlorophenyl)paraconic acid [Beil. XVIII-421] by distn. see (1).]

 \tilde{C} dis. in aq. alk. from which it is repptd. by CO_2 ; the alk. soln. of \tilde{C} couples with diazonium salts yielding azo dyestuffs (1).

C with aq. FeCl₃ gives a yellowish white ppt. which on stdg. assumes a pronounced violet color (1).

Č (1 mole) with PkOH (1 mole) in CHCl₃ yields an addn. cpd., Č.PkOH, or.-red. ndls. from hot CHCl₃, m.p. 139° (1).

--- 7-Chloro-1-naphthyl acetate: oil.

3:3810 (1) Erdmann, Kirchhoff, Ann. 247, 374-375 (1888).

3:3840 1,4-DICHLORONAPHTHOL-2

(3)

M.P. 123-124° (1)

122-123° (2)

121°

Ndls. from lgr.; eas. sol. alc., ether, or AcOH. [For prepn. of Č from 1,1-dichloro-2-keto-1,2-dihydronaphthalene, m.p. 54° (2), 48-50°

(3) (itself prepd. from naphthol-2 (1:1540) in AcOH + NaOAc soln. with Cl₂ (2) (3)), by shaking with satd, soln. of HCl gas in AcOH for 2-3 min. (2) (3) see indic. refs.; from 1,1,3,4-tetrachloro-2-keto-1,2,3,4-tetrahydronaphthalene [Beil. VII-371] by partial reduction with SnCl₂ in AcOH (poor yield) see (1); from 1-chloronaphthol-2 (3:1700) with SO₂Cl₂ at ord. temp. (4) (note that this prepn. undoubtedly involves intermediate forms. of 1,1-dichloro-2-keto-1,2-dihydronaphthalene (above) (2)) see indic. refs.; from 1,4,5-trichloronaphthol-2 [Beil. VI-650] by partial reduction with Na/Hg see (4).]

[C in AcOH with Cl₂ gives (1) 1,1,4-trichloro-2-keto-1,2-dihydronaphthalene [Beil.

VII-386], m.p. 86-87°, together with other oily by-products.]

Č with SnCl₂/AcOH/HCl in s.t. at 100° for 8 hrs. gives (72% yield (2)) (3) 4-chloronaphthol-2 (3:3045), mp. 103-104°.

 \tilde{C} in AcOH mixed with conc. HNO₃ (D=1.42) and cautiously warmed until the liq. shows intense red color, then poured into aq., yields (1) 4-chloro-3-nitronaphthoquinone-1,2 [Beil. VII-724], red ndls. from AcOH, m.p. 184° (1).

 \bar{C} with aq. alc. Na₂SO₃ boiled 72 hrs. gives in poor yield (2) 4-chloronaphthol-2-sulfonic acid-1, cryst. from aq. with ½ H₂O (not lost at 100° in vac.); note that this prod. on hydrolysis with H₂SO₄ gives (91% yield (2)) 4-chloronaphthol-2 (3:3045), m.p. 103-104°.

(D) 1,4-Dichloro-2-naphthyl acetate: m.p. 90-91° (1). [From C with AcCl (1).]

3:3840 (1) Zincke, Kegel, Ber. 21, 3387-3389 (1888). (2) Burton, J. Chem. Soc. 1945, 280-283. (3) Fries, Schimmelschmidt, Ann. 484, 293, 295-296 (1930). (4) Armstrong, Rossiter, Chem. News 63, 136 (1891); Proc. Chem. Soc. 7, 32 (1891).

3:3860 3,3'-DICHLOROBENZOPHENONE
$$C_{13}H_8OCl_2$$
 Beil. S.N. 652 (Di-(m-chlorophenyl) ketone)

M.P. 123.8-124.9° (1) B.P. 160-166° at 2 mm. (1)

[For prepn. of \tilde{C} from *m*-chlorobromobenzene [Beil. V-209, V₁-(115), V₂-(161)] (2) via conversion to *m*-chlorophenyl MgBr (cf. (3)) and reaction with *m*-chlorobenzonitrile [Beil. IX-339] (4), followed by hydrolysis (77% yield), see (1).]

(1). 3,3'-Dichlorobenzophenone 2,4-dinitrophenylhydrazone: mp. 235-238° (1).

3:3860 (1) Haller, Bartlett, Drake, Newmann, Cristol, et al., J. Am. Chem Soc. 67, 1600-1602 (1945). (2) Hartwell, Org. Syntheses 24, 22-24 (Note 5) (1944). (3) Hein, Retter, Ber. 71, 1968 (1938). (4) Korczynski, Fandrich, Compt. rend. 183, 421-423 (1926); Cent. 1926, II 1853; C.A. 21, 77 (1927).

3:3900 3-CHLOROPHTHALIC ANHYDRIDE

[See also 3-chlorophthalic acid (3:4820).]

[For prepn. of \bar{C} from 3-chlorophthalic acid (3:4820) by distn. see (4) (2); from 3-nitrophthalic anhydride [Beil. XVII-486, XVII₁-(256)] by htg with PCl₅ in s.t. 6 hrs. at 175° (5) or 9 hrs. at 220° (60% yield (1)) or with Cl₂ at 240° (6) see indic. refs.; from phthalic anhydride (1:0725) with Cl₂ at 240° in pres. of Fe or Fe salts see (7).]

[C with Cl₂ in fumg. H₂SO₄ in pres. of I₂ gives (8) a mixt. contg. 3 pts. 3,6-dichlorophthalic anhydride (3:4860), m.p. 194° cor., and 1 pt. 3,4-dichlorophthalic anhydride (3:3695), m.p. 120-121°, b.p. 329°.]

[The neutral dimethyl and diethyl esters corresp. to \bar{C} are unreported; ethyl hydrogen 3-chlorophthalate has m p. 118-119° (3).]

[\tilde{C} with PCl₅ (3) or with SOCl₂ + ZnCl₂ in s.t. at 200-240° (9) yields 3-chlorophthaloyl (di)chloride, b.p. 169-171° at 16 mm. (3)]

 \bar{C} with urea on fusion at 170° gives (3) 3-chlorophthalimide, cryst from AcOH, m.p. 233° (3), 236° (15). — \bar{C} with 1 mole aniline htd. at 200–220° until no more steam is evolved (14) or \bar{C} with 1 mole aniline in boilg. AcOH (14) gives quant. yield 3-chlorophthalimide (N-phenyl-3-chlorophthalimide), pale cream-colored ndls from AcOH, m.p. 189–190° (14); \bar{C} similarly treated with p-toluidine gives (80–90% yield (14)) N-(p-tolyl)-3-chlorophthalimide, colorless ndls. from AcOH, m.p. 160.5° (14).

[Č with pyrocatechol (1:1520) + AlCl₃ + NaCl htd. at 130-138° gives (10) an intermediate prod. (presumably 3-chloro-2-(o,m-dihydroxybenzoyl)benzoic acid), yel. cryst. from AcOH, mp. 187° (10), which with cone. H₂SO₄ yields (10) 8-chloro-1,2-dihydroxyan-thraquinone (5-chlorohystazarin), yel. cryst. from pyridine, mp. 187° (diacetate, m.p. 193° (10)). — Č with hydroquinone (1:1590) + AlCl₃ + NaCl htd. at 200-220° for 40-50 min. yields (11) 8-chloro-1,4-dihydroxyanthraquinone (5-chloroquinizarin), red cryst. from xylene, m.p. 243° (diacetate, m.p. 205°, dimethyl ether, m.p. 208° (11)).]

[\bar{C} with C_6H_6 + AlCl₃ yields (12) 6-(3?)-chloro-2-(benzoyl)benzoic acid, m.p. 233.5°, which with conc. H_2SO_4 for 4 hrs. at 95° gives (59% yield (12)) 1-chloroanthraquinone (3:4480), m.p. 162° (12). — \bar{C} with p-xylene + AlCl₃ gives (81% yield (13)) 6-(3?)-chloro-2-(2,5-dimethylbenzoyl)benzoic acid, pr. from AcOH, m.p. 215°, which on warming with 9 pts. fumg. H_2SO_4 (10% SO_3) gives (96% yield (13)) 1-chloro-5,8-dimethylanthraquinone, yel. ndls. from AcOH, m.p. 186°.]

Č on boilg. with dil. HCl (1) or Č on saponification with standard alk. (Sap. Eq. = 91.3) followed by acidifn. gives 3-chlorophthalic acid (3:4820) q.v.

3:3900 (1) Smith, J. Chem. Soc. 1933, 1643-1644. (2) Guareschi, Gazz. chim. ital. 17, 122 (1887). (3) von Braun, Larbig, Kredel, Ber. 56, 2338 (1923). (4) Krüger, Ber. 18, 1759 (1885). (5) Bogert, Boroschek, J. Am. Chem. Soc. 23, 751-752 (1901). (6) Imperial Chem. Ind., Ltd., Shaw, Thomas, Brit. 357,165, Oct. 15, 1931; Cent. 1931, II 3603. (7) Dvornikoff (to Monsanto

Chem. Co.), U.S. 2,028,383, Jan. 21, 1936; Cent. 1936, I 2830; C.A. 30, 1394 (1936).
(8) Villiger, Ber. 42, 3549 (1909).
(9) Kyrides (to Monsanto Chem. Co.), U.S. 1,951,364, March 20, 1934; Cent. 1934, II 333.
(10) Waldmann (to I.G.), Ger. 642,719, March 12, 1937; Cent. 1937, I 5048-5049; C.A. 31, 6261 (1937).

(11) Waldmann, J. prakt. Chem. (2) 136, 100 (1931). (12) Dougherty, Cleason, J. Am. Chem. Soc. 52, 1024-1027 (1930). (13) Mayer, Heil, Ber. 55, 2163 (1922). (14) Marriott, Robinson,

J. Chem. Soc. 1939, 136-137. (15) Drew, Pearman, J. Chem. Soc. 1937, 31.

3:3925 7-CHLORONAPHTHOL-2

M.P. 126.5° (1)

White lfts. from lgr.

[For prepn. of C from 7-hydrazinonaphthol-2 [Beil. XV-613] by treatment of its soln. in dil. HCl with CuSO₄ (19% yield) see (1).]

[\bar{C} (as sodium salt) treated with CO₂ at 230-250° and 45 atm. press. yields (2) 7-chloro-2-hydroxynaphthoic acid-3, yellowish lfts. from AcOH, m.p. 277-278° (2)]

0 7-Chloro-2-naphthyl acetate: lfts. from toluene, m.p. 104.5° (1). [From $\ddot{\textbf{C}}$ on refluxing with acetyl chloride (1).]

3:3925 (1) Franzen, Deibel, J. prakt. Chem. (2) 78, 154 (1878). (2) Lange, Luce, Jacobs (to I.G.), Ger. 564,128, Nov. 14, 1932; Cent. 1933, II 446.

3:3934 p-PHENYLPHENACYL CHLORIDE

(ω -Chloro-p-phenylacetophenone; chloromethyl p-xenyl ketone; 4-(chloroacetyl)biphenyl)

M.P. 126-127° (1) 122-123° (2) (3)

Pale vel. ndls. from dil. alc.

[For prepn. of C from biphenyl (1:7175) with chloroacetyl chloride (3:5235) + AlCl₃ (41% yield (2)) (3), or with chloroacetic acid anhydride (3:0730) + AlCl₃ (77% yield (2)), see indic. refs.]

[C with chloroacetyl chloride (3:5235) + AlCl₃ gives (52% yield (2)) 4,4'-bis-(chloroacetyl)biphenyl, ndls. from di-n-propyl ketone or cyclohexanone, m.p. 228-229° (2), 226-227° (4); note that this prod. with excess piperidine yields (4) 4,4'-bis-(piperidinoacetyl)biphenyl, brownish yel. pdr. from acetone, m.p. 143-144° (4).

[C with piperidine has not been directly reported but should yield 4-(piperidinoacetyl)biphenyl, ndis. from abs. alc., m.p. 93-94° (4), as has been demonstrated for the analogous p-phenylphenacyl bromide.]

Č with salts of acids should yield the corresp. p-phenylphenacyl esters (for table of examples see Vol. I, p. 652) although the usual reagt. for this purpose is the more common p-phenylphenacyl bromide.

 \tilde{C} with calcd. amt. of KMnO₄ in aq. alk. at 100° is oxidized (3) to p-phenylbenzoic acid [Beil. IX-671, IX₁-(280)], m.p. 217-218° (3) (228°).

3:3934 (1) Eastman Kodak Co., List No. 34 (1944). (2) Silver, Lowy, J. Am. Chem. Soc. 56, 2429-2430 (1934). (3) Collet, Bull. soc. chim. (3) 17, 510 (1897). (4) Carpenter, Turner, J. Chem. Soc. 1934, 872.

3:3945 5-CHLORONAPHTHOL-2

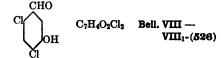
M.P. 128° u.c. (1)

Ndls.; sol. alc., AcOH, C₆H₆, CS₂. — Sublimes; volatile with steam.

[For prepn. of \bar{C} from salts of 2-hydroxynaphthalenesulfonic acid-5 [Beil. XI-282] by htg. with PCl₅, then distilling with steam, see (1).]

3:3945 (1) Claus, J. prakt. Chem. (2) 39, 317 (1889).

3:3952 4,6-DICHLORO-3-HYDROXY-BENZALDEHYDE



M.P. 130° (1) 129° (2)

Fairly eas. sol. hot aq.; eas. sol. C_6H_6 , alc.; insol. lgr. — Volatile with steam. \bar{C} has very pronounced sternutatory props. and also attacks moist skin producing painful blisters (2).

[For prepn. of \bar{C} from 4,6-dichloro-3-methylphenol (3:1745) via conv. to bis-(4,6-dichloro-3-methylphenyl) carbonate, chlorination of latter, and subsequent alk. hydrol. of the chlorination prod. see {1}; for formin. (in small amt. together with much 2,6 isomer) from 6-chloro-3-hydroxybenzaldehyde (3:3350) or from m-hydroxybenzaldehyde (1:0055) in AcOH with Cl_2 see {2}.]

 \bar{C} in 4 pts. AcOH + 1 pt. aq. treated grad. with 1 pt. conc. HNO₃ (D=1.4) yields (1) 4,6-dichloro-2-nitro-3-hydroxybenzaldehyde, m.p. 157° (1); this prod. with acetone and alk. yields (1) the corresp. indigoid, viz , 4,4,6,6-tetrachloro-7,7-dihydroxyindigo.

4,6-Dichloro-3-methoxybenzaldehyde: ndls. from C₆H₆, m.p. 117° (1).

3:3952 (1) Friedlander, Schenck, Ber. 47, 3048, 3051 (1914). (2) Hodgson, Beard, J. Chem. Soc. 1926, 148-149, 152.

3:3956 o-CHLOROPHENYLPROPIOLIC C₉H₅O₂Cl Beil. S.N. 950 ACID C=C—COOH

M.P. 131-132° (1) (2) 131° (3)

Cryst. from 50% AcOH or C6H6.

[For prepn. of C from o-chlorobenzaldehyde (3:6410) by conversion through o-chlorocinnamic acid to ethyl o-chlorocinnamate, thence by addn. of Br₂ to give ethyl β -(o-chlorophenyl)- α , β -dibromopropionate, followed by elimination of 2 HBr and saponification (or vice versa) with alc. KOH, and final acidification (68% yield (1)) (2) cf. (3), see indic. refs.]

 \bar{C} suspended in aq., treated with NaHCO₃ + CuCl₂, and steam-distilled (1) or \bar{C} with Cu(OAc)₂ (2) loses CO₂ giving (66% yield) o-chlorophenylacetylene (3:9497).

3:3956 (1) Bergmann, Bondi, Ber. 66, 282-283 (1933). (2) Otto, J. Am. Chem. Soc. 56, 1393-1394 (1934). (3) Wilson, Wenzke, J. Am. Chem. Soc. 57, 1265-1267 (1935).

3:3960 5-CHLORONAPHTHOL-1

M.P. 131.5° (1)

Ndls. from aq., lfts. from CS_2 ; spar. sol. aq. $-\bar{C}$ has characteristic odor.

[For prepn. of \tilde{C} from γ -(2-chlorophenyl)paraconic acid [Beil. XVIII-421] on rapid distn. see (1).]

[For condensation of C with subst. isatin chlorides in prepn of indigoid dyes see (2).]

C dis. in aq. alk. and this soln couples (1) with diazonium salts yielding azo dyestuffs.

C with aq. FeCl₃ gives a yellowish-white ppt. unchanged on stdg; C with Ca(OCl)₂ soln, gives a pale violet ppt. (1).

- Č (1 mole) in CHCl₃ on mixing with PkOH (1 mole) in CHCl₃ gives (1) ppt. of addn. epd., Č.PkOH, orange ndls. from hot CHCl₃, m.p. 160° (1).
 - **5-Chloro-1-naphthyl acetate:** lfts. from alc., m.p. 53° (1). [From C on protracted boilg, with AcCl (1).]

3:3960 (1) Erdmann, Kirchhoff, Ann. 247, 372-374 (1888). (2) I.G., Brit. 318,107, Oct. 23, 1929; Cent. 1930, I 1383.

3:3965 TETRACHLOROBENZO-QUINONE-1,2

(Tetrachloro-o-quinone)

 $\begin{array}{c} Cl \\ Cl \\ Cl \\ Cl \end{array}$ $\begin{array}{c} Cl \\ Cl \\ Cl \\ \end{array}$ $\begin{array}{c} Cl \\ Cl \\ \end{array}$

[See also tetrachloropyrocatechol (3:4875).]

Red cryst. pdr. (1), cryst. from dil. AcOH (2).

[For prepn. of C from tetrachloropyrocatechol (3:1520) by oxidn. with fumg. HNO₃ in AcOH (81% yield (1)) (2) (3) (4) (5) (6) see indic. refs.; from pyrocatechol (1:1520) (2) (3) or pyrocatecholsulfonic acid (7) with Cl₂ in AcOH see indic. refs.; from tetrachloropyrocatechol monomethyl ether (tetrachloroguaiacol) (8) or from tetrachloropyrocatechol dimethyl ether (tetrachloroveratrole) (8) by oxidn. with HNO₃ see indic. refs.]

[C adds 1 mole Cl₂ yielding (9) hexachlorocyclohexene-3-dione-1,2 [Beil. VII-575] q.v. which on reduction with SnCl₂ in AcOH (3) gives tetrachloropyrocatechol (3:4875).]

[C with PCl₅ (2 moles) htd. in s.t. at 200–210° for $\frac{1}{2}$ hr. gives (10) hexachlorobenzene (3:4939) and other products.]

[For complex behavior of \bar{C} on htg. with aq., with cold alcs., or with aniline see Beil. VII-602, VII₁-(338).]

 $\bar{\rm C}$ forms addn. cpds. with many hydrocarbons [e.g., $\bar{\rm C}$ with benzene gives $\bar{\rm C}.3{\rm C}_6{\rm H}_6$, m.p. 37-42° (11); $\bar{\rm C}$ with toluene gives $\bar{\rm C}.{\rm C}_7{\rm H}_8$, m.p. 45-50° (11); $\bar{\rm C}$ with hexamethylbenzene (1:7265) gives $\bar{\rm C}.{\rm C}_{12}{\rm H}_{18}$, greenish black ndls. from AcOH, m.p. 140-143° (11),

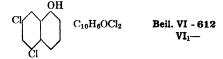
C with equiv. tetrachloropyrocatechol (3:4875) in least possible hot CHCl3 gives on

cooling the corresp. quinhydrone (6). — [For study of oxidn.-reductn. potential of system $\bar{C}/\text{tetrachloropyrocatechol}$ see (4) (5).]

3:3965 (1) Jackson, MacLaurin, Am. Chem. J. 37, 11-12 (1907). (2) Zincke, Ber. 20, 1779 (1887). (3) Zincke, Kuster, Ber. 21, 2729-2730 (1888). (4) Conant, Fieser, J. Am. Chem. Soc. 46, 1873, 1875 (1924). (5) Kvalnes, J. Am. Chem. Soc. 56, 2487-2489 (1934). (6) Jackson, Carleton, Am. Chem. J. 39, 497 (1909). (7) Datta, Bhoumik, J. Am. Chem. Soc. 43, 313 (1921). (8) Cousin, Compt. rend. 129, 967 (1899). (9) Zincke, Kuster, Ber. 22, 487 (1889). (10) Zincke, Kuster, Ber. 24, 927-928 (1891).

(11) Pfeiffer, Ann. 412, 294-296 (1916).

3:3985 5,7-DICHLORONAPHTHOL-1



M.P. 132° (1) (2)

Pale yel. pr. (from CS₂) (1) (2). — Somewhat sol. hot aq.

[For prepn. from γ -(2,4-dichlorophenyl)paraconic acid [Beil. XVIII-421] by distn. see (2)

C with FeCl₃ gives a white ppt. which on htg. with excess reagt. colors violet (2).

Č in dil. alk, soln, couples with diazotized naphthionic ac (1-aminonaphthalenesulfonic acid-4) giving intense purple color (2).

C on distn, with Zn dust yields naphthalene (1:7200) (2) (1).

5,7-Dichloro-1-naphthyl acetate: from C on protracted refluxing with 4 pts. AcCl; pr. (from CHCl₃ + lgr.), m p 110° (2).

3:3985 (1) Erdmann, Schwechten, Ber. 21, 3444 (1888). (2) Erdmann, Schwechten, Ann. 275, 284–285 (1893).

CHAPTER X

DIVISION A. SOLIDS

(3:4000-3:4499)

3:4000 4-CHLORONAPHTHO-QUINONE-1,2

M.P. 132-136° dec. (1)
[188° (2) see text]

Orange-red ndls. from C_6H_6 by addn. of lgr.; \bar{C} could not be further purified by recrystallization since some decompn. always occurred (1)

[For prepn. of \bar{C} from 1,4-dichloronaphthol-2 (3:3840) by conversion (59% yield) with HNO₃ in AcOH to 1,4-dichloro-1-nitro-2-keto-dihydronaphthalene, followed by subsequent elimination of NOCl by boiling with C_6H_6 (80% yield), see (1). — Note that the prod. of m.p. 188°, maroon ndls. from alc., obtd. (2) from 4-chloro-1,2-diaminonaphthalene (4-chloronaphthylenediamine-1,2) by air oxidn., is regarded as \bar{C} ; this discrepancy is unexplained.]

Č on reductive acetylation with Ac₂O + NaOAc + Zn dust loses its halogen atom giving (60% yield (1)) 1,2,4-triacetoxynaphthalene [Beil. VI-1133], m p. 134-135° (1).

[Č with 2,3-dimethylbutadiene (1:8050) in specially purified CHCl₃ in st. at 100° in dark for 72 hrs. undergoes a Diels-Alder type addition only very slowly (1); no intermediate addn. prod. could be isolated (difference from the isomeric 3-chloronaphthoquinone-1,2 (3:4704)), but on stdg. the soln. slowly deposits (15% yield (1)) 2,3-dimethylphenanthraquinone, mp. 237-238° u.c.; 242-243° cor. (1).]

4-Chloronaphthoquinone-1,2-oxime-2 (4-chloro-2-nitrosonaphthol-1) [Beil. VII₁-(385)]: pale yel. ndls., m.p. 157°. [Prepd. indirectly.]

3:4000 (1) Fieser, Dunn, J. Am. Chem. Soc. 59, 1019-1020 (1937). (2) Hodgson, Elliott, J. Chem. Soc. 1935, 1853.

3:4005 1,4,5-TRICHLORONAPHTHALENE

M.P. 133° (1) 131° (2) (3) (4) 129° u.c. (3)

Ndls. from alc. in which Č is spar. sol. — Volatile with superheated (3) steam. [For formn. of Č from sodium 1,5-dinitronaphthalenesulfonate-4 (1) with HCl + NaClO₃ 360

see (1); for prepn. of Č from 1,5-dichloro-4-nitronaphthalene [Beil. V-556] (3), from 1,4-dichloro-5-nitronaphthalene [Beil. V-556, V₁-(264)] (4) (3), from 4-chloro-1,5-dinitronaphthalene [Beil. V-561] (3), from 1-chloro-4,5-dinitronaphthalene [Beil. V-561] (3), from 4,5-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-162] (5), from 4-chloro-5-nitronaphthalenesulfonyl chloride-1 [Beil. XI-170] (6), from 5-chloro-4-nitronaphthalenesulfonyl chloride-1 [Beil. XI-170] (6), from 1-chloro-4-nitronaphthalenesulfonyl chloride-5 [Beil. XI-170] (6), or from 4-chloronaphthalene-1,5-bis-(sulfonyl chloride) [Beil. XI-213] (7) (2), each with PCl₆ as directed, see indic. refs.]

[C treated with ClSO₃H in CS₂ and reactn. prod. conv. to salts as directed (2) yields a mixt. of two sulfonates, viz., one derived from 1,4,5-trichloronaphthalenesulfonic acid-7 (corresp. sulfonyl chloride, m.p. 118° (2)) and the other derived from 1,4,5-trichloronaphthalenesulfonic acid-X (corresp. sulfonyl chloride, m.p. 178° (2)).

 $[\bar{C}$ on oxidn. with dil. HNO₃ in s.t. yields (3) a dichloro acid, presumably 3,6-dichlorophthalic acid (3:4870).]

3:4005 (1) Friedlander, Karamessinis, Schenk, Ber. 55, 47 (1922). (2) Turner, Wynne, J. Chem. Soc. 1941, 247, 254-255. (3) Atterberg, Ber. 9, 1187, 1733-1734 (1876). (4) Widman, Bull. soc. chim. (2) 28, 511 (1877). (5) Armstrong, Wynne, Chem. News 61, 273 (1890). (6) Cleve, Chem. Ztg. 17, 398 (1893). (7) Armstrong, Wynne, Chem. News 62, 163 (1890).

Colorless cryst. with camphoraceous odor; extremely volatile and readily sublimes; insol. aq. and volatile with steam; purified by sublimation or crystn. from boilg. MeOH.

[For prepn. of \bar{C} from 2,2,3-trimethylbutanol-3 (pentamethylethanol) [Beil. I-418, I₁-(207), I₂-(447)] (3) or its hydrate (1) with fumg. HCl (2) (3), with PCl₅ (1) or with AcCl (3:7065) (46% yield (4)) see indic. refs.; from 2,2,3-trimethylbutane ("triptane") (1:8544) with ter-butyl chloride (3:7045) + AlCl₅ by shaking 30-45 seconds (16% yield) see (4).]

C with alc. AgNO₃ ppts. AgCl even in cold (3).

 \tilde{C} with Mg in dry ether gives RMgCl; this upon oxidn. with O_2 and subsequent hydrolysis yields (2) 2,2,3-trimethylbutanol-2, m.p. 80° (2).

C converted to RMgCl and the latter treated with CO₂ yields (2) ter-butyl-methylacetic acid [Beil. II₂-(150)], m p. 80° (2).

3:4020 (1) Butlerow, Ann. 177, 183-184 (1875). (2) Richard, Ann. chim. (8) 21, 356-358 (1910). (3) Henry, Compt. rend. 142, 1024 (1906); Rec. trav. chim. 26, 104 (1907). (4) Bartlett, Condon, Schneider, J. Am. Chem. Soc. 66, 1533, 1537 (1944).

3:4030 2,4,6-TRICHLOROPHLORO-GLUCINOL

Cryst. from abs. alc. — Note that from aq. \bar{C} cryst. as a trihydrate (1), but on htg. this hydrate loses aq. before melting (2); note also that \bar{C} on recrystn. from toluene gives a solvated prod., m.p. $108-109^{\circ}$ (1). [For study of crystallography of \bar{C} see (4).]

 $\bar{\mathbf{C}}$ is alm. insol. aq. or cold $\mathbf{C}_6\mathbf{H}_6$; sol. alc. — $\bar{\mathbf{C}}$ readily sublimes.

[For prepn. of \bar{C} from phloroglucinol (1,3,5-trihydroxybenzene) (1:1620) with Cl_2 in CCl_4 (crude yield 76% (1)) or in AcOH (5) see indic. refs.; note that attempts (6) (7) to prepare \bar{C} from phloroglucinol (1:1620) with Cl_2 in aq. soln. were not effective owing to further decompn. of the prod. into dichloroacetic acid (3:6208) and/or the tetrahydrate of sym.-tetrachloroacetone (3:6050) cf. (1)

[For forms. of C from phloroglucinol (1:1620) with SO₂Cl₂ in dry ether see (3)]

[For formn. of \bar{C} from hexachlorocyclohexanetrione-1,3,5 ("hexachlorophloroglucinol") [Beil. VII-854, VII₁-(469)] by reduction with SnCl₂ or KI see (7)]

 \bar{C} dis. in hot cone. HCl from which on cooling it separates in fine ndls; \bar{C} with warm dil. HNO₃ is decomposed with forms. of oxalic acid (1.0445); \bar{C} with cone. H₂SO₄ dissolves unchanged on gentle warming, but on contd htg. HCl is evolved and soln turns deep sage-green (1).

 \tilde{C} dissolves in aq alk. but is repptd. unchanged upon acidification; note, however, that alk. soln. of \tilde{C} on stdg in air develops a purple color (1)

- $[\bar{C} \text{ in AcOH} \text{ added to excess Br}_2/\text{aq.}$ undergoes ring cleavage with form. of 1,1,3,5,5-pentabromo-1,3,5-trichloropentanedione-1,4 [Beil I-786], colorless cryst. from pet. ether, m.p. 93-95°, to a turbid liq. becoming clear at 98° (8).]
- 3:4030 (1) Webster, J. Chem. Soc. 47, 423-426 (1885). (2) Zincke, Kegel, Ber. 23, 1731-1732 (1890). (3) Peratoner, Finocchiaro, Gazz. chim. stal. 24, I 243-244 (1894). (4) Déverin, Bull. soc. saud. scc. natur. 59, 417-428 (1937), Cent. 1938, II 847, C.A. 34, 4320 (1940). (5) Hazura, Benedikt, Monatsh. 6, 706-707 (1885). (6) Hlasiwetz, Habermann, Ann. 155, 132-134 (1870). (7) Zincke, Kegel, Ber. 22, 1473-1477 (1889). (8) Zincke, Kegel, Ber. 23, 1720-1721 (1890). (9) Ciamician, Silber, Ber. 24, 2980-2981 (1891).

3:4040 2,6-DICHLORONAPHTHALENE

Tbls. from ether $+ C_6H_6$, ndls. from hot alc., pr. from AcOH. — Spar. sol. alc.; eas. sol. ether, C_6H_6 , or CHCl₃. — Volatile with steam.

[For prepn. of \tilde{C} from naphthalene-2,6-bis-(sulfonyl chloride) [Beil. XI-216] (8) (10), from 6-chloronaphthalene-2-sulfonyl chloride [Beil. XI-180] (45% yield (2)) (1) (9), from 6-bromonaphthalene-2-sulfonyl chloride [Beil. XI-184] (11), from salts of 2-hydroxy-naphthalenesulfonate-6 [Beil. XI-282, XI₁-(66)] (59% yield (3)) (4) (5), or from 6-bromonaphthol-2 [Beil. VI-651] (55% yield (12)) with PCl₅ as directed, see indic. refs; from 6-sulfonaphthylamine-2 [Beil. XIV-760, XIV₁-(735)] by treatment of corresp. diazonium chloride with PCl₅ in POCl₃ see (13) (14); from 2,6-diaminonaphthalene [Beil. XIII-208] via tetrazotization in HCl followed by htg. with Cu pdr see (6); from sodium β-naphthalenesulfonate [Beil. XI-171, XI₁-(38)] with KClO₃ + boilg. dil. HCl (50% yield) see (15).] (\tilde{C} in CHCl₃ satd with Cl₃ gives (9% yield (20)), 1.2 6-triplepropaphthylana (3:2515).

 $[\tilde{C} \text{ in CHCl}_3 \text{ satd. with Cl}_2 \text{ gives } (9\% \text{ yield } \{20\}) 1,2,6-\text{trichloronaphthalene } (3:2515), m.p. 92^\circ.]$

 \bar{C} on oxidn. with dil. HNO₃ (D=1.2) in s t at 150° (16) or better with dil. HNO₃ (D=1.13) in s t. at 190-200° (17) yields 4-chlorophthalic acid (3.4390), m.p. 148° u.c. (17). — \bar{C} on oxidn. with CrO₃/AcOH yields (18) 2,6-dichloronaphthoquinone-1,4 [Beil. VII-730], bright yel. ndls., m.p. 149-149° (18), this cpd. also accompanies (18) the 4-chlorophthalic acid of the same m.p. during HNO₃ oxidn. (above).

[\overline{C} on mononitration yields (16) two isomers, one m.p. 139-139.5°, the other m.p. 113.5-114° (16)

[Č in CS₂ treated with ClSO₃H yields (19) 2,6-dichloronaphthalenesulfonic acid-4 [Beil. XI-162] (corresp. sulfonyl chloride, m.p. 136°, corresp. sulfonamide, m.p. 269°).]

3:4040 (1) Forsling, Ber. 20, 80-81 (1887). (2) Beattie, Whitmore, J. Am. Chem. Soc. 55, 1548 (1933) (3) Weissberger, Sangewald, Z. physik. Chem. B-20, 146-147 (1933). (4) Claus, Zimmermann, Ber. 14, 1483-1484 (1881). (5) Pollak, Gebauer-Fulnegg, Blumenstock-Halward, Monatsh. 49, 197 (1928). (6) Veseley, Jakes, Bull. soc. chim. (4) 33, 949 (1923). (7) Tilden, Armstrong, Chem. News 58, 295 (1888). (8) Cleve, Bull. soc. chim. (2) 26, 245 (1876). (9) Arnell, Bull. soc. chim. (2) 45, 184 (1886). (10) Armstrong, Wynne, Chem. News 62, 163 (1890). (11) Sindall, Chem. News 60, 58 (1889). (12) Franzen, Stauble, J. prakt Chem. (2) 103, 370 (1921/22). (13) Erdmann, Ann. 275, 280 (1893). (14) Nakata, Ber. 64, 2067 (1931). (15) Kozlov, Talybov, J. Gen. Chem. (U.S.R.) 9, 1827-1833 (1939); C.A. 34, 4067 (1940). (16) Alén, Bull. soc. chim. (2) 36, 434 (1881). (17) Claus, Ber. 51, 320 (1882). (18) Claus, Müller, Ber. 18, 3073-3074 (1885). (19) Arinstrong, Wynne, Chem. News 61, 273-275 (1890). (20) Wynne, J. Chem. Soc. 1946, 61.

3:4052 2,3,5-TRICHLOROHYDROQUINONE OH $C_6H_3O_2Cl_3$ Beil. VI - 850 VI₁— VI₂-(846)

[See also 2,3,5-trichlorobenzoquinone-1,4 (3:4672).]

Colorless shining pr. from aq. rapidly losing their luster in air (3); transparent pr. with 1 mole AcOH from AcOH but solvated AcOH readily lost in air (5).

Č at 15° is sol. in 160 pts. aq. (6); Č is spar. sol. cold aq. but cas. sol. hot aq. in which it first melts to an oil (3); Č is eas. sol. alc. or ether.

C readily sublimes in lfts. (4); for study of sublimation press. see (7).

[For study of heat of forms. of \bar{C} see (8); for studies of heat of combustion of \bar{C} see (5) (9).]

[For detn. of chlorine in \bar{C} by hydrogenation at elevated temp. see (10); for patent on use of \bar{C} as vulcanization accelerator see (11).]

PREPARATION OF C

From trichlorobenzoquinone. [For prepn. of Č from 2,3,5-trichlorobenzoquinone-1,4 (3:4672) by reduction with aq. SO₂ (3) (4) (6) (12) in ether (1), or from "benzoquinone tetrachloride" (2,3,5,6-tetrachlorocyclohexanedione-1,4) [Beil. VII-557] with aq. SO₂ (13), see indic. refs.]

From other sources. [For formn. of \bar{C} (together with other products) from 2,5-dichlorobenzoquinone-1,4 (3:4470) or from 2,6-dichlorobenzoquinone-1,4 (3:3750) with boilg. conc. HCl see (14); from C_6H_6 with KClO₃ + H_2SO_4 see (16).]

CHEMICAL BEHAVIOR OF C

Reduction. [\bar{C} with Na/Hg in acid soln. is hardly affected and does *not* (3) give hydro-quinone; however, for anal. of \bar{C} by quant. detn. of chlorine with H₂ at elev. temp. see (10).]

Oxidation. \bar{C} on oxidn., e.g., with CrO₃ at 0° (5), conc. HNO₃ (4) (3), AgNO₃ (4), or FeCl₃ (4), gives 2,3,5-trichlorobenzoquinone-1,4 (3:4672); note, however, that with insufficient oxidizing agent the corresp. quinhydrone (see below) may separate.

[For study of oxidn -reductn. potential of system $\bar{C} + 2,3,5$ -trichlorobenzoquinone-1,4 (3:4672) see (2) (17) (18).]

C (1 mole) with 2,3,5-trichlorobenzoquinone-1,4 (3:4672) (1 mole) in CHCl₃ soln. gives on evapn. (2) (19) the corresp. quinhydrone, green-black cryst., m.p. 114-115° (2), 103° (19).

[Note also that Č in aq. KOH exposed to air first turns green, then red, and finally brown (4), and this soln. on stdg. or boilg. in air gradually separates the corresp. potassium salt of chloranilic acid (3:4970) (3).]

Other reactions of \bar{C} . $[\bar{C}$ with PCl₅ (2 moles) on htg. gives (3) a mixture of pentachlorobenzene (3:2290) and hexachlorobenzene (3:4939).]

- ---- Trichlorohydroquinone dimethyl ether (3,4,5-trichloro-1,4-dimethoxybenzene): unreported.
- Trichlorohydroquinone diethyl ether (3,4,5-trichloro-1,4-diethoxybenzene): ndls. from alc., m.p. 68.5° (3). [From C with C₂H₈I + KOH in s.t. (3).]
- Trichlorohydroquinone diacetate: ndls. by sublimation, m.p. 153° (3). [From C with AcCl under reflux (3).]
- Trichlorohydroquinone dibenzoate: ndls. from CS₂, m.p. 174° (14). [From C̄ with BzCl on htg. (14).]

3:4052 (1) Biltz, Giese, Ber. 37, 4017 (1904). (2) Conant, Fieser, J. Am. Chem. Soc. 45, 2206-2207 (1923). (3) Graebe, Ann. 146, 22-30 (1868). (4) Städeler, Ann. 69, 321-326 (1849). (5) Valeur, Ann. chim. (7) 21, 496-499 (1900). (6) Stenhouse, Ann. Suppl. 6, 218 (1868). (7) A. S. Coolidge, M. S. Coolidge, J. Am. Chem. Soc. 49, 100-104 (1927). (8) Sjöstrom, Svensk Kem. Tvd. 48, 121-124 (1936); Cent. 1937, I 58; C.A. 30, 6634 (1936). (9) Swietoslawski, Starczewska, J. chim. phys. 23, 399-401 (1925). (10) ter Meulen, Heslinga, Rec. trav. chim. 42, 1093-1096 (1923).

(11) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; Cent. 1933, I 3134; C.A. 27, 2845 (1933). (12) Graebe, Ann. 263, 28 (1891). (13) Peratoner, Genco, Gazz. chim. ital. 24, II 389-390 (1894). (14) Levy, Schultz, Ann. 210, 153-154 (1881). (15) Krafft, Ber.

797-800 (1877). (16) Carius, Ann. 142, 129-138 (1867). (17) Conant, J. Am. Chem. Soc.
 293-297 (1927). (18) Kvalnes, J. Am. Chem. Soc. 56, 667-670 (1934). (19) Ling, Baker, J. Chem. Soc. 63, 1322-1323 (1893).

3:4065 3-CHLORO-4-HYDROXYBENZ- HOCHO
$$C_7H_6O_2Cl$$
 Beil. VIII - 81 ALDEHYDE $VIII_1-$

```
M.P. 139° cor. (1) B.P. 149-150° at 14 mm. (1) 132-134° (2) 127-128° (3)
```

Ndis. from aq. (1). — Very spar. sol. cold aq., eas. sol. hot aq.; spar. sol. CHCl₃; eas. sol. alc., ether (1).

[For prepn. of $\bar{\rm C}$ from p-hydroxybenzaldehyde (1:0060) with ${\rm Cl_2}+{\rm CHCl_3}$ see (1) (2); from 3-chloro-4-hydroxybenzyl alcohol by htg. with alk. sodium m-nitrobenzenesulfonate see (3); from o-chlorophenol (3:0255) + CH₂O under specified circumstances see (4) or with chloral (3:5210) see (5).]

C with FeCl₃ gives no coloration (3). — C forms a NaHSO₃ cpd. (3).

Č in EtOAc hydrogenated with H₂ at 40 lb./sq. in. for 45 min. in presence of Raney Ni cat. gives (2) 3-chloro-4-hydroxybenzyl alc., cryst. from C₆H₆, m.p. 127° (2).

- 3-Chloro-4-hydroxybenzaldoxime: ndls. from aq. or CHCl₃, m p. 144-145° (1).
- --- 3-Chloro-4-hydroxybenzaldehyde phenylhydrazone: unrecorded.
- ---- 3-Chloro-4-hydroxybenzaldehyde p-nitrophenylhydrazone: unrecorded.
- 3-Chloro-4-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.
- 3-Chloro-4-hydroxybenzaldehyde semicarbazone: yel. ndls. from very dil. AcOH, m.p. 210° dec. (1); 212° (3).

3:4065 (1) Biltz, Ber. 37, 4031-4034 (1904). (2) Buehler, Brown, Holbert, Fulmer, Parker, J. Org. Chem. 6, 904 (1941). (3) Hanus, J. prakt. Chem. 158, 263 (1941). (4) Geigy and Co., Ger. 105,798; Cent. 1900, I 523. (5) Haakh, Smola, Austrian 151,159, March 25, 1935; Cent. 1935, I 439.

3:4085 2-CHLORO-3-HYDROXYBENZ- CHO $C_7H_5O_2Cl$ Beil. S.N. 745 ALDEHYDE

M.P. 139.5° (1) 139-139.5° (3) 139° cor. (4)

Colorless cryst. from dil. AcOH (1) becoming pale pink on prolonged exposure to air (1). — Č has pronounced sternutatory props. (1) (3).

[For prepn. of \tilde{C} from m-hydroxybenzaldehyde (1:0055) + Cl_2 (32.6% yield (4)) see (1) (3) (4); for indirect prepn. via 2-nitro-3-hydroxybenzaldehyde, reductn., and appropriate diazo reactns. see (1).]

 \tilde{C} in 50% AcOH mononitrated as directed (2) by grad. addn. of HNO₃ (D=1.3) then after a min. poured onto ice gives 100% yield of mixt. of 4-nitro and 6-nitro derivs.; extraction with aq. at 90° dissolves the latter leaving residue of almost pure 4-nitro deriv.; from the soln. of 6-nitro isomer a little dissolved 4-nitro cpd. is distilled out with steam (2).

4-Nitro-2-chloro-3-hydroxybenzaldehyde: pale yel. ndls. from AcOH, m.p. 166° (2). [Corresp. oxime, insol. aq., yel. ndls. from alc., m.p. 170° (2); p-nitrophenylhydrazone, deep or. ndls. from hot AcOH, m.p. 294-295° dec. (2); semicarbazone, sulfur-yel. ndls.

from hot alc., m.p. 271-272° dec. (2); methyl ether, colorless ndls. from dil. alc. or dil. AcOH, m.p. 107° (2).]

6-Nitro-2-chloro-3-hydroxybenzaldehyde: colorless ndls. from aq., m.p. 153° (2). [Corresp. oxime, exceedingly sol in aq. or alc, colorless ndls. from CHCl₃, m.p. 175° (2); p-nitrophenylhydrazone, or.-red ndls. from hot dil. AcOH, m.p. 232-233° (2); semicarbazone, pale yel. ndls. from alc., m.p. 234° dec. (2); methyl ether, colorless ndls. from AcOH, m.p. 134° (2).]

Č in CHCl₃ treated with Br₂ in CHCl₃ as directed (5) gives (86% yield (5)) 4-bromo-2-chloro-3-hydroxybenzaldehyde, cryst. from 50% AcOH, m.p. 139-140° cor. (5). [This deriv. depresses m.p. of \bar{C} (5).] [4,6-Dibromo-2-chloro-3-hydroxybenzaldehyde has m.p. 104-105° (5).]

C with 50% KOH at 60-70° undergoes Cannizzaro reacting giving (4) 2-chloro-3-hydroxy-benzyl alc. (87% theory (4)), cryst. from toluene, mp. 132° cor (4), and 2-chloro-3-hydroxy-benzoic acid (96% theory (4)) (3:4395), cryst. from aq., mp. 156° (4)

C in aq. 20% NaOH (1) or aq. NaHCO₃ (1), treated with Me₂S()₄, yields methyl ether (2-chloro-3-methoxybenzaldehyde), volatile with steam, cryst. from dil alc., m.p. 56-57° (1). [This ether depresses m.p. of corresp. deriv. (m.p. 52°) of the isomeric 4-chloro-3-hydroxybenzaldehyde (3:3780)] [On oxidn. with alk. KMnO₄ (1) this methyl ether yields 2-chloro-3-methoxybenzoic ac., m.p. 160° (1).]

- **2-Chloro-3-hydroxybenzaldoxime:** colorless ndls from dil alc., m.p. 149° (1).
- ---- 2-Chloro-3-hydroxybenz ldehyde phenylhydrazone: unrecorded.
- **② 2-Chloro-3-hydroxybenzaldehyde** *p*-nitrophenylhydrazone: or -red ndls from hot alc., m.p. 244-245° (1).
- ---- 2-Chloro-3-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded
- **② 2-Chloro-3-hydroxybenzaldehyde semicarbazone:** pale yel ndls, mp. 236-237° (1).
- **D** 2-Chloro-3-acetoxybenzaldehyde: rhombic cryst. from alc., m p. 62° (1).
- © 2-Chloro-3-benzoxybenzaldehyde: rhombic cryst. from alc., m.p. 88° (1).

3:4085 (1) Hodgson, Beard, J. Chem. Soc. 1926, 149-155 (2) Hodgson, Beard, J. Chem. Soc. 1926, 2031-2036. (3) Bissell, Kranz (to National Amline and Chem. Co.), U.S. 1,776,803, Sept. 30, 1930; Cent. 1931, II 159, C.A. 24, 5768-5769 (1930). (4) Lock, Monatsh. 55, 309-311 (1930). (5) Lock, Monatsh. 62, 187-188 (1933).

3:4095 2,4-DICHLOROPHENOXYACETIC $C_8H_6O_3Cl_2$ Beil. S.N. 522 ACID Cl OCH_2COOH

White odorless cryst. from C_6H_6 ; alm. insol. aq. — Neut. Eq. = 221.0.

[For prepn. of \bar{C} from 2,4-dichlorophenol (3:0560) with chloroacetic acid (3:1370) in aq. NaOH (87% yield) see (1).]

[For general survey of \overline{C} as plant hormone see (1) (3) cf. (4); for use of solns. of \overline{C} in polyethylene glycols for regulating growth of plants see (5); for use of \overline{C} as weed killer see (6).]

3:4095 (1) Zimmermann, Ind. Eng. Chem. 35, 596-601 (1943). (2) Pokorny, J. Am. Chem. Soc. 63, 1768 (1941). (3) Zimmermann, Hitchcock, Contrib. Boyce Thompson Inst. 12, 321-343 (1942); C.A. 36, 6199 (1942). (4) Avery. Berger, Shalvia, Botan. Gaz. 104, 281-287 (1942); C.A. 37, 1471 (1943). (5) Mitchell, Hamner, Botan. Gaz. 105, 474-483 (1944); C.A. 38, 4654 (1944). (6) Harner, Tukey, Science 100, 154-155 (1944).

3:4102 m-CHLOROPHENYLPROPIOLIC C₉H₅O₂Cl Beil. S.N. 950 ACID ——C=C—COOH

M.P. 140-141° (1)

Cryst. from AcOH.

[For prepn. of \bar{C} from *m*-chlorobenzaldehyde (3:6475) by conversion through *m*-chlorocinnamic acid to ethyl *m*-chlorocinnamate, thence by addn. of Br₂ to give ethyl β -(*m*-chlorophenyl)- α , β -dibromopropionate, followed by climination of 2 HBr and saponification (or vice versa) with alc. KOH, and final acidification (yield not stated), see {1}.

Č with Cu(OAc)₂ loses CO₂ yielding (1) *m*-chlorophenylacetylene (3:9500) (cf. also under o-chlorophenylpropiolic acid (3:3956)).

3:4102 (1) Otto, J. Am. Chem. Soc. 56, 1393-1394 (1934).

Ndls. from ether; cryst. from CCl₄, CS₂, C₆H₆ + EtOH, or C₆H₆ (for studies on crystal-lographic props. see (2) (8) (5) (15)). — Insol. cold and spar. sol. hot alc.; fairly sol. cold ether, C₆H₆, CHCl₃, or CS₂. — \bar{C} has penetrating and disagreeable odor. — Sublimes easily.

[For prepn. of \bar{C} from 2,4,5-trichloroaniline [Beil. XII-627] (9) or from 2,5-dichloro-p-phenylenediamme [Beil. XIII-118] (16) via diazotization and use of Cu_2Cl_2 reactn. (64% yield (16)) see indic. refs; from p-dichlorobenzene (3:0980) with $S_2Cl_2 + AlCl_3$ in SO_2Cl_2 (67% yield (1)) (17) or from o-dichlorobenzene (3:6055) with $Cl_2 + cat$. (18) see indic. refs.]

[For formn. of \bar{C} from C_6H_6 with Cl_2 in pres. of I_2 (5), Fe (44% yield (13)), or AlCl₃ (19), or Cu (20), or from chlorobenzene with $Cl_2 + Cu$ (20), or from c-dichlorobenzene (3:6055) with $Cl_2 + cat$. (18) or Al/Hg (21), or from m-dichlorobenzene (3:5960) with $Cl_2 + L$ (21) or AlCl₃ (4), or from p-dichlorobenzene with Cl_2 in pres. of Fe (39% yield (13)), see indic. refs.; from dry C_6H_6 with anhyd. AuCl₃ (22) or on electrol. in aq. HCl/AcOH soln. see (23); from lower chloro derivs. of C_6H_6 with FeCl₃ see (7); from 2,4,5-trichlorotoluene (3:2100) with Cl_2 see (24); from benzaldehyde (1:0195) by htg. with $SbCl_5$ see (11).]

[For form. of \tilde{C} from 2,5-dichloro-4-nitroaniline on diazotization and treatment with Cu_2Cl_2 see (25) (14) (note abnormal replacement of nitro group); from nitrobenzene with $SO_2Cl_2 + N_2O_4$ see (10); from resorcinol 4,6-bis-(sulfonyl chloride) or hydroquinone 2,5-

bis-(sulfonyl chloride) with PCl₅ in s.t. at 180° see {12} (26); from 4,6-dichlorobenzene 1,3-bis-(sulfonyl chloride) (27) or from 1,3-bis-(methylmercapto)benzene-4,6-bis-(sulfonyl chloride) (28) with SOCl₂ at 170-200° see indic. refs.; from 2,5-dichlorobenzene-1,4-bis-(sulfonyl chloride) with PCl₅ in s.t. 4 hrs. at 180° see (6); from 2,3,5,6-tetrachloro-N-nitroacetanilide (39) by refluxing in toluene or xylene (other products are also formed) see (39).]

[For behavior of \bar{C} with liq. Cl₂ yielding addn. products see (29); for behavior with NH₃ at elevated temps, see (30); \bar{C} with $S_2Cl_2 + AlCl_3 + SO_2Cl_2$ yields (17) hexachlorobenzene (3:493)).]

[C htd. with NaOMe as directed yields according to conditions (13) (31) (32) (38) 2,4,5-trichlorophenol (3:1620) or its methyl ether.]

 \overline{C} on mononitration, e.g., on boilg. with 5 pts. HNO₃ (D=1.52) for $\frac{1}{2}$ hr. (3) (13) (34), yields 1,2,4,5-tetrachloro-3-nitrobenzene [Beil. V-247], m.p. 99-100° (33) (35), 99° (34) (13), 98° (9), some tetrachlorobenzoquinone (chloranil) (3:4978) (insol. in pet. ether) also being formed (9) (34) (13) (33). [For studies on chem. of this mononitro cpd. see (36).]

 $\tilde{\mathbf{C}}$ on dinitration by boilg. 5-6 hrs. with mixt. of 10 pts. HNO₃ (D=1.52)+10 pts. fumg. H₂SO₄ (25% SO₃) gives (71% yield (33)) 1,2,4,5-tetrachloro-3,6-dinitrobenzene, cryst. from C₆H₆ by addn. of alc., m.p. 227-228° (33), 232-233° (35).

Č with 4 pts. chlorosulfone acid refluxed for hr. gives (78% yield (37)) hexachlorobenzene (3:4939), m.p. 218-219° u.c. (37).

3:4115 (1) Silberrad, J. Chem. Soc. 121, 1020 (1922). (2) Fels, Z. Krist. 32, 365 (1900). (3) Dadieu, Pongratz, Kohlrausch, Monatsh. 61, 434 (1932). (4) Ohvier, Rec trav. chim. 39, 411-413 (1920). (5) Jungfleisch, Ann. chim. (4) 15, 277-283 (1868). (6) Gebauer-Fulnegg, Fidor, Monatsh. 48, 634 (1927). (7) Thomas, Compt. rend. 126, 1212 (1898). (8) Bodewig, Z. Krist. 3, 400 (1879). (9) Beilstein, Kurbatow, Ann. 192, 236-237 (1878). (10) Battegay, Denivelle, Bull. soc. chim. (4) 47, 609 (1930).

(11) Gnehm, Banziger, Ann. 296, 67 (1897). (12) Litvay, Riesz, Landau, Ber. 62, 1867 (1929). (13) Holleman, Rec. trav. chim. 39, 736-737, 745, 749 (1920). (14) Hodgson, J. Soc. Dyers Colourists 42, 368 (1926). (15) Groth, Chem. Krist 4, 7 (1917). (16) Schoutissen, J. Am. Chem. Soc. 55, 4538-4539 (1933). (17) Roberts and Co. & Silberrad, Brit. 193, 200, March 15, 1923; Cent. 1925, I 904. (18) Mills (to Dow Chem. Co.), U.S. 1,934,675, Nov. 7, 1933, Cent. 1934, I 1390; C.A. 28, 494 (1934). (19) Mouneyrat, Pouret, Compt. rend. 127, 1028 (1898). (20) Tei, Komatsu, Mem. Coll. Sci. Kyoto Imp. Univ. 10-A, 326-330 (1927); Cent. 1928, I 2370.

(21) Cohen, Hartley, J. Chem. Soc. 87, 1363–1365 (1905). (22) Kharasch, Isbell, J. Am. Chem. Soc. 53, 3053 (1931). (23) Fichter, Glantsstein, Ber. 49, 2475–2481 (1916). (24) Beilstein, Kuhlberg, Ann. 152, 247–248 (1869). (25) Holleman, van Haeften, Rec. trav. chim. 40, 71 (1921). (26) Quilico, Gazz. chim. ital. 57, 800–802 (1927). (27) Pollak, Wienerberger, Monatsh. 35, 1472 (1914). (28) Pollak, Monatsh. 35, 1460 (1914). (29) van der Linden, Rec. trav. chim. 55, 425–427 (1936); 57, 342–344 (1938). (30) Heslinga, Rec. trav. chim. 43, 178–180, 182 (1924).

(31) Aktien-Gesell. für Anilin-Fabr., Ger. 349,794, March 9, 1922; Cent. 1922, IV 45; Ger. 411,052, March 23, 1925; Cent. 1925, I 2411. (32) Clark, Crozier, Trans. Roy. Soc. Can. (3) 19. III 153-156 (1925). (33) Berckmans, Holleman, Rec. trav. chim. 44, 851-852 (1925). (34) Dyson, George, Hunter, J. Chem. Soc. 1926, 3044. (35) Qvist, Salo, Acta Acad. Abcensis Math. et Phys. 8, No. 4 (1934); Cent. 1934, II 595; Cent. 1936, I 540. (36) Peters, Rowe, Stead, J. Chem. Soc. 1943, 233-235. (37) Huntress, Carten, J. Am. Chem. Soc. 62, 513 (1940). (38) de Crauw, Rec. trav. chim. 50, 787 (1931). (39) Peters, Rowe, Stead, J. Chem. Soc. 1943, 372-373.

3:4135 TETRACHLORORESORCINOL

M.P. 141° (1) 140° (2) Long colorless ndls. from hot aq. — Faintly pleasant phenolic odor. [New comml. prod. (1942) in U.S.A.] — Eas. sol. alc., ether, AcOH, C₆H₆; fairly eas. sol. hot aq.; spar. sol. cold aq.

[For prepn. from "hexachlororesorcinol" (3:3470) by reduction with SnCl₂ in AcOH see (1).]

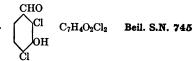
C is sol. in aq. alk. (2). — C in aq. soln. gives with FeCl₃ a blue color (2).

C in AcOH on treatment with Cl2 yields "hexachlororesorcinol" (3:3470), m.p. 115°.

Tetrachlororesorcinol diacetate: m.p. 145° (1), 144° (2). [Note that m.p. of this deriv. is close to that of C and should be tested by method of mixed m.p.'s.]

3:4135 (1) Zincke, Fuchs, Ber. 25, 2689-2690 (1892). (2) Fries, Hartmann, Ber. 54, 199 (1921).

3:4140 2,4-DICHLORO-3-HYDROXYBENZ-ALDEHYDE



M.P. 141° (1)

Colorless cryst. from AcOH. \bar{C} has pronounced sternutatory props. and blisters moist skin. — [Note that the m.p. of a mixt. of \bar{C} with isomeric 2,6-dichloro-3-hydroxybenz-aldehyde (3:4160), m.p. 140°, is depressed to 111° (1)]

[For prepn. of C from 4-chloro-3-hydroxybenzaldehyde (3.3780) in AcOH with Cl₂ at room temp. (100% yield) see (1).]

 \tilde{C} (1 pt.) in AcOH (4 pts.) on nitration at 65° with 1 pt. conc. HNO₃ (D=1.42) yields (2) 2,4-dichloro-3-hydroxy-6-nitrobenzaldehyde (2), colorless ndls. from its deep yellow soln. in AcOH or from hot aq., m.p. 107° (2) (p-nitrophenylhydrazone, or. ndls. from AcOH, m.p. 279-280° (2), semicarbazone monohydrate, yel. ndls. from dil. alc., softens 140-150° (2)).

Č dislvd. in boilg. 10% NaOH (2 moles) and treated with Me₂SO₄ (1.3 moles) yields (1) 2,4-dichloro-3-methoxybenzaldehyde, m.p. 82° (1) (p-nitrophenylhydrazone, old-gold ndls., m.p. 258-260° (1)), which on oxidn. yields 2,4-dichloro-3 methoxybenzoic acid, colorless ndls., m.p. 163° (1).

- © 2,4-Dichloro-3-hydroxybenzaldoxime: fine colorless ndls. from alc., m.p. 188° (1).
- **② 2,4-Dichloro-3-hydroxybenzaldehyde** *p*-nitrophenylhydrazone: or.-red ndls., m.p. 277-278° dec. (1).

3:4140 (1) Hodgson, Beard, J. Chem. Soc. 1926, 147-155. (2) Hodgson, Beard, J. Chem. Soc. 1926, 2030-2036.

C7H5O2Cl 3:4150 o-CHLOROBENZOIC ACID Beil. IX - 334 COOH IX_{1} -(138) M.P. 142° (1) (2) (3)139.9° (15)139.8-140.0° (16)141.8° (4) 139.5-140° 141° (5) (6) (7) (8) (181) (17)140-142° (9) 139.5° (38) 139-140° 140.65° (10)(18) (19)139° 140.3° (11) (29)(20) (21) (22) 138° 140.2° (23) (24) (58) $\langle 12 \rangle$ 140° 137° (13) (14) (26) (27) (49) (25) (63) (97) (36)

Cryst. from hot aq., C_6H_6 , dioxane/ C_6H_6 , or alc. — \bar{C} is spar. sol. cold aq.; e.g., \bar{C} is sol. at 0° in 881 pts. aq. (27); at 25°, 100 ml. satd. aq. soln. conts. 0.213 g \bar{C} (21) (= 0.0136 mole per liter (21) (28)) — \bar{C} is eas. sol. hot aq, alc., ether (26) — At 14–16°C 100 ml. satd. soln. of \bar{C} in acetone conts. 28.4 g. \bar{C} , in ether 17 g. \bar{C} , in EtOAc 13.2 g. \bar{C} , in 75% AcOH 6.2 g. \bar{C} ; in C_6H_6 0.9 g. \bar{C} ; in CCl_4 0.6 g. \bar{C} ; in CS_2 0.5 g. \bar{C} ; in lgr. 0.07 g. \bar{C} (10). — For study of soly. of \bar{C} in acetone (41), C_6H_6 (42), heptane (29), chlorobenzene (3: 7903) (30), o-chlorotoluene (3: 8245) (30), or m-chlorotoluene (3. 8275) (30) see indic. refs.

For study of distribution at 25° of \bar{C} between aq. + toluene (31), aq. + xylene (32), or aq. + CHCl₃ (31) (32) (for use of CHCl₃ in sepn. of \bar{C} from aq. suspension of 3-chlorophthalic acid (3:4820) (33)) see indic. refs.; for adsorption of \bar{C} on charcoal from its solns. in EtOH (34), acetone (4), C_6H_6 (4), or aq. (35) see indic. refs.; for soly. of \bar{C} in aq. solns. of various salts (including Na \bar{A}) see (28) (21).

 \bar{C} can be sublimed in vac. (12). — \bar{C} is but very slightly volatile with steam (for details see (11)). — For crystallographic data see (36) (37). — For purification of \bar{C} (by use of decolorizing carbon on soln. of \bar{C} in aq. Na₂CO₃ followed by repptn. with 6 N HCl) see (38).

Binary systems contg. \bar{C} : for f.p./compn. data on system $\bar{C} + H_2O$ see (39); for f.p./compn. data and diagram on system $\bar{C} + BzOH$ (1:0715), euteetic, m.p. 91.1°, contg. about 41 wt. % \bar{C} , see (10) (41); for f.p./compn. data on systems $\bar{C} + o$ -toluic acid (1:0690) (20) or $\bar{C} + o$ -hydroxybenzoic acid (salicylic acid) (1:0780) (20) see indic. refs.

For f.p./compn. data and diagrams on systems \bar{C} + m-chlorobenzoic acid (3:4392) (eutectic, m.p. 110.7°, contg. 52-53 mole % \bar{C} (6) (40) (10) (15)) see indic. refs ; on system \bar{C} + p-chlorobenzoic acid (3:4940) (eutectic, m.p. 132°, contg. abt. 86 mole % \bar{C}) see (10) (15).

For f.p./compn. data and diagrams on systems $\tilde{C}+o$ -bromobenzoic acid (41), $\tilde{C}+o$ -iodobenzoic acid (42), $\tilde{C}+o$ -nitrobenzoic acid (43), $\tilde{C}+m$ -nitrobenzoic acid (43) see indic. refs.

Ternary systems contg. $\bar{\mathbf{C}}$. [For influence of addn. of benzoic acid (6) or of p-chlorobenzoic acid (3:4940) (40) to the eutectic of $\bar{\mathbf{C}}$ with m-chlorobenzoic acid (3:4392) see indic. refs.; for influence of addn. of $\bar{\mathbf{C}}$ to the eutectic of benzoic acid with m-chlorobenzoic acid see (40); for data on system $\bar{\mathbf{C}} + m$ -chlorobenzoic acid (3:4392) + p-chlorobenzoic acid (3:4940), eutectic, m.p. 104.9°, contg. respectively 48.3, 44.0, and 7.7 mole % of the three isomers, see (15).]

Miscellaneous. [For study of fate of \tilde{C} in animal organism see (44) (45); note that contrary to earlier (45) results with dogs and rabbits conjugation with glycine to yield the expected N-(o-chlorobenzoyl)glycine (o-chlorobippuric acid) [Beil. IX-336], m.p. 176° (45), does (44) occur. — For study of use of \tilde{C} (or its salts) as preservatives see (46); for detectn. of \tilde{C} in foods see (179). — For use of \tilde{C} as vulcanization regulator see (47) (48).]

Preparation. [For prepn. of \bar{C} from o-chlorotoluene (3:8245) by oxidn. with boilg aq. KMnO₄ (yields: 90% (14), 74–78% (18), 68–71% (24)) (49) (13), with nitrosulfonic acid (from fumg. HNO₃ + dry SO₂) at 100° (50), with air in the pres. of various catalysts (51) (52) (53), or in aq. alk. at 260° under press. (54), see indic. refs; for formn. of \bar{C} from o-chlorophenyl benzyl ketone by auto-oxidn. in light and air see (56); for formn. of \bar{C} from o-chlorobenzaldehyde (3:6410) by oxidn. with CrO₃ (57), with alk. KMnO₄ (58), or by auto-oxidn. in Ac₂O (59) see indic. refs.]

[For prepn. of \bar{C} from o-aminobenzoic acid (anthranilic acid) [Beil. XIV-312, XIV₁-(529)] via diazotization and use of Cu₂Cl₂ (yields: 90% (24), 87% (178)) (preferably under CO₂ (60)), or CuH (60% yield (61)), or Cu (62) see indic. refs.]

[For prepn. of \bar{C} from o-chlorobenzonitrile [Beil. IX-336] by hydrolysis with H₂SO₄ (14), with dil. HCl in s.t. at 150° (63), or boilg. KOH (14) see indic. refs.; from o-chlorobenzoyl chloride (3:6640) by hydrolysis with aq. (91) or aq. alk.; from o-chlorobenzotri-

chloride (3:6880) by hydrolysis (64) (65), e.g., with aq. in s.t. at 150° (27) or by boilg. conc. HNO₃ (65) see indic. refs.; from o-chlorobenzal (di)chloride (3:6625) with CrO₃ (57) or with boilg. aq. for 20 hrs. followed by oxidn. with KMnO₄ (75% yield (7)); from a mixt. of o-chlorobenzotrichloride + o-chlorobenzal (di)chloride by hydrol. with 70% H₂SO₄ or 80% AcOH or 5% NaOH at 90-100° in stream of air to effect immediate oxidn. (67); from o-chlorobenzoyl-o-chlorotriphenylmethane by hydrolytic cleavage with 20% MeOH/KOH 5 hrs. at b p. (8); from o-chlorophenylnitrolic acid by hydrolysis with boilg. aq. (19) see indic. refs.]

[For form. of \bar{C} (together with other prods.) from benzoic acid (1:0715) with KClO₃ + HCl (68), with NaOCl (6) (69), see indic refs.]

[For formn. of \bar{C} from o-sulfobenzoic acid imide (saccharin) [Beil. XXVII-168, XXVII₁-(266)] with KClO₃ + HCl see (9); from 3-chlorophthalic acid (3:4820) by cat. monode-carboxylation see (70); from o-nitrotoluene [Beil. V-318, V₁-(158), V₂-(243)] (71), from sodium o-toluenesulfonate [Beil. XI-83, XI₁-(22)] (72), or from o-toluenesulfonyl chloride [Beil. XI-86, XI₁-(23)] (71) with SOCl₂ in s.t. at elevated temp. followed by treatment with aq. see indic refs.]

Chemical behavior. [\bar{C} (as Na \bar{A}) on reduction with Na/Hg (27) (25) (73) or \bar{C} (as K \bar{A}) on fusion with sodium formate (74) of (75) is dehalogenated yielding benzoic acid (1:0715) (for study of reduction of \bar{C} with H₂ + Ni in aq. alk at ord. temp. see (76)). — \bar{C} on electrolytic reduction in alc. H₂SO₄ yields (77) o-chlorobenzyl alc. [Beil. VI-444, VI₁-(222)], ndls. from aq. alc., m p. 72° (77)]

 \bar{C} behaves normally as a monobasic acid: e.g., \bar{C} on titration with standard dil. aq. alk. gives Neut. Eq. 156.5; ionization const at 25° is 13.2×10^{-4} (78) (79) cf. (80) (81) (21) (1). — [For study of acid strength of \bar{C} in various alcohols (82) (83) (84) (5) (85) (86) (22) or in acctonitrile (87) see indic. refs. — For solubility of \bar{C} in aq. solns. of various salts incl. Na \bar{A} see (28) (21). — For sepn. of \bar{C} from p-chlorobenzoic acid (3:4940) by use of difference in their acidic strength see (88). — For use of \bar{C} as standard in alkalimetry (89) and in iodimetry (90) see indic refs]

Salts of inorg. bases. [NH₄ $\bar{\Lambda}$ (91) (92) (note that this salt with benzotrichloride (3:6880) in pres. of suitable cat. yields (93) o-chlorobenzontrile). — Hydroxylamine salt: m.p. 104.5° (94). — Na $\bar{\Lambda}$ (use as preservative) (46) — K $\bar{\Lambda}$.½H₂O (91) (forms liq. cryst. on fusion (95)). — Ag $\bar{\Lambda}$, scales from boilg aq. (25) (100) (note that this salt with I₂ in C₆H₆ under reflux does not (96) yield phenyl o-chlorobenzoate, m.p. 37°, and thus differs from corresp. salt of m-chlorobenzoic acid (3:4392)). — Ca $\bar{\Lambda}_2$.H₂O (26) (97), much more sol. aq. than corresp. salts of m-chlorobenzoic acid (3:4392) or p-chlorobenzoic acid (3:4940) (97); insol. either cold or hot alc. (98); on dry distn. gives (18% yield (99)) xanthone (1:7275), m p. 174°. — Ba $\bar{\Lambda}_2$.3H₂O from spont evapn. of aq. soln. (98) (9). — Ba $\bar{\Lambda}_2$ from hot conc. aq. soln. (25) (26) (use in sepn. of \bar{C} from isomers (40)); spar. sol. aq. (100). — Note that Pb $\bar{\Lambda}_2$ (25) (100) and Cu $\bar{\Lambda}_2$ (25) (100) are spar. sol. aq., while salts of Ca, Sr, Mg, Zn, Fe, Mn, Co, Ni, and Cd are sol (100). — For sepn. of \bar{C} from BzOH (1:0715) by use of Cu salts see (6).]

Salts of organic bases. \bar{C} with equiv. amt. benzylamine in boilg. EtOAc followed by evapn. of solvent yields (101) benzylammonium o-chlorobenzoate, m.p. 148.4–149.4° u.c., 150.5–151.5° cor, Neut Eq. 263.6 (note that the m.p. of this salt is but very slightly differom that of corresp. salt of m-chlorobenzoic acid (3:4392)). — \bar{C} similarly treated with α -phenylethylamine yields (101) α -phenylethylammonium o-chlorobenzoate, m.p. 128.4–129.4° u.c., 130.9–131.9° cor., Neut. Eq. 277.6 (note that m.p. of this salt, although better separated from those of the isomeric acids than the preceding case, is very close to those of the corresp. salts of m-methoxybenzoic acid, p-methoxybenzoic acid, and o-nitrobenzoic acid).

Č (1 mole) in alc. mixed with codeine (1 mole), m.p. 155°, htd. several minutes, solvent evapd. and resulting sirup recrystd. from aq. yields (102) codeine o-chlorobenzoate, C₁₈H₂₁-O₃N.Č, m.p. 134° on "Maquenne block"; note that this value although close to that of corresp. prod. from o-bromobenzoic acid is widely different from that of corresp. salts of either m-chlorobenzoic acid (3:4392) or p-chlorobenzoic acid (3:4940) which are 96° and 162° respectively. — Č (1 mole) in alc. (or CHCl₃) with strychnine (1 mole) in alc., boiled for a few minutes, then cooled, yields (103) strychnine o-chlorobenzoate, C₂₁H₂₂-O₂N₂.Č, m.p. 170° u.c. on "Maquenne block"; note that this melting point is somewhat lower than that (185°) for the corresp. salt of m-chlorobenzoic acid (3:4392) and widely different from that (251°) of the corresp. salt of p-chlorobenzoic acid (3:4940).

[For optical data on cinchonine salt see (104); for salt (m.p. 108-110°) with phenylmercuric hydroxide see (105).]

 \tilde{C} with alcohols gives by conventional processes the corresp. esters; for details on methyl o-chlorobenzoate (3:6695) and ethyl o-chlorobenzoate (3:6800) see these compds. — [For study of rate of esterification of \tilde{C} with MeOH (106) (111) (17) (112), with EtOH (2) (17) (113), or with cyclohexanol (1:6415) (107) see indic. refs.]

 \bar{C} with P_2O_5 in toluene boiled for 4 hrs. (108), or \bar{C} (109) or its sodium salt (110) refluxed with oxalyl (di)chloride (3:5060) in C_6H_6 , yields o-chlorobenzoic acid anhydride, ndls. from lt. pet. (108) or alc. (109), m.p. 79.6° (108), 78-79° (109); note that \bar{C} (2 moles) with oxalyl (di)bromide refluxed in C_6H_6 similarly gives good yields (110) of the above anhydride, but that Na \bar{A} with oxalyl (di)bromide can also be used (110) to give o-chlorobenzoyl bromide, b.p. 143-145° at 37 mm. (110).

 \tilde{C} with PCl₅ (114) (45) (115), or with PCl₃ + ZnCl₂ (114), or with SOCl₂ (114) (45) (116) (117), or with SOCl₂ + pyridine (118), or with o-chlorobenzotrichloride (3:6880) + ZnCl₂ (119) yields o-chlorobenzoyl chloride (3:6640) q v. for data on yields.

Č with KOH or NaOH on fusion (128) (27) (25), or Č with aq. piperidine in pres. of Cu powder in s.t. at 160° for 4 hrs. (121), or Č with aq. piperidine + Na₂CO₃ + amyl alc. + Cu powder refluxed 6 hrs. (124), or Č (as KĀ) with aq. NaOAc + Cu(OAc)₂ in s.t. at 140–150° for 9–10 hrs. (126), or Č with aq. Ca(OH)₂ + Cu cpds. at 160–170° under press. (122) gives (83% yield (126)) o-hydroxybenzoic acid (salicylic acid) (1:0780), accompanied in some cases (120) by substantial amounts of m-hydroxybenzoic acid (1:0825). — For use of alk. fusion as means of detect. of Č in wine see (123). — Note that Č with aq. KOH (even in pres. of copper) (124), or Č with aq. Ba(OH)₂ in s.t. at 190–200° (125), does not yield salicylic acid or any chloride ion.

Reaction of C with phenols. C on suitable treatment condenses with phenols yielding σ-aryloxybenzoic acids: e.g., C (as KĀ) with Na phenolate and Cu powder at 180–190° for 5 min. (127) (128), or C (as KĀ) with phenol + Cu powder or Cu salts (129) (130), or C (as KĀ) with anhydrous KOAc/NaOAc + Cu powder at 245–255° for 5 hrs. (126) gives (90% yield (127)) σ-phenoxybenzoic acid [Beil. X-65, X₁-(28)], lfts. from dil. alc., m.p. 113°; note that this prod. with conc. H₂SO₄ on gentle warming loses H₂O and ringcloses in quant. yield (131) to xanthone (1:7275), m.p. 174°. — [For analogous condensations of C with σ-cresol (1:1400) (127) (128) (60), m-cresol (1:1730) (127), p-cresol (1:1410) (127) (128), σ-anphthol (1:1500) (132), β-naphthol (1:1540) (127) (128), σ-chlorophenol (3:0495) (133), m-chlorophenol (3:0495) (133), m-nitrophenol (133), p-nitrophenol (133), including conv. to the corresp. xanthones, see indic. refs.; many other analogous cases are known but cannot be included here.

Reaction of C with amines. C (or its salts) with primary or secondary aliphatic or aromatic amines in the pres. of K₂CO₃ and Cu powder on htg. condenses with elimination of HCl (or its equivalent) to yield products of type o-HOOC—C₅H₄—NHR; these products by ring closure through elimination of water yield in turn the corresponding acridones; the

reaction has been executed for countless cases of which only a few of the more important examples can be cited here; for the most comprehensive single survey see (134).

 \tilde{C} (as KĀ) htd. with aq. aniline + Cu powder (134) (135), Cu salts (135), or \tilde{C} htd. with aniline + Cu powder (136) or Cr powder (137), or \tilde{C} htd. with aniline + anhydrous K_2CO_3 + CuO (134) (38) gives (yields: 97% (134), 82–93% (38), 87% (137)) N-phenylanthranilic acid (diphenylamine-o-carboxylic acid) [Beil. XIV-327, XIV₁-(533)], cryst. from alc., m.p. 182–183° rap. htg. (38); this prod. with conc. H_2SO_4 at 100° loses aq. and ring-closes (yields: 91–96% (38)) (138) (139) to acridone [Beil. XXI-335, XXI₁-(312)], sublimable yel. ndls., m p. 354° cor.

[For details on analogous reaction of C with o-toluidine (134) (135) (136) (140), m-toluidine (134) (141), p-toluidine (134) (135), α-naphthylamine (134) (135), ρ-naphthylamine (134) (135), o-aminophenol (134), o-anisidine (134), m-anisidine (134), p-anisidine (134), p-aminobenzoic acid (134), p-phenylenediamine (134), p-aminodimethylaniline (124), see indic. refs.; scores of other examples cannot be cited here.]

Substitution of nucleus of \bar{C} . — [\bar{C} in fumg. H_2SO_4 or chlorosulfonic acid + a little sulfur treated with Br_2 (1 mole) at $60-70^\circ$ gives (70-75% yield (143)) 5-bromo-2-chlorobenzoic acid [Beil. IX-355], ndls., m.p. 165-167° (143).]

 \bar{C} on mononitration under various conditions, e.g., \bar{C} (2 wt. pts.) dislvd. in conc. H₂SO₄ (15 wt. pts.) and treated below 50° with a mixt. of HNO₃ (D=1.5) (1 wt. pt.) in conc. H₂SO₄ (2.5 wt pts.) (144) gives mainly (yields: 78.5% (144), 35% (145), 32–38% (146)) (147) (148) (14) (149) 2-chloro-5-nitrobenzoic acid [Beil. IX-403], ndls. from aq., m.p. 165° (149) (14) (172), 164–165° (144) (145), 164° (146) (148), accompanied by a small amt. 2-chloro-3-nitrobenzoic acid [Beil. IX-402], m.p. 185° (148), 181° (150). — [Note that both the other nitro-2-chlorobenzoic acids are known, viz., 2-chloro-4-nitrobenzoic acid [Beil. IX-404], ndls. from aq., m.p. 140° (151), 139–140° (152), and 2-chloro-6-nitrobenzoic acid, m.p. 161° (151), but are prepd. by other methods.]

Č on direct dinitration, e.g., with conc. H₂SO₄ + KNO₃ at 100° (153) (154) or at 130° (155) or Č with conc. H₂SO₄ + fumg. HNO₃ at 130–140° (156), gives (94% yield (155)) 2-chloro-3,5-dinitrobenzoic acid [Beil. IX-415], ndls. from aq., m.p. 199–200° (153) (154), 199° (156), 198.5° cor. (155) (for use of this prod. in detection of Č see (180)); this prod. is also obtd. by further nitration of 2-chloro-3-nitrobenzoic acid (above) with conc. H₂SO₄ + KNO₃ at 170° (157). — [Note that of the 5 other isomeric dinitro-2-chlorobenzoic acids which are possible only one is known, viz, 2-chloro-4,5-dinitrobenzoic acid, m.p. 165° cor. (158), obtd. from 2-chloro-4-nitrobenzoic acid (above) by further nitration with fumg. HNO₃ + conc. H₂SO₄ (80% yield (158)).]

- --- Methyl o-chlorobenzoate: oil, b.p. 234°. (See 3:6695.)
- --- Ethyl o-chlorobenzoate: oil, b.p. 243°. (See 3:6800.)
- p-Nitrobenzyl o-chlorobenzoate: m.p. 106° (159). [From C (as NaA) with p-nitrobenzyl bromide (m.p. 99°) in boilg. dil. alc. (159); note that the m.p. of this ester is almost identical with that (107°) of the corresp. prod. from m-chlorobenzoic acid (3:4392).]
- Dependent of this prod. is only slightly lower than that (87.6°) of the corresp. prod. similarly obtd. from p-chlorobenzoic acid (3:4940).
- --- p-Chlorophenacyl o-chlorobenzoate: unreported.
- p-Bromophenacyl o-chlorobenzoate: m.p. 107.0° cor. (161), 106° (23) (162). [From C (as NaA) with p-bromophenacyl bromide (m.p. 109°) in boilg. alc. (80% yield (23)).]

- ---- p-Iodophenacyl o-chlorobenzoate: unreported.
- p-Phenylphenacyl o-chlorobenzoate: m.p. 123° (163). [From C (as NaA) with p-phenylphenacyl bromide (m p. 126°) in boilg. alc. (163).]
- --- S-Benzylthiuronium o-chlorobenzoate: unreported.
- © S-(p-Chlorobenzyl)thiuronium o-chlorobenzoate: cryst. from dioxane, m.p. 159° cor. (164). [From \tilde{C} (as Na \tilde{A} or K \tilde{A}) in aq. with 1 equiv of S-(p-chlorobenzyl)-thiuronium chloride, m.p. 197° (10% in alc.) (164); note that the m.p. of this prod. is closely adjacent to that (m.p. 157° cor.) of the corresp. salt of m-chlorobenzoic acid (3:4392).]
- ⑤ S-(p-Bromobenzyl)thiuronium o-chlorobenzoate: m.p. 168° cor. (165). [From Č (as KĀ or NaĀ) in aq. with 1 equiv. of S-(p-bromobenzyl)thiuronium bromide (m.p. 213°) in alc. (165); note that m.p. of this prod. is only slightly higher than that (163° cor.) for the corresp. prod. from p-chlorobenzoic acid (3:4940).]
- © o-Chlorobenzamide: cryst. from alc. or alc./ether, mp. 142.4° cor. (166), 142° (167), 141° (14), 140.5° (91), 139° (25). [From Č by refluxing with \$\text{AcOH}\$ + (\$\text{NH}_4\$)2CO₃ (37-39% yield (167)), from o-chlorobenzoyl chloride (3:6640) with conc. aq. \$\text{NH}_4\$OH (166) (14) (91) (25), or from ethyl o-chlorobenzoate (3:6800) with conc. aq. \$\text{NH}_4\$OH (25).] [Note that o-chlorobenzamide on htg. with \$\text{AlCl}_3\$.NaCl (large excess) gives (93% yield (168)) o-chlorobenzonitrile [Beil. IX-336], m.p. 43-44° (168), 42-43° (169), b.p. 232° (169).]
- © o-Chlorobenzhydrazide: ndls. from alc., m p. 117 118° (170), 109-110° (171). [From ethyl o-chlorobenzoate (3:6800) q.v. with hydrazine hydrate (170) (171); for use as reagt. for identification of aldehydes and ketones see (170).]
- ---- N-(o-Chlorobenzoyl) N-phenylhydrazide: unreported.
- © o-Chlorobenzanilide: ndls. from alc. or pet. ether; mp. 114° (172) (173) (174), 117-118° (175) (176). [From o-chlorobenzoyl chloride (3:6640) with excess aniline (25) (172) in pres. of a tertiary amine (80% yield (174)); also from oxime of o-chlorobenzophenone (3:0715) by Beckmann rearr. (175) (173) (176)] [Note that this prod. must not be confused with benz-o-chloroanilide, m.p. 99-100°.]
- © o-Chlorobenz-p-toluidide: cryst. from dil alc., m.p. 131° (177). [From o-chlorobenzoyl chloride (3:6640) with p-toluidine (177).]
- o-Chlorobenz-α-naphthalide: unreported.
- ---- o-Chlorobenz-β-naphthalide: unreported.
- 3:4150 (1) Dippy, Williams, Lewis, J. Chem. Soc. 1935, 343-346. (2) Kailan, Antropp, Monalsh. 52, 297, 303-307 (1929). (3) Fels, Z. Krist. 37, 485 (1903). (4) Berger, Rec. trav. chrm. 50, 379, 389, 395 (1931). (5) Wooten, Hammett, J. Am. Chem. Soc. 57, 2289-2296 (1935). (6) Smith, J. Chem. Soc. 1934, 213-218. (7) Asinger, Lock, Monalsh. 62, 333-334 (1933). (8) Bergmann, Schuchardt, Ann. 487, 254-255 (1931). (9) P. Bertolo, A. Bertolo, Gazz. chim. ital. 62, 487-493 (1932). (10) Bornwater, Holleman, Rec. trav. chim. 31, 223. 230-236, 242-248 (1912). (11) Sidgwick, J. Chem. Soc. 117, 403-406 (1920). (12) Andrews, Lynn, Johnson, J. Am. Chem. Soc. 48, 1282 (1926). (13) Koopal, Rec. trav. chim. 34, 144 (1915). (14) Montagne, Rec. trav. Chim. 19, 50-51, 53, 56-57, 64-65, 68, 72 (1900). (15) Johnston, Jones, J. Phys. Chem. 32, 599-601 (1928). (16) Hobbs, Weith, J. Am. Chem. Soc. 65, 968 (1943). (17) Kellas, Z. physik. Chem. 24, 222, 225, 230, 240-241 (1897). (18) Clarke, Taylor, Org. Syntheses, Coll. Vol. 2 (1st ed.), 135-136 (1943); 10, 20-21 (1930). (19) Charlton, Earl, Kenner, Lucciano, J. Chem. Soc. 1932, 40. (20) Lettré, Barnbeck, Lege, Ber. 69, 1151-1154 (1936).
- (21) Osol, Kirkpatrick, J. Am. Chem. Soc. 55, 4430-4440 (1933). (22) Kuhn, Wassermann, Helv. Chim. Acta 11, 31-34, 41 (1928). (23) Kelly, Howard, J. Am. Chem. Soc. 54, 4383-4385 (1932). (24) Graebe, Ann. 276, 54-56 (1898). (25) Kekulé, Ann. 117, 152-159 (1861). (26) Limpricht, von Uslar, Ann. 102, 259-264 (1857). (27) Kolbe, Lauteman, Ann. 115, 186-187, 196 (1860). (28) Philip, Garner, J. Chem. Soc. 95, 1466-1473 (1909). (29) Sidgwick, Ewbank, J. Chem. Soc. 119, 981, 984, 988 (1921). (30) Chapus, Compt. rend. 191, 258 (1930).
 - (31) Smith, White, J. Phys. Chem. 33, 1958, 1970 (1929). (32) Smith, J. Phys. Chem. 25, 221,

- 228 (1921). (33) Jaeger (to Selden Co.), U.S. 1,685,634, Sept. 25, 1928; Cent. 1929, I 807. (34) Griffin, Richardson, Robertson, J. Chem. Soc. 1928, 2708. (35) Freundlich, Z. physik. Chem. 57, 433 (1907). (36) Steinmetz, Z. Krist. 53, 465-466 (1913). (37) Groth, Chem. Krist. 4, 463-464 (1917). (38) Allen, McKee, Org. Syntheses, Coll. Vol. 2 (1st ed.) 15-17 (1943); 19, 6-9 (1939). (39) Flaschner, Rankin, Monatsh. 31, 43 (1910). (40) Hope, Riley, J. Chem. Soc. 121, 2518-2527 (1922).
- (41) Lettré, Barnbeck, Fuhst, Hardt, Ber. 70, 1411-1412 (1937). (42) Lettré, Lehmann, Ber. 71, 416-417 (1938). (43) Lettré, Ber. 73, 386-390 (1940); C.A. 34, 5831 (1940). (44) Quick, Cooper, J. Biol. Chem. 96, 83-101 (1932). (45) Novello, Miriam, Sherwin, J. Biol. Chem. 67, 555-557 (1926). (46) Sabalitschka, Dietrich, Desinfektion 11, 67-71, 94-104 (1926); Cent. 1927, I 2670; C.A. 20, 3712 (1926). (47) Goodyear Tire and Rubber Co., French 761,220, March 14, 1934; Cent. 1934, II 854. (48) Williams (to du Pont Co.), U.S. 2,034,889, March 24, 1936, Cent. 1936, II 2457, C.A. 30, 3280 (1936). (49) Seelig, Ann. 237, 154 (1887). (50) Varma, Narayan, J. Indian Chem. Soc. 4, 285-286 (1927).
- Maxted, Dunsby, J. Chem. Soc. 1928, 1441. (52) Maxted, Coke, Brit. 237,688, Aug. 21, 1925; Cent. 1928, I 1712. (53) Charlot, Ann. chim. (11) 2, 469 (1934). (54) Schrader, Ges. Abhandl. Kenntus Kohle 4, 310-341 (1920); Cent. 1921, I 537; C.A. 15, 2850-2851 (1921). (55) This ref. deleted. (56) Jenkins, J. Am. Chem. Soc. 57, 2733 (1935). (57) Henry, Ber. 2, 136 (1869). (58) Mayer, English, Ann. 417, 78 (1918). (59) van der Beek, Rec. trav. chim. 51, 412 (1932). (60) Anschutz, Claasen, Ber. 55, 683-684 (1922).
- (61) Neogi, Mitra, J. Chem. Soc. 1928, 1332. (62) Atkinson, Holm-Hansen, Nevers, Marino, J. Am. Chem. Soc. 65, 476 (1943). (63) Henry, Ber. 2, 492-493 (1869). (64) Britton (to Dow Chem. Co.), U.S. 1,878,463, Sept. 20, 1932, Cent. 1933, I 311; C.A. 27, 308 (1933). (65) M.L.B., Ger. 229,873, Jan. 6, 1911; Cent. 1911, I 358. (56) Anschutz, Ann. 454, 99 (1927). (67) Heller (to Chem. Fabrik von Heyden), Ger. 639,578, Dec. 8, 1936, Cent. 1937, I 2025; C.A. 31, 3943 (1937). (68) Claus, Bucher, Ber. 20, 1623 (1887). (69) Lossen, Ger. 146,174, Nov. 6, 1903; Cent. 1903, II 1224. (70) Jaeger (to Selden Co.), U.S. 1,953,231 & 1,953,232, April 3, 1934; Cent. 1934, II 669, 1688.
- (71) Meyer, Monatsh. 36, 730 (1915).
 (72) M.L.B., Ger. 282,133, Feb. 15, 1915, Cent. 1915,
 I 464.
 (73) Reichenbach, Bellstein, Ann. 132, 309-311 (1864).
 (74) Meyer, Ber. 3, 363-364 (1870).
 (75) Ador, Meyer, Ber. 4, 260 (1871).
 (76) Kelber, Ber. 54, 2257-2259 (1921).
 (77) Mettler, Ber. 38, 1750 (1905).
 (78) Ostwald, Z. physik. Chem. 3, 255 (1889).
 (79) Bodforss,
 Z. physik. Chem. 102, 53 (1922).
 (80) Wightman, Jones, Am. Chem. J. 46, 92-93 (1911).
- (81) Saxton, Meier, J. Am. Chem. Soc. 56, 1918-1921 (1934).
 (82) Dippy, J. Chem. Soc. 1941, 550-552.
 (83) Elliott, Kilpatrick, J. Phys. Chem. 45, 451-465, 466-471, 472-485, 485-492 (1941).
 (84) Kilpatrick, Mears, J. Am. Chem. Soc 62, 3047-3051, 3051-3054 (1940).
 (85) Larsson, Z. physik. Chem. A-169, 207 223 (1934).
 (86) Bright, Briscoe, J. Phys. Chem. 37, 787-796 (1933).
 (87) M. Kilpatrick, M. L. Kilpatrick, Chem. Revs 13, 131-137 (1933).
 (88) Mills (to Dow Chem. Co.), U. S. 1,942,826, Jan. 9, 1934, Cent. 1934, I 2196, C. A. 28, 1719 (1934).
 (89) Murgulescu, Alexa, Z. anal. Chem. 125, 260-267 (1943); C. A. 37, 4320 (1943).
 (90) Murgulescu, Latiu, Z. anal. Chem. 125, 267-268 (1943); C. A. 37, 4320 (1943).
- (91) Rivals, Ann. chim. (7) 12, 521 525 (1897). (92) McMaster, Godlove, J. Am. Chem. Soc. 37, 2183 (1915). (93) I G., Brit. 323,948, Feb. 6, 1930; Cent 1930, I 2630 (94) Oesper, Ballard, J. Am. Chem. Soc. 47, 2424-2427 (1925). (95) Vorlander, Huth, Ber. 43, 3129 (1910). (96) Birckenbach, Meisenheimer, Ber. 69, 723-729 (1936). (97) Beilstein, Schlun, Ann. 133, 242 (1865). (98) Beilstein, Ann. 179, 288-289, Notes (1875). (99) Lawson, Perkin, Robinson, J. Chem. Soc. 125, 652 (1924). (100) Ephrann, Ber. 55, 3482 (1922).
- (101) Buehler, Carson, Edds, J. Am Chem. Soc. 57, 2181-2182 (1935). (102) Poe, Strong, J. Am. Chem. Soc. 57, 380 (1935). (103) Poe, Suchy, J. Am. Chem. Soc. 56, 1640-1641 (1934). (104) Poe, Swisher, J. Am. Chem. Soc. 57, 748-749 (1935). (105) Andersen (to Lever Bros.), U.S. 2,177,049, Oct. 24, 1939; C.A. 34, 1036 (1940). (106) Hartman, Borders, J. Am. Chem. Soc. 59, 2107-2111 (1937). (107) Hartman, Storms, Gassmann, J. Am. Chem. Soc. 61, 2167-2169 (1939). (108) Rule, Patterson, J. Chem. Soc. 125, 2161 (1924). (109) Adams, Wirth, French, J. Am. Chem. Soc. 40, 424-427 (1918). (110) Adams, Ulich, J. Am. Chem. Soc. 42, 607-609 (1920).
- (111) Michael, Oechslin, Ber. 42, 318-330 (1909). (112) Sudborough, Turner, J. Chem. Soc. 101, 237-240 (1912). (113) Wightman, Wiesel, Jones, J. Am. Chem. Soc. 36, 2254 (1914). (114) Clark, Bell, Trans Roy. Soc. Can. (3) 27, III, 97-103 (1933). (115) Emmerling, Ber. 8, 883 (1875) (116) Frankland, Carter, Adams, J. Chem. Soc. 101, 2476 (1912). (117) Meyer, Monatsh. 22, 427 (1901). (118) Norris, Bearse, J. Am. Chem. Soc. 62, 953-956 (1940). (119) Scottish Dyos, Ltd. & Bangham, Thomas, Brit. 308, 231, April 18, 1929, Cent. 1929, II 1348; C.A. 24, 129 (1930). (120) Ost, J. prakt. Chem. (2) 11, 389-391 (1875).

(121) Ullmann, Kipper, Ber. 38, 2121-2122 (1905). (122) Boehringer und Söhne, Ger. 288,116, Oct. 19, 1915; Cent. 1915, II 1269. (123) Olejnicek, Hanzelka, Chem. Obzor 16, 147-151, 168-170, 187-191, 211-215 (1934); Cent. 1936, I 1983. (124) Tuttle, J. Am. Chem. Soc. 45, 1910-1916 (1923). (125) Meyer, Beer, Lasch, Monatsh. 34, 1669 (1913). (126) Rosenmund, Harms, Ber. 53, 2229-2231 (1920). (127) Ullmann, Zlokasoff, Ber. 38, 2112-2119 (1905). (128) A.G.F.A., Ger. 158,998, March 1, 1905, Cent. 1905, I 843. (129) Ullmann, Ber. 37, 853-854 (1904). (130) A.G.F.A., Ger. 150,323, March 22, 1904; Cent. 1904, I 1043.

(131) Graebe, Ber. 21, 503 (1888). (132) Knapp, J. prakt. Chem. (2) 146, 116-117 (1936). (133) Dhar, J. Chem. Soc. 117, 1061-1062, 1067-1069 (1920). (134) Ullmann, Ann. 355, 312-358 (1907). (135) M.L.B., Ger. 145, 189, Oct. 24, 1903; Cent. 1903, II 1097. (136) Ullmann, Ber. 36, 2382-2384 (1903). (137) Chakrabarty, Dutt, J. Indian Chem. Soc. 5, 514, 518 (1928). (138) Graebe, Lagodzinski, Ber. 25, 1734-1736 (1892); Ann. 276, 45-46 (1893). (139) Matsumura, J. Am. Chem. Soc. 57, 1533 (1935). (140) Lehmstedt, Bruns, Klee, Ber. 69, 2403 (1936).

(141) Lehmstedt, Schrader, Ber. 70, 842-849 (1937). (142) Magidson, Grigorowski, Ber. 69, 404 (1936). (143) I.G., French 835,727, Dec. 29, 1938; Cent. 1939, I 2295; C.A. 33, 5004 (1939). (144) Lehmstedt, Ber. 64, 2384-2385 (1931). (145) Bogert, Hirschfelder, Lauffer, Collection Czechoslov. Chem. Commun. 2, 385-386 (1930). (146) Dey, Doraiswami, J. Indian Chem. Soc. 10, 315-316 (1933). (147) Deese (to du Pont Co.), U.S. 2,100,242, Nov. 23, 1937; Cent. 1938, I 1876; C.A. 32, 596 (1938). (148) Holleman, de Bruyn, Rec. trav. chim. 20, 207-210 (1901). (149) Hübner, Ann. 222, 195-198 (1883). (150) Kenner, Stubbings, J. Chem. Soc. 119, 598 (1921).

(151) Lehmstedt, Schrader, Ber. 70, 1536-1537 (1937). (152) Magidson, Grigorowski, Ber. 66, 869 (1933). (153) Cohn, Monatsh. 22, 386-387 (1901). (154) Kalle & Co., Ger. 106,510, Dec. 23, 1898; Cent. 1900, I 742. (155) Ullmann, Ann. 366, 82-83 (1909). (156) Purgotti, Contardi, Gazz. chim. ital. 32, I 527-528 (1902). (157) Holleman, Rec. trav. chim. 20, 235-236 (1901). (158) Goldstein, Studer, Helv. Chim. Acta 20, 1409 (1937). (159) Reid, J. Am. Chem. Soc. 39, 132 (1917). (160) Chen, Trans. Science Soc. China 7, 73-80 (1931).

(161) Lund, Langvad, J. Am. Chem. Soc. 54, 4107 (1932). (162) Chen, Shih, Trans. Science Soc. China 7, 81-87 (1931). (163) Kelly, Morisani, J. Am. Chem. Soc. 58, 1502 (1936). (164) Dewey, Sperry, J. Am. Chem. Soc. 61, 3251-3252 (1939). (165) Dewey, Shasky, J. Am. Chem. Soc. 63, 3526-3527 (1941). (166) Remsen, Reed, Am. Chem. J. 21, 289-290 (1899). (167) Kao, Ma, Science Repts. Natl. Tsing Hua Univ. A-1, 21-22 (1931). (168) Norris, Klemka, J. Am. Chem. Soc. 62, 1432-1435 (1940). (169) Henry, Ber. 2, 492-493 (1869). (170) Sun, Sah, Science Repts. Natl. Tsing Hua Univ. A-2, 359-363 (1934); Cent. 1935, I 57; C.A. 29, 466 (1935).

(171) Kalb, Gross, Ber. 59, 732 (1926). (172) Hubner, Ann. 222, 194-196 (1883). (173) Meisenheimer, Meis, Ber. 57, 295 (1924). (174) Shah, Deshpande, J. Unv. Bombay 2, No. 2, 125-127 (1933); Cent. 1934, II 3110; C.A. 28, 6127 (1934). (175) Montagne, Koopal, Rec. trav. chim. 29, 143-144 (1910). (176) Porter, Wilcox, J. Am. Chem. Soc. 56, 2688 (1934). (177) Schreib, Ber. 13, 465 (1880). (178) Bryd, Roczniki Chem. 7, 436-445 (1927), C.A. 22, 2372 (1928). (179) Fischer, Z. Untersuch. Lebensm. 67, 161-162 (1934). (180) Deshusses, Mutt. Lebensm. Hyg. 34, 211-217 (1943); C.A. 38, 2586 (1944).

(181) Herz, Wittole, Monatsh. 74, 277 (1943).

3:4155 5,8-DICHLORONAPHTHOL-2

$$ho$$
OH ho Cl_0H $_6$ OCl2 Beil. S.N. 538

376

M.P. 141-142° (1)

[For prepn. from 5,8-dichloro-2-aminonaphthalene by htg. with dil. H₂SO₄ for 8 hrs. at 195-205° under pressure see (1) (2).]

--- 5,8-Dichloro-2-naphthyl methyl ether: m.p. 74° (2).

3:4155 (1) Soc. Chem. Ind., Basel, Swiss 202,854, May 1, 1939; Cent. 1939, II 3196. (2) Goldstein. Viaud, Helv. Chim. Acta, 27, 883-888 (1944); C.A. 39, 926 (1945).

3:4160 2,6-DICHLORO-3-HYDROXYBENZ-ALDEHYDE

CHO C₇H₄O₂Cl₂ Beil. S.N. 74.5 Cl Cl OH

M.P. 142-142.2° (1) 140.5° cor. (2) (3) 140° (4)

Colorless cryst. from hot aq. — \bar{C} has pronounced sternutatory properties and also attacks moist skin producing painful blisters. — [\bar{C} when mixed with 2-chloro-3-hydroxy-benzaldehyde (3:4085), m.p. 139.5° (4), depresses m.p. to 116° (4).]

[For prepn. of \bar{C} from m-hydroxybenzaldehyde (1:0055) with Cl_2 (2 moles) in AcOH soln. (yields: 51.5% (2) cf. (3), 38% (4)) (1) (other prods. also being formed) see indic. refs.; from 2-chloro-3-hydroxybenzaldehyde (3:4085) with Cl_2 (1 mole) in AcOH see (4); from 6-chloro-3-hydroxybenzaldehyde (3:3350) with Cl_2 (1 mole) in AcOH (\bar{C} is main prod. (5) but 4,6-dichloro-3-hydroxybenzaldehyde (3:3952) is also formed (4) (5)) see indic. refs.]

[For condens. of \bar{C} with p-chlorophenol (3:0475) and use of prod. as mothproofing agent see (6); for condens. of \bar{C} with 2,4-dihydroxybenzoic acid (1:0843) (7) or with o-cresotinic acid (2-hydroxy-3-methylbenzoic acid) (8) and use of products as dye intermediates see indic. refs]

C in 50% aq. KOH at 60-70° first ppts. yel. K salt of C which grad. dissolves and is replaced by a colorless cryst. ppt.; after stdg. 4 hrs. acidification with dil. H₂SO₄ gives (93.8% yield (2)) 2,4-dichlorophenol (3:0560), m.p. 42° (2).

 \bar{C} in AcOH with Br₂ gives (70% yield (3)) 4-bromo-2,6-dichloro-3-hydroxybenzaldehyde, cryst. from C_6H_7 + lgr., m p. 104-105° (3) (methyl ether, m.p. 82°, oxime, m.p. 193° cor. (3)).

 $\bar{\rm C}$ (1 pt.) in AcOH (4 pts.) on nitration with 1 pt. conc. HNO₃ (D=1.42) at 65° yields (4) 2,6-dichloro-3-hydroxy-4-nitrobenzaldehyde, bright yel. ndls. from AcOH or pl. from aq, m.p. 80° (4) (Ag salt, crimson ndls. from hot aq.; oxime, deep yel. ndls. from dil. alc., m.p. 195°; p-nitrophenylhydrazone, deep red ndls. from hot AcOH, m.p. 279-280° dec.; semicarbazone, light-yel. lfts. from hot alc., m.p. 255-256° (4)).

C dislvd. in hot aq. NaHCO₃ and treated with Me₂SO₄ for 15 min. yields (4) (3) the corresp. methyl ether, viz., 2,6-dichloro-3-methoxybenzaldehyde, m.p. 103-104° (3), 102° (4) (p-nitrophenylhydrazone, old-gold ndls., m.p. 214-215° (4)); this methyl ether upon oxidn. with alk. KMnO₄ gives (4) 2,6-dichloro-3-methoxybenzoic acid, ndls. from dil. alc., m.p. 149.5° (4).

- ② 2,6-Dichloro-3-hydroxybenzaldoxime: ndls. from dil. alc., m.p. 174-175° (4).
- D 2,6-Dichloro-3-hydroxybenzaldehyde p-nitrophenylhydrazone: deep or.-red. ndls.,
 m.p. 205-206° (4).

3:4160 (1) Bissell, Kranz (to National Aniline and Chem. Co.), U.S. 1,776,803, Sept. 30, 1930; Cent. 1931, I 159; C.A. 24, 5768-5769 (1930). (2) Lock, Monath. 55, 311 (1930). (3) Lock, Monath. 662, 184-185, 193-194 (1933). (4) Hodgson, Beard, J. Chem. Soc. 1926, 148-149, 152-153, 155. (5) Hodgson, Beard, J. Chem. Soc. 1926, 2031, 2034-2035. (6) Weiler, Wenk, Stötter (to I.G.), Ger. 530,219, July 24, 1931; Cent. 1932, I 3012. (7) Weiler (to F. Bayer & Co.), U.S. 1,532,790, April 7, 1925; Cent. 1925, II 352. (8) I.G., Brit. 263,879, March 2, 1927; Cent. 1927, I 2364.

3:4170 3-CHLORONAPHTHOL-1

$$\begin{array}{c|c} OH & C_{10}H_7OCl & \textbf{Beil. VI } --\\ & & VI_{1}--\\ & & VI_{2^-}(\textbf{581}) \end{array}$$

Ndls. from lgr. (2), C₆H₆, alc. or 80% AcOH (1) — Volatile with steam (1).

[For prepn. of \bar{C} from 3-chloronaphthylamine-1 (1) via diazotization and hydrolysis of the diazonium salt with steam see (1); from 2,3,4-trichloronaphthol-1 [Beil. VI-613] by partial reduction with HI (D=1.7) in AcOH on boilg 7 hrs. (100% yield) see (2).]

C is sol. in aq. alk., and the result. soln. couples with solns. of diazonium salts (1).

Č with Br₂ aq. (and alk.?) gives 3-chloro-2,4-dibromonaphthol-1, pr. from 90% formic acid, m.p. 112° (1).

[Č in 10% aq. KOH shaken with Me₂SO₄ for 20 min. gives (81% yield (2)) 3-chloronaphthol-1 methyl ether, oil, b.p. 162-164° at 18 mm. (2).]

- **3-Chloro-1-naphthyl acetate:** ndls. from $\lg r$, mp. 69° (2). [From \tilde{C} with acetyl chloride in C_6H_6 on refluxing 3 hrs in C_6H_6 (66% yield (2))]
- 3-Chloro-1-naphthyl benzoate: ndls. from lgr., m.p. 118-119° (2). [From C in 10% aq. KOH on shaking with BzCl (71% yield (2)).]

3:4170 (1) Hodgson, Elliott, J. Chem. Soc. **1934**, 1707. (2) Franzen, Stauble, J. prakt. Chem. (2) **103**, 385–387 (1922).

Many recorded m.p.'s lower than these values [cf. Beil. IX-343 and (3)] were on samples now known to have been impure.

Cryst. from lgr. (1) or mixt. of $C_6\overline{H}_6 + \text{lgr.}$ (4) (3); pr. from aq., tbls. from C_6H_6 , ndls. from alc. — Can also be purified by distn. in vac. (1). — Volatile with steam (?).

[For prepn. of \bar{C} from 2,6-dichlorotoluene (3:6270) (57% yield (4)) via bromination to 2,6-dichlorobenzyl bromide, conversion to corresp. acetate, and oxidn. of latter with KMnO₄ see (1) (4); from 2,6-dichlorobenzaldehyde by oxidn. with KMnO₄ see (2); for older less satisfactory methods see Beil IX-343.]

 \bar{C} on htg. begins to lose CO₂ at 235° (5) [\bar{C} htd. with a large excess 50% aq. KOH at 150° for 24 hrs. was recovered unchanged to extent of 90% (9)]

C on nitration under stated conditions (1) gives 94% yield 2,6-dichloro-3-nitrobenzoic acid, cryst. from toluene, m.p. 152° (1).

 \bar{C} (as $K\bar{A}$) htd. with anilme + $K_2CO_3 + Cu$ in amyl alc. gives small yield of diphenylaminecarboxylic acid-2, cryst. from C_6H_6 , m.p. 181° (1). [Note loss of both chlorine atoms.]

 \bar{C} htd. with acetamide for 6 hrs. at 225-235° gave 93% yield (5) m-dichlorobenzene (3:5960), b.p. 172°.

 \overline{C} htd. with PCl₅ (6) or with SOCl₂ + pyridine (4) yields 2,6-dichlorobenzoyl chloride, b.p. 142-143° at 21 mm. (6), 126-128° at 18 mm. (7).

- Methyl 2,6-dichlorobenzoate: from $Ag\bar{A} + MeI$ (8); b.p. 250° (8).
- Ethyl 2,6-dichlorobenzoate: from AgĀ + EtI (8) or from Č via SOCl₂, followed by EtOH (82% yield (5)); cannot be prepared by direct esterification (8); b.p. 264-265° (8). [This ester on htg. with AlCl₃ at 120-130° for 2½ hrs. gives EtCl (91%) and Č (92%) (5).]
- D 2,6-Dichlorobenzamide: ndls. from alc., m.p. 202° (8), 198° (7). [This amide htd. with NaCl.AlCl₃ over free flame evolves HCl and gives (67% yield (5)) 2,6-dichlorobenzonitrile, ndls. from lgr., m.p. 142.5-143 5° (5), 143° (9); the nitrile can be reconverted to the amide with alk. H₂O₂ (9).]
- 2,6-Dichlorobenzanilide: unrecorded.

3:4200 (1) Lehmstedt, Schrader, Ber. 70, 1530-1531 (1937).
 (2) Davies, J. Chem. Soc. 119, 873 (1921).
 (3) Bornwater, Holleman, Rec. trav. chim. 31, 227, 230 (1912).
 (4) Norris, Bearse, J. Am. Chem. Soc. 62, 953-956 (1940).
 (5) Norris, Klemka, J. Am. Chem. Soc. 62, 1432-1435 (1940).
 (6) Cohen, Briggs, J. Chem. Soc. 83, 1213-1214 (1903).
 (7) Dilthey, Quint, Heinen, J. prakt. Chem. (2) 152, 71 (1939).
 (8) Reich, Bull. soc. chim. (4) 21, 219 (1917).
 (9) Ref. 8, pp. 222-223.
 (10) Lock, Bock, Ber. 70, 922 (1937).

[See also cis-1,2-dichloro-1,2-diphenylethylene (3:1380).]

Colorless tbls. from alc.; \tilde{C} is much less sol. in alc. than its *cis* isomer (3:1380); 100 pts. abs. alc. at 24 4° dis. 0.71 pt. \tilde{C} , but soly. of \tilde{C} is diminished by pres. of its stereoisomer (10). — \tilde{C} (like its isomer) is very sol. ether.

Note that $\bar{\mathbb{C}}$ (the higher-melting tolane dichloride) has now been shown (4) to have the trans configuration, many earlier reports to the contrary notwithstanding.

Note also that $\bar{\mathbb{C}}$ with 1,1,2,2-tetrachloro-1,2-diphenylethane (tolane tetrachloride) (3:4496) gives an isomorphous mixt. (2), formerly erroneously regarded as an individual cpd. designated as "ditolane hexachloride."

PREPARATION OF C

Note that in all processes (below) for prepn. of Č more or less of the lower-melting (cis) stereoisomer is always formed.

FROM DINUCLEAR INITIAL MATERIALS

From diphenylacetylene (tolane). [For prepn. of \bar{C} from tolane [Beil. V-656, V₁-(319), V₂-(568)] with Cl_2 in CHCl₃ see (7).]

From trans-1,2-diphenylethylene (stilbene). [For prepn. of \bar{C} from stilbene (1:7250) with PCl₅ (2 moles) in POCl₃ at 170° see {12}.]

From 1,1,2,2-tetrachloro-1,2-diphenylethane (tolane tetrachloride). [For prepn. of \bar{C} from tolane tetrachloride (3:4496) by removal of two adjacent chlorine atoms by use of Zn dust in EtOH (1) (6) (7) (10), Zn dust in AmOH (6), Fe powder in boilg. AcOH (14) (6) (note that in this method ratio of \bar{C} to lower m.p. stereomer is 1:5 (6)), or by use of excess conc. (2 N) MeMgCl (11), or with H_2 + hydrazine hydrate in MeOH/KOH at b.p. for $1\frac{1}{2}$ hrs. (3) see indic. refs.]

From benzoin. [For formn. of \tilde{C} from benzoin (1:5210) with PCl₅ at 0° (much benzoylphenyl-dichloromethane ("chlorobenzil") [Beil. VII-436, VII₁-(234)] also being formed) see (20).]

From Mononuclear Initial Materials

From benzotrichloride. [For prepn. of \tilde{C} from benzotrichloride (3:6540) with Cu powder (yield of total mixed stereoisomers 68% (15), 23.5% (16) (17)), by action of excess conc. (2 N) MeMgCl (yield total mixed stereoisomers 22% (11)), by action of hydrazine hydrate + Pd in MeOH/KOH (35% yield (3)), or for formn of \tilde{C} (together with other products) by pyrolysis over hot Pt (18) see indic. refs.]

From benzal (di)chloride. [For form. of \tilde{C} (together with other prods.) from benzal (di)chloride (3:6327) by pyrolysis over hot Pt see (18).]

FROM MISCELLANEOUS SOURCES

[For formn. of \bar{C} from CaC₂ with satd. soln. of Cl₂ in C₆H₆ see (13); from benzoyl-phenyl-diazomethane (azibenzil) [Beil. VII₁-(395), XXIV-208] with oxalyl (di)chloride (3:5060) in C₆H₆ (38.5% yield \bar{C}) see (9); from 1,1,2-trichloro-1,2-diphenylethane [Beil. V-601] by elimination of HCl with alc. KOH see (19); for formn. of \bar{C} from its lower-melting stereoisomer (3:1380) by distn. (about 32% conversion to \bar{C} (10)) (12) (6) see indic. refs.]

CHEMICAL BEHAVIOR OF C

 $\ddot{\mathbf{C}}$ on htg. is partially transformed (6) (12) to the lower-melting isomer (3:1380); on distn. conversion is about 68% (10).

Reduction of C. C with conc. HI and red P in s.t. at 170° for 20 hrs. gives (16) (20) bibenzyl (1:7149), m.p. 52°.

Elimination of 2 chlorine atoms. \bar{C} with Na/Hg in alc. (1) (16), or \bar{C} with Zn dust in boilg. alc. (7) (10), or \bar{C} with alc. KOH in s.t. at 180° (12) gives diphenylacetylene (tolane) [Beil. V-656, V₁-(319), V₂-(568)], m.p. 60°.

Addn. of halogens. \bar{C} with Cl_2 in C_6H_6 soln. yields (13) 1,1,2,2-tetrachloro-1,2-diphenylethane (tolane tetrachloride) (3:4496). — \bar{C} does not (12) add Br₂, and the expected prod. 1,2-dibromo-1,2-diphenylethane is unreported from any other source. Nitration of \bar{C} . The nitration of \bar{C} has never been studied, and neither mono nor dinitro

derivs. are reported from any other source.

3:4210 (1) Zinin, Ber. 4, 288-289 (1871). (2) Marckwald, Karczag, Ber. 40, 2994-2995 (1907). (3) Busch, Weber, J. prakl. Chem. (2) 146, 50-52 (1936). (4) Bergmann, J. Chem. Soc. 1936, 403, 405. (5) Arends, Ber. 64, 1939 (1931). (6) Blank, Ann. 248, 17-25, 33-34 (1888). (7) Liebermann, Homeyer, Ber. 12, 1973-1974 (1874). (8) Stelling, Z. physik. Chem. B-24, 425 (1934). (9) Staudinger, Ber. 49, 1971-1972 (1916). (10) Eiloart, Am. Chem. J. 12, 231-253 (1890).

(11) Fuson, Ross, J. Am. Chem. Soc. 55, 723 (1933). (12) Limpricht, Schwanert, Ber. 4, 379 (1871). (13) Davidson, J. Am. Chem. Soc. 40, 397-399 (1918). (14) Lachowicz, Ber. 17, 1165 (1884). (15) Reitzenstein, Breuning, J. prakt. Chem. (2) 83, 115-116 (1911). (16) Hanhart, Ber. 15, 899-900 (1882). (17) Onufrowicz, Ber. 17, 835 (1884). (18) Loeb, Ber. 36, 3060-3061 (1903). (19) Sudborough, J. Chem. Soc. 71, 221-222 (1897). (20) Redsko, J. Russ. Phys-Chem. Soc. 21, 426 (1889); Ber. 22 (Referate) 760 (1889).

M.P. 144-145° (1) 144° (2) (3) (5) 143° (4)

[See also 2,3-dichlorobenzoquinone-1,4 (3:2885).]

Ndls. from aq. with 2 H_2O lost at 100° or over conc. H_2SO_4 (1); eas. sol. alc., insol. cold lgr.; sublimes.

[For prepn. of \bar{C} from hydroquinone (1:1590) in ether with SO₂Cl₂ (1) (6), in AcOH with Cl₂ (30% yield (4)) (7) (6), in ether with EtOCl (3), or in MeOH with Cl₂ (9) see indic. refs.; from chlorobenzoquinone (3:1100) in ether with HCl gas (12% yield (5)) (1) (4) (6) (yield is small (5), reaction difficult to control (4), sometimes fails (8) (6)); from p-benzoquinone dichloride (2,3-dichlorocyclohexene-5-dione-1,4) [Beil. VII-573] by reductn. with SO₂ (1) (6) or SnCl₂ + HCl (2), or with Ac₂O + H₂SO₄ followed by hydrolysis of the resultant diacetate (2).]

[For use as antioxidant and gum inhibitor in cracked gasoline see (10); in aq. petroleum emulsion as insecticidal oil spray see (11).]

C with FeCl₃ gives a greenish black quinhydrone (1)

C in AcOH with excess Br₂ yields (6) 4,5-dibromo-2,3-dichlorohydroquinone, golden-yel. lfts. from lgr., m.p. 294° (6).

 \bar{C} reduces NH₄OH/AgNO₃ and Fehling's soln. (1); \bar{C} on oxidn. with MnO₂ + dil. H₂SO₄ (1) (4) (5) or with CrO₃/AcOH (7) gives (yields: 88% (4), 60% (1)) 2,3-dichlorobenzo-quinone (3:2885) q.v. [For study of oxidn.-reductn. potential of \bar{C} see (4).]

- ② 2,3-Dichlorohydroquinone diacetate: colorless ndls. from dil. alc., m p. 121° (6) (2). [From $\ddot{C} + Ac_2O$ (6), or from p-benzoquinone dichloride (see above) with $Ac_2O + H_2SO_4$, (2).]
- **D 2,3-Dichlorohydroquinone dibenzoate:** colorless cryst. from CS₂ or pet. ether, m.p. 173-174° (1). [From \bar{C} in dil. aq. alk. with BzCl (1).]
- D 2,3-Dichlorohydroquinone dimethyl ether: pinkish white ndls. from dil. alc., m.p. 124° (6). [From C in dil. alk. with Me₂SO₄ (6)] [Note that corresp. deriv. of 2,5-dichlorohydroquinone (3:4690) has m.p. 125-127° but that a mixt. of the two derivs. is depressed to m.p. 97° (6).]

3:4220 (1) Peratoner, Genco, Gazz. chim. ital. 24, II 375-396 (1894). (2) Dimroth, Eber, Wehr, Ann. 446, 141, 144 (1926). (3) Goldschmidt, Endres, Dirsch, Ber. 58, 576 (1925). (4) Conant, Fieser, J. Am. Chem. Soc. 45, 2204-2205 (1923). (5) Oliveri-Tortorici, Gazz. chim. ital. 27, II 584-585 (1897). (6) Gebauer-Fulnegg, Malnic, Monatsh. 47, 403-404 (1926). (7) Eckert, Endler, J. prakt. Chem. (2) 104, 82 (1922). (8) Den Hollander, Rec. trav. chim. 39, 481-482 (1920). (9) Plazek, Roczniki Chem. 10, 761-776 (1930); Cent. 1931, I 1428; C.A. 25, 1504 (1931). (10) Clarke, Towne (to Texas Co.), U.S. 2,023,871, Dec. 10, 1935; Cent. 1936, I 2671; C.A. 38, 851 (1936).

(11) Yates (to Shell Development Co.), U.S. 1,778,240, Oct. 14, 1930; Cent. 1931, I 2799; C.A. 24, 5928 (1930).

Neut. Eq. 186.5

382

Wh. ndls. (from hot aq.). [For prepn. from o-chlorophenol (3:5980) by htg. with chloroacetic ac. (3:1370) and aq alk see (1) (2) (3)]

C refluxed with 1½ pts. thionyl chloride for 1½ hrs gives (90% yield (1)) o-chlorophenoxyacetyl chloride, b p. 136° at 12 mm., m p. 184° (1)

The methyl ester (b.p. 186-188°) and the ethyl ester, ndls. (from alc.), m.p. 32°, have been prepd. from the acid chloride (1) (5).

- o-Chlorophenoxyacetamide: from the acid chloride by treatment with excess (NH₄)₂CO₃; ndls. readily sol. in hot aq., alc., or C₆H₆, m.p. 149 5° (1).
- o-Chlorophenoxyacetanilide: from the acid chloride by action of aniline (2 moles) in C₆H₆; ndls. (from alc.), m.p. 121° (1).
- 3:4260 (1) Minton, Stephen, J. Chem. Soc. 121, 1599-1601 (1922). (2) Behaghel, J. prakt. Chem. 114, 297-298 (1926). (3) Koelsch, J. Am. Chem. Soc. 53, 304-305 (1931) Branch, J. Am. Chem. Soc. 65, 1555-1564 (1943). (5) Bacher, Raiford, Proc. Iowa Acad. Sci. **50**, 247-251 (1943); C.A. **38**, 2327 (1944).

[C is best prepd (nearly quant. yield (2)) by alk, hydrolysis of its acetate (see below) or by similar treatment (67% yield (3)) of its benzoate (see below) or (39% yield (3)) of its benzenesulfonate (see below); for formn. of C from 4-amino-4'-hydroxybiphenyl by diazotization, etc., see (1); from 4'-chloro-4-aminobiphenyl (2) by diazotization and hydrolysis see (2).]

C on chlorination with Cl2 in CCl4 soln. gives (92% yield (4)) 2-chloro-4-(p-chlorophenyl)phenol, m.p. 71-72° (corresp. acetate, m.p. 74.5-75°; corresp. benzoate, m.p. 125-126°: corresp. benzenesulfonate, m.p. 100-101°) (4).

- **4-(p-Chlorophenyl)phenyl acetate:** m.p. 113° (2) [From \bar{C} by acetylation, or from the acetate of 4-hydroxybiphenyl (1:1585) with Cl2 in CCl4 + trace of I2 (47% yield (2)) or similarly in AcOH (5).] [Note that the m.p. of this prod. has also been given without details of prepn. as 72° (6).
- **182°** (3). [From \bar{C} by benzoylation or from the benzoate of 4-hydroxybiphenyl (1:1585) with Cl₂ in CCl₄ soln. + trace of I₂ (55% vield (3)).]
- 1 4-(b-Chlorophenyl) phenyl benzenesulfonate: m.p. 74-75° (3). [From C with benzenesulfonyl chloride + aq. 10% NaOH (3), or from the benzenesulfonate ester of 4-hydroxybiphenyl (1:1585) with Cl₂ in CCl₄ soln. + trace I₂ (21% yield (3)).1

3:4262 (1) Angeletti, Gatti, Gazz. chim. ital. 58, 633 (1928). (2) Savoy, Abernathy, J. Am. Chem. Soc. 64, 2219-2221 (1942). (3) Savoy, Abernathy, J. Am. Chem. Soc. 64, 2719-2720 (1942). (4) Savoy, Abernathy, J. Am. Chem. Soc. 65, 1464-1465 (1943). (5) Schmidt, Savoy, Abernathy, J. Am. Chem. Soc. 65, 296-297 (1943). (6) Hodgson, J. Chem. Soc. 1942, 583.

M.P. 147 (1)

Cryst. from AcOH.

[For prepn. of \bar{C} from p-chlorobenzaldehyde (3:0765) by conversion through p-chlorocinnamic acid to ethyl p-chlorocinnamate, thence by addn. of Br₂ to give ethyl β -(p-chlorophenyl)- α , β -dibromopropionate, followed by elimination of 2 HBr and saponification (or vice versa) with alc. KOH, and final acidification (yield not stated), see (1)

 \bar{C} with $Cu(OAc)_2$ loses CO_2 yielding (1) p-chlorophenylacetylene (3:0590) (cf. also under o-chlorophenylpropiolic acid (3:3956))

3:4265 (1) Wilson, Wenzke, J. Am. Chem. Soc. 57, 1265-1267 (1935).

3:4270 4,4'-DICHLOROBENZOPHENONE
$$C_{13}H_8OCl_2$$
 Beil. VII - 420 VII₁-(228)

M.P.	148°	(1)	B.P.	353° at 757 mm.	(2)
	147.75°	(2) (20)		243° at 38 mm. (15)
	147°	(19)			
	146.5-147.5° cor.	(40)			
	146°	(3) (37)			
	145°	(4) (5) (6)			
		(7) (8) (16)			
	144-145°	(9) (10)			
	144.5°	(11) (14)			
	144°	(12)			
	142-143°	(13) (22)			

Colorless lits from alc; eas sol ether, acetone, AcOH, CHCl₃, CS₂. — [For f.p./compn. data on systems \bar{C} + benzophenone (1:5150) and \bar{C} + diphenylamine see (12).]

[For prepn. of \bar{C} from p-chlorobenzoic acid (3:4940) + chlorobenzene (3:7903) + AlCl₃ (82% yield (1)) or from p-chlorobenzoyl chloride (3:6550) + chlorobenzene (3:7903) + AlCl₃ in CS₂ in direct sunlight (yields: 90% (17), 75–80% (2), 36% (9)) (37) (some isomeric 2,4'-dichlorobenzophenone (3:1565) also being formed) see indic. refs.; from chlorobenzene (3:7903) + AlCl₃ + CO₂ at 80–150° and 10 atm. press. (p-chlorobenzoic acid is main prod.) see (18); from p-chlorophenyl MgCl + CO₂ (together with p-chlorobenzoic acid) see (8).]

[For prepn. of C from dichloro-bis-(p-chlorophenyl)methane (4,4'-dichlorobenzophenone

dichloride) (see below) by hydrolysis with boilg. dil. alc. {14} or conc. H₂SO₄ {14} (15) (6) (19) see indic. refs.; from tetra-(p-chlorophenyl)ethylene glycol (see below) on fusion or on boilg. with AcOH see (20); from 4,4'-dibromobenzophenone with PCl₅ at 150° see (21); from 4,4'-dichloro-3-nitrobenzophenone (see below) via reduction to amine, diazotization, and treatment with SnCl₂ + NaOH see (2).]

[For formn. of \bar{C} by oxidation with $CrO_3/AcOH$ of 4,4'-dichlorobenzilic acid (2), of bis-(p-chlorophenyl)methane (7), of tris-(p-chlorophenyl)methane (16), of 1,1,4,4-tetra-(p-chlorophenyl)butyne-2 (91% yield (4)), or of 1,1,4,4-tetra-(p-chlorophenyl)butyne-1,2,3 (94% yield (5)) see indic. refs.; from oxidn. of β , β -di-(p-chlorophenyl)propionic acid with aq. KMnO₄ see (10); from 2,2-dimethyl-5,5-bis-(p-chlorophenyl)pentanone-3 [α -(p,p'-dichlorophenyl)propiophenone] by oxidn. with alk. KMnO₄ see (22); from β , β -di-(p-chlorophenyl)propiophenone by oxidn. with aq. KMnO₄ in NaOH + pyridine soln. see (13); from bis-(p-chlorophenyl)methyleneacetophenone with KMnO₄ in acetone (71% yield) see (3)]

[For formn. of C from 1,1-di-(p-chlorophenyl)ethane (3:0995) (39), from 1-chloro-2,2-bis-(p-chlorophenyl)ethylene (3:1430) (84% yield (40)), or from 1,1-dichloro-2,2-bis-(p-chlorophenyl)ethylene (3:2438) (40), all by oxidn. with CrO₃/AcOH, see indic. refs.]

[$\tilde{\mathbf{C}}$ on reduction with 3% Na/Hg in 90% alc. (20), with Al/Hg in 80% alc. (6) (11), with Zn dust + AcOH on boilg. (20), with Zn dust + alc. KOH (20) or NaOH (23), or simply with boilg. alc. KOH (24) gives (yields: 100% (23), 96% (6) (11) di-(p-chlorophenyl)carbinol (4,4'-dichlorobenzhydrol) [Beil. VI-680, VI₁-(327)], cryst. from alc., m.p. 94° (20), 93° (24), 91.5° (23), 89-90° (6) (11) (corresp. 3,5-dinitrobenzoate, m.p. 174-176° (41)); note that in some cases this main prod. is accompanied by tetra-(p-chlorophenyl)ethylene glycol (see below). — $\tilde{\mathbf{C}}$ on reduction with Zn dust + AcOH + dil. H₂SO₄ (25), or in alc. in bright sunlight for 5 days (20) ef (26), gives (85% yield (20)) tetra-(p-chlorophenyl)ethylene glycol [Beil. VI-1058, VI₁-(523)], m p. 180° (6) (11), 175° (20) (accompanied by smaller amts. of other prods.)

[\bar{C} with sodium phenylacetylene in dry ether gives (57% yield (3)) bis-(p-chlorophenyl)-ethynyl-carbinol, m.p. 163-164° (3); \bar{C} with diphenylmethyl sodium gives (27) bis-(p-chlorophenyl)-diphenylmethyl-carbinol, m.p. 183-184° (27); \bar{C} with McMgI in dry ether gives (39) (19) not only some bis-(p-chlorophenyl)-methyl-carbinol, m.p. 67.0-68 5° (39), but also (68% yield (19)), by loss of H₂O, unsym.-di-(p-chlorophenyl)cthylene, m.p. 91°(3:2475); \bar{C} with β-(diphenylvinyl)MgBr gives (12% yield (28)) 1,1-di-(p-chlorophenyl)-3,3-diphenylpropen-2-ol-1, m.p. 85°, which on htg. at 130-150° loses H₂O yielding 1,1-di-(p-chlorophenyl)-3,3-diphenylpropadiene-1,2, m.p. 93-95° (28); \bar{C} with ethyl bromoacetate + Zn in C₆H₆ gives (30% yield (28) ethyl β , β -di-(p-chlorophenyl)- β -hydroxypropionate, m.p. 102° (28).]

[Č with PCl₅ at 150° gives (17) (15) (29) dichloro-di-(p-chlorophenyl)methane (4,4'-dichlorobenzophenone dichloride), m.p. 52-53° (15), 52.5° (17).]

[$\bar{\mathbf{C}}$ on fusion with NaOH yields (7) chlorobenzene (3:7903) + p-chlorobenzoic acid (3:4940). — $\bar{\mathbf{C}}$ with 10% aq. NaOH in pres. of Cu 5 hrs. at 190° under press. yields (30) 4,4'-dihydroxybenzophenone [Beil. VIII-317, VIII₁-(641)], m.p. 214° (30).]

[C with hydrazine hydrate in isopropyl alc. in s.t. at 150–160° for 7 hrs. gives (56% yield (42)) 4,4'-dichlorobenzophenone hydrazone, m.p. 91–93°, which on Wolff-Kishner reduction gives (21% yield (42)) 4,4'-dichlorodiphenylmethane (3:1057).]

[C with aq. NH₄OH in pres. of CuO + NH₄NO₃ + KClO₃ under press. at 180° (1) cf. (31) gives (92% yield (1)) 4,4'-diaminobenzophenone [Beil. XIV-88, XIV₁-(391)], m.p. 245-246° (1), 242.5° (31); some half reactn. prod., viz., 4-amino-4'-chlorobenzophenone, m.p. 185° (1), is also formed. — For similar reactn. of C with diethylamine leading to 4-chloro-4'-diethylaminobenzophenone see (32). — For reactn. of C with N-methyl-a-

phenylindole and use in prepn. of dyes see (33); with ethylbutyl-m-toluidine see (34); with aminoanthraquinone derivs. see (35) (36).]

- [$\bar{\rm C}$ on nitration with 10 wt. pts. fumg. HNO₃ (D=1.47) in cold (37) or with 5 pts. abs. HNO₃ at 0° (2) gives (81% yield (37)) 4,4'-dichloro-3,3'-dinitrobenzophenone, cryst. from AcOH, m.p. 132.5° (2), 132-133° (38), 120° (37); $\bar{\rm C}$ on trinitration at 130° with 1.8 wt. pts. conc. H₂SO₄ contg. 2 pts. KNO₃ gives (37) 4,4'-dichloro-3,3',5-trinitrobenzophenone, cryst. from AcOH, m.p. 140° (37); $\bar{\rm C}$ on tetranitration with 10 pts. fumg. H₂SO₄ + 1 pt. KNO₃ at 150° gives (37) 4,4'-dichloro-3,3',5,5'-tetranitrobenzophenone, cryst. from AcOH, m.p. 202° (37).] [A mono-nitrated $\bar{\rm C}$, viz., 4,4'-dichloro-3-nitrobenzophenone. ndls. from alc., m.p. 87° (2), 88-89° (38) has been obtd. indirectly.]
 - 4,4'-Dichlorobenzophenone oxime: ndls. from alc., m.p. 136-136.5° (1), 136° (7), 135° (8) (9), 134° (5). [From \(\bar{C}\) with excess NH₂OH in alc. at 100° (9).] [This prod. by Beckmann rearr. with conc. H₂SO₄ yields p-chlorobenz-p-chloroanilide, m.p. 213-213.5° (1).]
 - ---- 4,4'-Dichlorobenzophenone phenylhydrazone: not reported.
 - ---- 4,4'-Dichlorobenzophenone p-nitrophenylhydrazone: not reported.
 - ---- 4,4'-Dichlorobenzophenone 2,4-dinitrophenylhydrazone: m.p. 238-240° (40).
- 3:4270 (1) Newton, Groggins, Ind. Eng. Chem. 27, 1397-1399 (1935). (2) Montagne, Rec. trav. chim. 21, 24-29 (1902). (3) Meyer, Schuster, Ber. 55, 822-823 (1922). (4) Brand, Horn, Bausch, J. prakt. Chem. (2) 127, 246-247 (1930). (5) Brand, Bausch, J. prakt. Chem. (2) 127, 235-236 (1930). (6) Cohen, Boeseken, Rec. trav. chim. 38, 115-116, 123 (1919). (7) Stephen, Short, Gladding, J. Chem. Soc. 117, 523 (1920). (8) Bodroux, Bull. soc. chim. (3) 31, 29 (1904). (9) Dittrich, Ann. 264, 175-178 (1891). (10) Fuson, Kozacık, Eaton, J. Am. Chem. Soc. 55, 3803 (1933).
- (11) Bosseken, Cohen, Cent. 1915, 1375-1376. (12) Schaum, Rosenberger, Z. anorg. allgem. Chem. 136, 335-336 (1924). (13) Eaton, Black, Fuson, J. Am Chem. Soc. 56, 688 (1934). (14) Norris, Green, Am. Chem. J. 26, 496-497 (1901). (15) Norris, Twieg, Am. Chem. J. 30, 398 (1903). (16) Fischer, Hess, Ber. 38, 337-338 (1905). (17) Montagne, Rec. trav. chim. 25, 384, 389 (1906). (18) I.G., Brit. 307,223, March 28, 1929; Cent. 1929, I 3145; Meyer, Hopff (to I.G.), Ger. 524,186, May 11, 1931; Cent. 1931, II 497. (19) Bergmann, Bondi, Ber. 64, 1469-1470 (1931). (20) Montagne, Rec. trav. chim. 24, 114-120 (1905).
- (21) Cone, Robinson, Ber. 40, 2160-2161 (1907). (22) Weinstock, Fuson, J. Am. Chem. Soc. 56, 1242 (1934). (23) Norris, Tibbetts, J. Am. Chem. Soc. 42, 2091 (1920). (24) Montagne, Moll van Charante, Rec. trav. chim. 31, 313-314 (1912). (25) Montagne, Rec. trav. chim. 25, 411-414 (1906). (26) Cohen, Boeseken, Rec. trav. chim. 39, 258 (1920). (27) Bergmann, J. Chem. Soc. 1936, 412-413. (28) Bergmann, Hoffmann, Meyer, J. prakt. Chem. 135, 255, 261 (1932). (29) Schonberg, Schutz, Ber. 62, 2331 (1929). (30) Britton (to Dow Chem. Co.), U.S. 1,961,630, June 5, 1934; Cent. 1934, II 1846; C.A. 28, 4744 (1934).
- (31) Britton, Bryner (to Dow Chem. Co.), U.S. 1,946,058, Feb. 6, 1934; Cent. 1934, I 3396; C.A 28, 2364 (1934). (32) Hammond, Harris (to Heyden Chem. Co.), U.S. 2,223,517, Dec. 3, 1940, C.A. 35, 1808 (1941). (33) Wolff (to I G.), Brit. 417,014, Oct. 25, 1934; Ger. 604,429, Oct. 20, 1934; French 761,372, March 17, 1934; Swiss 170,094, Sept. 11, 1934; Cent. 1935, I 801. (34) Wolff, Werner (to I.G.), Ger. 606,642, Dec. 3, 1934; Cent. 1935, I 1621. (35) B.A.S.F., Ger. 220,579, April 5, 1910; Cent. 1910, I 1471. (36) Kranzlein, Vollmann, Boedeker, Ger. 574,966, April 21, 1933; Cent. 1933, I 4046. (37) Consonno, Gazz. chim. ital. 34, I 376-377 (1904). (38) Maron, Fox, Ber. 47, 2781 (1914). (39) Grummitt, Buck, Becker, J. Am. Chem. Soc. 67, 2266 (1945). (40) Haller, Bartlett, Drake, Newman, Cristol, Magerlein, Mueller, Schneider, J. Am. Chem. Soc. 67, 1599, 1602 (1945).
- (41) Grummitt, Buck, J. Am. Chem. Soc. 67, 693-694 (1945). (42) Grummitt, Jenkins, J. Am. Chem. Soc. 68, 914 (1946).

3:4280 2-CHLORO-4-HYDROXYBENZ- $C_7H_5O_2Cl$ Beil. VIII - 81 $VIII_1$ —

Colorless ndls. from AcOH (1) or aq. (2). — Volatile with steam but much less so than the isomeric 4-chloro-2-hydroxybenzaldehyde (3:0960) (1).

[For prepn. of \bar{C} from *m*-chlorophenol (3:0255) via Reimer-Tiemann reactn. see (1); via anhyd. HCN + AiCl₃ + C₆H₆ (50% yield) see (2); for prepn. (alm. 100% yield (1)) from 2-chloro-4-nitrotoluene via 2-chloro-4-aminotoluene and subsequent diazo reactn. see (1).]

C does not reduce NH₄OH/AgNO₃ or Fehling soln. (1).

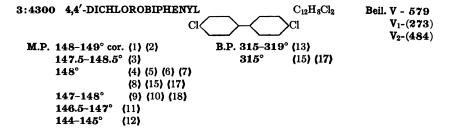
 \bar{C} with aq. FeCl₃ gives only a slight ppt. [dif from 4-chloro-2-hydroxybenzaldehyde (3:0960)]; the copper and chromium salts are lighter green in color than those from that isomer (1).

Č on mononitration as specified (3) yields 5-nitro-2-chloro-4-hydroxybenzaldehyde, vol. with steam, colorless ndls. from alc., m.p. 125° (3). [This product yields a phenylhydrazone, silky dark purple ndls. from alc., m.p. 166° sl. dec; a p-mtrophenylhydrazone, deep or. ndls. from AcOH, m.p. 266° dec.; and a semicarbazone, light or. ndls from dil. AcOH, m.p. 266° dec. (3).]

Č on dinitration as specified (3) yields 3,5-dinitro-2-chloro-4-hydroxylenzaldehyde, not volatile with steam, pale yel. massive pr. from aq , m.p. 93° (3). [This product yields a phenylhydrazone, br.-purple ndls from alc., m.p. 210° dec.; a p-nitrophenylhydrazone, red-br. ndls. from dil. AcOH, m.p. 267° dec.; and a semicarbazone, lt. br. ndls. from dil. AcOH, m.p. 192° dec (3).]

- 2-Chloro-4-hydroxybenzaldoxime: cryst. from alc., m p 194° (2).
- --- 2-Chloro-4-hydroxybenzaldehyde phenylhydrazone: unrecorded.
- **D** 2-Chloro-4-hydroxybenzaldehyde p-nitrophenylhydrazone: dark red pl. from ale. or vermilion red cryst. from AcOH, m.p. 288° dec. (1).
 - --- 2-Chloro-4-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.
- 2-Chloro-4-hydroxybenzaldehyde semicarbazone: yel cryst. from alc, m.p. 214°
 (1).
- **② 2-Chloro-4-acetoxybenzaldehyde:** colorless ndls. from dil AcOH, m.p. 51 5° (1).
- ② 2-Chloro-4-benzoxybenzaldehyde: colorless ndls. from alc, m.p. 96 5° (1). [Note that this ③ does not give good distinction from isomeric 4-chloro-2-hydroxybenzaldehyde (3:0960) whose corresponding benzoate has m.p. 98.5° (1).]

3:4280 (1) Hodgson, Jenkinson, J. Chem Soc. **1927**, 1740-1742. (2) Gattermann, Ann. **357**, 334 (1907). (3) Hodgson, Jenkinson, J. Chem. Soc. **1928**, 2274-2275.



Colorless cryst. from toluene + lt. pet. (2), from 50% AcOH (14), or from alc. (11). [For prepn. of $\bar{\mathbf{C}}$ from 4,4'-diaminobiphenyl (benzidine) [Beil. XIII-214, XIII₁-(58)] via tetrazotization and use of Cu powder (9), Cu₂Cl₂ (3), or HgCl₂ complex (82% yield (10)), see indic. refs.; from biphenyl (1:7175) in AcOH with Cl₂ (41% yield (2)) (convenient for prepn. small amts. $\bar{\mathbf{C}}$) see (2); from 4,4'-dinitrobiphenyl with SOCl₂ in s.t. for 10 hrs. at 200-210° see (7); from p-chloroiodobenzene [Beil. V-221, V₁-(119)] with Cu powder at 200-250° (82% yield) see (15).]

[For formn. of \tilde{C} from chlorobenzene (3:7903) by pyrolysis see (16) (12) (for discussion of formn. during mfg. of phenol from chlorobenzene see (19)); from biphenyl (1:7175) with Cl_2 in pres. of $SbCl_5$ (17) or I_2 (13) see indic. refs.; from 4,4'-dihydroxybiphenyl (1:1640) with PCl_5 see (13); from 4,4'-dichlorobiphenyl-3,3'-diarboxylic acid on htg. see (18); from 4,4'-dichloro-3,3'-diaminobiphenyl via tetrazotization and htg. with alc. see (14); from decompn. of bis-(p-chlorobenzoyl) peroxide on htg. see (6)]

[For manuf of \bar{C} or mixts. of dichlorobiphenyls contg. \bar{C} from biphenyl with Cl_2 see (20) (21) (22) (23); for use as insecticide see (24)]

[C htd. under press with conc. aq. NH₄OH in pres. of Cu₂Cl₂ and Ca (OH)₂ gives (99.5% yield (25)) 4,4'-diaminobiphenyl (benzidne); C with aq. over Cu + silica gel at 525-600° gives (26) 4,4'-dihydroxybiphenyl (1:1640)]

 \bar{C} on mononitration in 15 pts. AcOH with 10 pts. HNO₃ (D=1.46) at 100° for ½ hr. (2), or in nitrobenzene soln. with HNO₃ (D=1.52) as directed (2), gives alm. quant. yield of 4,4'-dichloro-2-nitrobiphenyl, cryst from alc or CCl₄, m.p. 102° (2) (27). [This prod. does *not* react with piperidine (27)]

 \bar{C} on dinitration by soln in 7½ pts HNO₃ (D=1.52) in an ice bath gives (2) mixt. contg. 81.3% 4,4'-dichloro-2,3'-dinitrobiphenyl and 18.7% 4,4'-dichloro-2,2'-dinitrobiphenyl. By recryst. from AcOII 4,4'-dichloro-2,3'-dinitrobiphenyl is obtd in ndls., m p. $141-142^{\circ}$ (2), 140° (28), which on warming with piperidine for a few seconds yields (28) 4-chloro-4'-piperidino-2,3'-dinitrobiphenyl, or ndls from alc., m p. 132° (28) (note that the principal dinitration prod. of \bar{C} is the 2,3'-dinitro- \bar{C} and not the 2,2'-isomer as formerly (29) supposed). — From the mother liq. of the above dinitration may be obtd. (2) the true 4,4'-dichloro-2,2'-dinitrobiphenyl, m.p. $138-139^{\circ}$ (2); this does not react with piperidine

 \bar{C} on trinitration with 10 pts. HNO₃ (D=1.52) for 2 hrs. at 100° gives (2) (30) 4,4′-dichloro-2,3′,5′-trinitrobiphenyl, ndls. from AcOH, m.p. 166-167° (2), 164-165° (30); this prod. warmed with piperidine gives 4-chloro-4′-piperidino-2,3′,5′-trinitrobiphenyl, crimson pr. from AcOH, m.p. 182° (2).

 \bar{C} on oxidn. with CrO₃ in AcOH yields (13) p-chlorobenzoic acid (3:4940), m.p. 237° (13).

3:4300 (1) Williamson, Rodebush, J. Am. Chem. Soc. 63, 3019 (1941). (2) Shaw, Turner, J. Chem. Soc. 1932, 288-289, 294-296. (3) Brotscher, Helv. Phys. Acta 1, 358 (1928). (4) Griess, J. Chem. Soc. 20, 101 (1867). (5) Mieleitner, Z. Krist. 55, 66 (1920). (6) Fichter, Adler, Helv. Chim. Acta 9, 285 (1926). (7) Mascarelli, Gatti, Gazz. chim. ital. 59, 870 (1929). (8) Brüll, Gazz. chim. ital. 65, 24 (1935). (9) Weissberger, Williams, Z. physik. Chem. B-3, 309 (1929). (10) Schwechten, Ber. 65, 1607 (1932).

Pickett, Walter, France, J. Am. Chem. Soc. 58, 2296 (1936).
 Meyer, Hofmann, Monatsh. 38, 143 (1917).
 Schmidt, Schultz, Ann. 207, 338-344 (1881).
 Holt, J. Chem. Soc. 1934, 1432.
 Ullmann, Ann. 332, 54-55 (1904).
 Kramers, Ann. 189, 137-140 (1877).
 Kramers, Ann. 189, 142-145 (1877).
 Schultz, Rohde, Vicari, Ann. 352, 130 (1907).
 Hale, Britton, Ind. Eng. Chem. 20, 122 (1923).
 Malowan (to Swann Research, Inc.), U.S. 1,951,577, March 20, 1934; Cent. 1934, II 3183; C.A. 28, 3427 (1934).

(21) Federal Phosphorus Co, French 703,216, April 27, 1931, Cent. 1931, II 1635. (22) Britton, Stoesser (to Dow Chem. Co.), U.S. 1,835,754, Dec. 8, 1931; Cent. 1932, I 1440. (23) Prahl, Mathes (to F. Raschig), Ger. 580,512, July 13, 1933; Cent. 1933, II 1763. (24) I.G.,

Ger. 513,775, Dec. 2, 1930; Cent. 1931, I 1965. {25} Booth (to Swann Research, Inc.), U.S. 1,954,469, April 10, 1934; Cent. 1934, II 1846; C.A. 28, 3744 (1934), Federal Phosphorus Co., Brit. 370,774, May 4, 1932; Cent. 1932, II 1237. {26} Booth (to Swann Research, Inc.), U.S. 1,925,367, Sept. 5, 1933, Cent. 1934, I 128; C.A. 27, 5342 (1933). (27) LeFevre, Turner, J. Chem. Soc. 1926, 2045. (28) Dennett, Turner, J. Chem. Soc. 1926, 477, 479-480. (29) Borsche, Scholten, Ber. 56, 609 (1917). (30) Vernon, Rebernak, Ruwe, J. Am. Chem. Soc. 54, 4456-4467 (1932).

3:4315 6,7-DICHLORONAPHTHOL-1

M.P. 151° (1) (2) 149–150° (3)

Cryst from CHCl₃ (3).

[For prepn. from β -(3,4-dichlorobenzal)propionic ac [Beil. IX-614] by distn. see (1) (2) (3); \bar{C} is sepd. from the smaller proportion of 7,8-dichloronaphthol-1 (3:2635) by the greater soly. of the latter in lgr. (3).]

C on oxidn. with $K_2Cr_2O_7 + dil$. H_2SO_4 yields (3) 4,5-dichlorophthalic ac (3:4890), which during m.p. detn. is converted to 4,5-dichlorophthalic anhydride (3:4830), m.p. 184-185° (3).

Č in alk. soln. coupled with diazotized naphthionic acid (1-aminonaphthalenesulfonic acid-4) gives a deep red-bluish color which upon acidification becomes dark yellow (3). [Dif. from 7,8-dichloronaphthol-1 (3:2635) q.v.]

6,7-Dichloro-1-naphthyl acetate: ndls. from dil. alc., or compact pr. from CHCl₃ lgr., m.p. 102-103° (3).

3:4315 (1) Armstrong, Wynne, Chem. News **71**, 253 (1895). (2) Armstrong, Wynne, Proc. Chem. Soc. **11**, 78-79 (1895); Ber. **29**, Referate, 223-224 (1896). (3) Erdmann, Schwechten, Ann. **275**, 286-288 (1893).

3:4325 3,3-DICHLORO-2,2-DIMETHYLBUTANE

M.P. 151-152° (1)

Colorless cryst. subliming readily even at ord. temp.

[For prepn of \bar{C} from ter-butyl methyl ketone (pinacolone) (1:5425) with PCl_5 at 0-5° (1) (2) (3) (4) (5) (6) (7) (9) see indic. refs Note that \bar{C} (by loss of HCl) is always accompanied by more or less 3-chloro-2,2-dimethylbutene-3 (3:7340) and other prods.]

C on htg. with phenol + KOAc yields (8) 3-chloro-2,2-dimethylbutene-3 (3:7340).

 \bar{C} on htg. at 150-230° with powdered KOH (moistened with alc.) gives (65% yield (6)) (9) (2) ter-butylacetylene [Beil. I-256], b.p. 37.8° at 760 mm., $D_0^{20} = 0.6683$, $n_{\alpha}^{20} = 1.37257$ (6); note that use of NaOH instead of KOH gives by loss of 1 HCl only 3-chloro-2,2-dimethylbutene-3 (3:7340) and no ter-butylacetylene (9).

3:4325 (1) Bartlett, Rosen, J. Am. Chem. Soc. 64, 544 (1942). (2) Delacre, Bull. soc. chim. (3) 35, 343-344 (1906). (3) Favorskii, J. Russ. Phys.-Chem. Soc. 19, 425 (1887); Ber. 20, Referate 781 (1887). (4) Delacre, Bull. acad. roy. Belg. 1906, 7-41; Cent. 1906, I 1233-1234. (5) Delacre, Cent. 1906, II 496. (6) Ivitzky, Bull. soc. chim. (4) 35, 357-358 (1924). (7) Meerwein, Wortman, Ann. 435, 201, Note 4 (1924). (8) Meerwein, Wortman, Ann. 435, 194, Note 1 (1924). (9) de Graef, Bull. soc. chim. Belg. 34, 428-429 (1925).

3:4330 2-CHLORONAPHTHOIC ACID-1

M.P. 152-153° (1) 151-152° (2)

151° (4)

Cryst. from C_6H_6 (2). — Sol. in 1000 pts. aq. at 20° or in 126 pts. aq. at 100°; eas. sol. alc., ether (1).

[For prepn. of \bar{C} from 2-hydroxynaphthoic acid-1 [Beil. X-328, X₁-(144)] with PCl₅ (3 moles) in s.t. at 180-190° for 8 hrs. followed by treatment with aq. see (1) (2); from 1-chloroformylnaphthyl-2-phosphoric acid dichloride [Beil. X-329] with PCl₅ (2 moles) in s.t. at 180-190° followed by treatment with aq. see (1) (2); from 2-chloro-1-(chloromethyl)-naphthalene (4) by oxidn. with dil HNO₃ for 15 days see (4).]

 \bar{C} in aq. susp. with 2% Na/Hg yields (1) α -naphthoic acid (1:0785), m.p. 160° (1).

C does not esterify upon treatment in MeOH with HCl gas (3).

Salts: CaĀ_{2.2}H₂O; sol. in 150 pts. cold aq. or 75 pts. hot aq.; loses water of hydration completely at 180° (1).

- Methyl 2-chloro-1-naphthoate: pr. from alc. + toluene, m.p. 50° (1) (2), b.p. 176-180° at 18.5 mm. (2). [From AgA with MeI in s.t. at 100° (1) or from C with ethereal diazomethane (2)] [This ester is very resistant to hydrolysis (1) (2).]
- Ethyl 2-chloro-1-naphthoate: unreported.
- --- p-Bromophenacyl 2-chloro-1-naphthoate: unreported.

3:4330 (1) Rabe, Ber. 22, 394-396 (1889). (2) Bergmann, Hirshberg, J. Chem. Soc. 1936, 333-334. (3) Meyer, Ber. 28, 184 (1895). (4) Horn, Warren, J. Chem. Soc. 1946, 144.

3:4335 2,4,5-TRICHLOROPHENOXYACETIC

 $C_8H_5O_3Cl_3$

Beil. S.N. 522

ACID Cl Cl—OCH₂.COOH

M.P. 153° (1)

Colorless cryst. from C_6H_6 ; alm. insol. aq. — Neut. Eq. = 255.5.

[For prepn. of \bar{C} from 2,4,5-trichlorophenol (3:1620) with chloroacetic acid (3:1370) in aq. NaOH (85% yield) see (1).]

[For use of \bar{C} as weed killer see (2); for general survey of activity of \bar{C} as plant hormone see (4) (5)]

[For prepn. of ethylene glycol bis-(2,4,5-trichlorophenoxyacetate), m.p. 140°, and its use as plasticizer see (3).]

3:4335 (1) Pokorny, J. Am. Chem. Soc. 63, 1768 (1941) (2) Hamner, Tukey, Science 100, 154-155 (1944). (3) Grether, Shawver, DuVall (to Dow Chem. Co.), U.S. 2,121,226, June 21, 1938; C.A. 32, 6257 (1938). (4) Zimmerman, Ind. Eng. Chem. 35, 596-601 (1943). (5) Hitchcock, Zimmerman, Contrib. Boyce Thompson Inst. 14, 21-38 (1945); C.A. 39, 5289 (1945); Proc. Am. Soc. Hort. Sci. 45, 187-189 (1944); C.A. 39, 4918 (1945).

3:4340 2,5-DICHLOROBENZOIC ACID Cl
$$C_7H_4O_2Cl_2$$
 Beil. IX - 342 COOH IX_1 -(141)

Ndls. from aq. or dil. alc. — Somewhat volatile with steam. — Sol. in 1193 pts. aq. at 11° (12); in 1177 pts. at 14° (11).

[For prepn. of \bar{C} from 2,5-dichlorotoluene (3:6245) by htg. with dil. HNO₃ in s.t. at 140° (60% yield (4)) (5) (13) (2) (8) (7) or htg. with KMnO₄ (14) see indicated refs.; for prepn. of \bar{C} from 2,5-dichlorobenzaldehyde (3:1145) via Cannizzaro reactin. (84% yield (1)) see (1) (4); for prepn. (90-95% yield (9)) from 5-chloro-2-aminobenzoic acid via diazo reactin + CuCl see (9) (11); from 2,5-dichloroaniline via 2,5-dichlorobenzointrile (m.p. 130°) and its hydrolysis with fumg. HCl at 180° see (15); for prepn. of \bar{C} from benzoic acid + KClO₃ + HCl see (12) (21); for still other misc. methods see Beil. 1X-342, IX₁-(141).

For f p./compn. data on mixtures of \bar{C} with *m*-chlorobenzoic acid, m.p. 154.4° (3:4392), and with 2,3-dichlorobenzoic acid, m.p. 154.4° (3:4650), see (2).

 \ddot{C} on htg with 3 pts. conc. H_2SO_4+2 pts. aq. loses CO_2 at 220° yielding p-dichlorobenzene (3:0980) (5).

The direct nitration of \bar{C} is unrecorded. [However, 2,5-dichloro-3-nitrobenzoic acid, ndls. from AcOH, m.p. 220°, and 2,5-dichloro-6-nitrobenzoic acid [Beil. 1X-404], m.p. 143_144°, have both been prepd. by oxidn. (16) of the corresp. aldehydes.]

 \tilde{C} with PCl₅ (17) or with SOCl₂ (18) yields 2,5-dichlorobenzoyl chloride, b p. 137° at 15 mm. (17), 95.3-95.5° at 1 mm. (18). [For formn. in chlorination of benzoyl chloride see (2).]

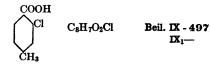
- Methyl 2,5-dichlorobenzoate: unrecorded.
- Ethyl 2,5-dichlorobenzoate: b.p. 271° cor. (12). [For study of hydrolysis see (20).]
- 2.5-Dichlorobenzamide: woolly ndls. from aq., m.p. 155° (12).
- D 2,5-Dichlorobenzanilide: from 2,5-dichlorobenzoyl chloride (above) + aniline (11), pr from C₆H₆, m p. 240° (11).
- **D** 2,5-Dichlorobenz-3-nitroanilide: from 2,5-dichlorobenzoyl chloride (above) + m-nitroaniline (19), ndls. from aq. MeOH, m.p. 151-152° u.c. (19).

3:4340 (1) Lock, Ber. 66, 1531 (1933). (2) Hope, Riley, J. Chem. Soc. 123, 2470-2480 (1923). (3) Bornwater, Holleman, Rec. trav. chim. 31, 227-230 (1912). (4) de Crauw, Rec. trav. chim. 50, 773 (1931). (5) Lellmann, Klotz, Ann. 231, 319 (1885). (6) Gassmann, Hartmann, J. Am. Chem. Soc. 63, 2394 (1941). (7) Cohen, Dakin, J. Chem. Soc. 79, 1130 (1901). (8) Turner, Wynne, J. Chem. Soc. 1936, 712. (9) Eller, Klemm, Ber. 55, 222 (1922). (10) Twiss, Farinholt, J. Am. Chem. Soc. 58, 1564 (1936).

(11) Hühner, Ann. 222, 201-203 (1883). (12) Beilstein, Ann. 179, 290-293 (1875). (13) Feldmann, Kopeliowitsch, Arch. Pharm. 273, 491 (1935). (14) Ullmann, Wagner, Ann. 371, 388 (1910); 355, 364 (1907). (15) Noelting, Kopp. Ber. 38, 3509 (1905). (16) Hodgson, Beard, J. Chem. Soc. 1927, 2381-2382. (17) Cohen, Briggs, J. Chem. Soc. 83, 1214 (1903). (18) Norris, Ware, J. Am. Chem. Soc. 61, 1418-1420 (1939). (19) Simpson, Stephenson, J. Chem. Soc. 1942, 356. (20) Blakey, McCombie, Scarborough, J. Chem. Soc. 1926, 2863-2868.

(21) Biswas, Das-Gupta, J. Indian. Chem. Soc. 19, 497-498 (1942); CA. 37, 5709 (1943).

3:4355 2-CHLORO-4-METHYLBENZOIC ACID



Colorless ndls. from alc.; spar. sol. cold, more sol. hot, aq.; cas. sol. alc., ether, CHCl₃, hot C₆H₆.

[For prepn. of \bar{C} from 3-chloro-4-isopropyl-1-methylbenzene (3-chloro-p-cymene) (3:8770) by oxidn. with 15 pts. boilg. HNO₃ (D=1.24-1.29) (other products are also formed) see (2); from 3-chloro-4-methylbenzomtrile, m.p. 61-62° (1), by hydrol. with boilg. aq. KOH (100% yield) see (1).]

Salts. NH₄ \bar{A} , K \bar{A} , Na \bar{A} H₂O, all very eas. sol. both in aq. and in alc. (1); Ca \bar{A}_2 .2H₂O, Ba \bar{A}_2 .5H₂O, eas. sol. hot aq. (1); Ag \bar{A} , spar. sol. cold aq. but eas. sol. hot aq. (1).

[\tilde{C} on mononitration by soln. in fumg. HNO₃ (D=15) at ord. temp. followed by stdg. several hrs. ppts. 2-chloro-5-nitro-4-methylbenzoic acid [Beil. IX-503], cryst. from hot aq or alc., m.p. 180° u.c. (1), 180–181.5° u.c. (3), 180–181° (4) (note that the isomeric 2-chloro-3-nitro-4-methylbenzoic acid [Beil. IX-503], m.p. 192° u.c. (3), may be formed from \tilde{C} under certain conditions (3)).]

 $|\bar{C}|$ on dinitration with mixt. of 1 pt. fumg. HNO₃ (D=1.52) + 4 pts. conc. H₂SO₄ gives (3) either in cold or on htg. exclusively 2-chloro-3,5-dinitro-4-methylbenzoic acid [Beil. IX-506], ndls. from alc., m.p. 233° u.c. (3)]

- Ethyl 2-chloro-4-methylbenzoate: oil, b.p. not reported; $D_4^{21.4} = 1.1591$ (5), $n_{He}^{21.4} = 1.52443$ (5)
- —— 2-Chloro-4-methylbenzamide: ndls. from alc., m.p. 182° (1). [From partial alk. hydrolysis of 2-chloro-4-methylbenzonitiile (see above) (1)]

3:4355 (1) Claus, Davidsen, J. prakt Chem (2) 39, 491–496 (1889). (2) Fileti, Crosa, Gazz. chim ital. 16, 288-290 (1886). (3) Claus, Davidsen, Ann. 265, 345-346, 348-349 (1891). (4) Fileti, Crosa, Gazz. chim. ital. 18, 312 (1888). (5) von Auwers, Harres, Z. physik. Chem. A-143, 18 (1929).

Pr. (from hot aq.). - Spar. sol cold aq.

[For prepn from p-chlorophenol (3:0475) by htg. with chloroacetic ac. (3:1370) and aq. alk see (1) (4) (5) (6).]

C htd. with conc. HCl in s.t. at 150° yields p-chlorophenol (3:0475) (3).

 \bar{C} refluxed with $1\frac{1}{2}$ pts. thionyl chloride for $1\frac{1}{2}$ hrs. gives (90% yield) p-chlorophenoxyacetyl chloride, b.p. 142° at 17 mm., m.p. 18.8° {1).

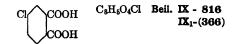
The methyl ester (b.p. 177-180°) and the ethyl ester, ndls. (from alc.), m.p. 49°, have been prepared from the acid chloride (1)

p-Chlorophenoxyacetamide: from the acid chloride by treatment with excess (NH₄)₂CO₃; ndls. from alc., m.p. 133° (1).

p-Chlorophenoxyacetanilide: from the acid chloride by action of aniline (2 moles) in C_6H_6 ; ndls. (from alc.), m.p. 125° (1).

3:4375 (1) Minton, Stephen, J. Chem. Soc. 121, 1599-1601 (1922). (2) Michael, Am. Chem. J. 9, 216 (1887). (3) Peratoner, Gazz. chrm. ital. 28, I 239 (1898). (4) Behaghel, J. prakt. Chem. 114, 297-298 (1926). (5) Koelsch, J. Am. Chem. Soc. 53, 304-305 (1931). (6) Hayes, Branch, J. Am. Chem. Soc. 65, 1555-1564 (1943).

3:4390 4-CHLOROPHTHALIC ACID



M.P. 157°	(1)	
156°	(2)	
151°	(3)	
150-150.5°	(4)	
150° in s.t.	(5)	
148° u.c.	(6)	

[See also 4-chlorophthalic anhydride (3:2725).]

Ndls. from alc.; cryst from CoH6 or CCl4. — Eas. sol. aq., alc., ether, or AcOH.

[For prepn. of \bar{C} from 4-chlorophthalic anhydride (3:2725) by warming with aq. or from dimethyl 4-chlorophthalate (3) or diethyl 4-chlorophthalate (5) by hydrol with alk. see indic. refs.; from neutral sodium phthalate in aq. alk. on treatment with Cl₂ see (3) (7) (8) (9) (10); from 4-chloro-2-methylbenzoic acid (3:4700) (11) (12), from 5-chloro-2-methylbenzoic acid (3:4670) (11), from 4-chloro-2-methylacetophenone [Bcil. VII-306] (2), or from 7-chloro-1,2,3,4-tetrahydronaphthalene (1) by oxidn. with alk. KMnO₄ see indic. refs.; from 6-chloroindanone-1 [Beil. VII-361] on evapn. with hot 25% HNO₃ see (4); from 1,6-dichloronaphthalene (3:0810) (13), 2,6-dichloronaphthalene (3:4040) (14) (6), 2,7-dichloronaphthalene (3:3445) (14), 6-chloronaphthol-2 (3:3500) (6), or 4-chloro-2-methylbenzoic acid (above) (12) on oxidn. with dil. HNO₃ in s.t. as directed see indic. refs.; from the trichloride of 4-sulfophthalic acid [Beil. XI-407] with PCl₅ in s.t. at 220° followed by KOH hydrolysis of the 4-chlorophthalyl (di)chloride see (15); from 4-sulfophthalic anhydride (16) by htg. with HCl + NaClO₃ see (16)

C on htg. above m.p. gives 4-chlorophthalic anhydride (3:2725).

[\bar{C} on fusion with KOH (11) or with NaOH at 165-175° (10) gives (100% yield (10)) 4-hydroxyphthalic acid [Beil. X-499, X_1 -(255)], m p. 204-205°, with conv. to corresp. anhydride, m p. 171° (note that this same prod. is also obtd. from the isomeric 3-chlorophthalic acid (3:4820)).]

[Č htd. under press. at 350° with aq. + cat. loses CO₂ presumably yielding (17) m-chlorobenzoic acid (3:4392) and/or p-chlorobenzoic acid (3:4940).]

 $[\bar{C} \text{ with NH}_3 \text{ gas} + \text{cat. as directed (18) yields 4-chlorophthalonitrile, m.p. 130-132° (19).}]$

[For use of C as softener for cellulose derivatives see (20); for reaction of C with naphthalene + AlCl₃ yielding intermediates for vat dyes see (21).]

 \bar{C} on htg. with resorcinol + few drops conc. H_2SO_4 , then dissolving in alk., gives fluorescein reactn. (2) $-\bar{C}$ is unstable toward KMnO₄ (2).

Salts. BaĀ, CaĀ, dif. sol. aq.; BaĀ.H₂Ā, spar. sol. even in hot aq. (11) (for table of heavy metal salts see (22)).

Esters. Dimethyl 4-chlorophthalate; from Ag₂Ā with MeI (15), from 4-chlorophthalyl (di)chloride (above) with MeOH (15), or from C in MeOH with HCl gas (3); ndls. from

lgr., m.p. 38° (3), 37° (15), b.p. 186–187° at 32 mm. (3); diethyl 4-chlorophthalate; from \dot{C} in alc. with HCl gas (15) or from diethyl 4-aminophthalate via diazotization and use of Cu₂Cl₂ reactn. (70% yield (5)), b.p. 300–305° (15), 185–190° at 25 mm. (5), 173–174° at 16 mm. (1).

3:4390 (1) von Braun, Larbig, Kredel, Ber. 56, 2337-2338 (1923). (2) Mayer, Albert, Schön, Ber. 65, 1297 (1932). (3) Ayling, J. Chem. Soc. 1929, 253-256. (4) Miersch, Ber. 25, 2116 (1892). (5) Blicke, Smith, J. Am. Chem. Soc. 51, 1869 (1929). (6) Claus, Dehne, Ber. 15, 320-321 (1882). (7) Moore, Marrack, Proud, J. Chem. Soc. 119, 1788-1789 (1921). (8) Egerer, Monatsh. 34, 81-83 (1913). (9) Scottish Dyes, Ltd., Beckett, Bangham, Thomas, Brit. 348,632, June 11, 1931; Cent. 1931, II 1194. (10) Rushchinskii, Compt. rend. acad. sci. (U.R.S.S.) 1933, 118-121; Cent. 1935, I 1617.

(11) Krüger, Ber. 18, 1758-1759 (1885). (12) Claus, Stapelberg, Ann. 274, 289 (1893). (113) Cleve, Bull. soc. chim. (2) 29, 499 (1878). (14) Alén, Bull. soc. chim. (2) 36, 433-434 (1881). (15) Rée, Ann. 233, 237-238 (1886). (16) Waldmann, Schwenk, Ann. 487, 290-291 (1931). (17) Jaeger (to Selden Co.), U.S. 1,953,231, Apr. 3, 1934; Cent. 1934, II 1688. (18) Imperial Chem. Ind., Ltd., French 766,944, July 6, 1934; Cent. 1934, II 2749. (19) Soc. Chem. Ind. Basel, French 844,567, July 27, 1939; C.A. 34, 7299 (1940). (20) Dreyfus, French 749,792, July 29, 1933; Cent. 1934, I 3154.

(21) B.A.S.F., French 599,038, Dec. 31, 1925, Cent. 1926, I 2850. (22) Ephraim, Ber. 55, 3482 (1922).

3:4392	m-CHLOROBE ACID	NZOIC C	Соон	$\mathrm{C_7H_5O_2Cl}$	Beil. IX - 337 IX ₁ -(139)
M.P.	159°	(105)	154.5°	(11) (12)	
	158°	(1) (2) (3)	154.4°	(13)	
	157.5°	(3) (4)	154.25°	(14)	
	157°	(5)	154-155°	(15)	
	156.2°	(6)	154°	(16) (17) (18) (60)	
	155-156° cor.	(7)	153-154°	(24)	
	156°	(26)	153.5°	(19)	
	155°	(8)	153°	(20) (21) (26) (28)	(35)
	154.8-155.0° cor	. (62)		(70) (84)	
	154.9°	(8)	152°	(22) (47)	
	154.8-154.9°	(9)			
	154.8°	(10)			

Pr. from hot aq., 30% AcOH or C_6H_6 . — \tilde{C} is spar. sol. cold aq., e.g., 1 pt. \tilde{C} is sol. at 0° in 2840 pts. aq. (23); 100 ml. satd. aq. soln. at 25° conts. 0.0385 g. \tilde{C} (60). — \tilde{C} is eas. sol. hot aq., alc., ether. — At 14–16° C 100 ml. of satd. soln. of \tilde{C} in ether conts. 14 g. \tilde{C} ; in C_6H_6 , 0.66 g. \tilde{C} ; in CS_2 , 0.62 g. \tilde{C} ; in CCl_4 , 0.08 g. \tilde{C} (8). — For study of soly. of \tilde{C} in m-chlorotoluene (3:8245), or in m-chlorotoluene (3:8275) see (10); in acetone or C_6H_6 see (6); for soly of \tilde{C} in aq. solns. of various salts including Na \tilde{A} see (60). — For distribution coefficients of \tilde{C} at 25° between aq. + toluene or between aq. and CHCl₃ see (102).

 \tilde{C} can be sublimed under reduced press. (24) (14). — \tilde{C} is but very slightly volatile with steam (for details see (12)). — For study of adsorption of \tilde{C} by charcoal from acetone or C_{aHa} soln, see (6).

Binary systems contg. \bar{C} : [For f.p./compn. data on system \bar{C} + H₂O see (25). — For f.p./compn. data and diagram of system \bar{C} + benzoic acid (1.0715) (eutectic, m.p. 96.0° (20), 95.4° (27) (8), contg. 36 wt. % \bar{C} (27) (20) (8) (28)) see indic refs. — For f.p./compn. data on systems \bar{C} + m-toluic acid (1:0705) (26), \bar{C} + m-hydroxybenzoic acid (1:0825) (26), see indic refs.]

[For f.p./compn. data on system $\bar{C}+o$ -chlorobenzoic acid (3:4150) (eutectic, m.p. 110.7°, contg. 47–48 mole % \bar{C} (20) (27) (8) (19)) see indic. refs.; on system $\bar{C}+p$ -chlorobenzoic acid (3:3940) (eutectic, m.p. 140.9°, contg. 80 mole % \bar{C} (8) (19) cf. (104)) see indic. refs.; on system $\bar{C}+2$,5-dichlorobenzoic acid (3:4340) (eutectic, m.p. 119.7°, contg. 51–58 mole % \bar{C}) see (13).]

[For f.p./compn. data on systems $\bar{C} + o$ -bromobenzoic acid (28), $\bar{C} + m$ -bromobenzoic acid (28), $\bar{C} + p$ -bromobenzoic acid (28), m-iodobenzoic acid (29), o-nitrobenzoic acid (30), m-nitrobenzoic acid (30) see indic. refs.]

Ternary systems contg. \bar{C} : [For influence of addn. of benzoic acid (20) or of p-chlorobenzoic acid (3:4940) (27) to eutectic of \bar{C} with o-chlorobenzoic acid (3:4150) see indic. refs. — For influence of addn. of o-chlorobenzoic acid (3:4150) to eutectic of \bar{C} with benzoic acid (1:0715) see (27); for data on system $\bar{C} + o$ -chlorobenzoic acid (3:4150) + p-chlorobenzoic acid (3:4940) see (19).]

Miscellaneous. [For study of fate of \bar{C} in animal organism see (31) cf. (102) (note that although from man \bar{C} is excreted (34) as N-(m-chlorobenzoyl)glycine (m-chlorobippuric acid) [Beil. IX-339], m.p. 143-144° (31), yet from dog and rabbit no evidence for this conjugation product has been found (31). — For study of use of \bar{C} as a preservative see (32). — For use of \bar{C} as vulcanization regulator see (33)

Preparation. [For prepn. of \bar{C} from benzoic acid (1:0715) by chlorination with Cl₂ (38) in pres. of FeCl₃ (70% yield (8)), with KClO₃ + conc. HCl (35) (36) (37) (38), with aqua regia at 100° (yield 32% (39)) (7), with SbCl₅ (35) (40) (84), with MnO₂ + conc. HCl in s.t. at 150° (41), with NaOCl soln. (20) (42), or with Ca(OCl)₂ soln (42) (35) (38) see indic. refs. (note that in all these cases numerous other chlorination products are also formed); from cinnamic acid (1:0735) by chlorination and oxidn with Ca(OCl)₂ soln. see (35) (38).]

[For prepn. of \bar{C} by oxidn. of *m*-chlorotoluene (3:8275) with $K_2Cr_2O_7 + H_2SO_4$ (43), with 5% aq. KMnO₄ (75% yield (4)) (8), with dil. HNO₃ in s.t. at 130-140° for 8 hrs. (47), or in aq. alk. at 260° under press. with air (44) see indic. refs.; from 3-chlorobiphenyl (3:8940) or from 3,3'-dichlorobiphenyl (3:0180) by oxidn. with $CrO_3/AcOH$ in pres of V_2O_5 see (45); from *m*-chlorobenzaldehyde (3:6475) by oxidn. with alk KMnO₄ see (3).]

[For prepn. of C from m-chlorobenzal (di)chloride (3:6710) by hydrolysis with aq. followed by KMnO₄ oxidn. (7% yield (2)) or from its mixt. with m-chlorobenzotrichloride (3:6845) by hydrolysis with 70% H₂SO₄ or 80% AcOH or 5% NaOH at 90-100° in stream of air to effect immediate oxidn. (46) see indic. refs.]

[For prepn. of \bar{C} from *m*-chlorobenzonitrile [Beil. IX-339], m.p. 40.5° (48), by hydrolysis with conc. H₂SO₄ (3), from *N*-(*m*-chlorobenzoyl)glycine (*m*-chlorohippuric acid) by hydrolysis with HCl (35) (36), see indic. refs.]

[For prepn. of C from m-aminobenzoic acid [Beil. XIV-383, XIV₁-(558)] via dizactization and use of Cu_2Cl_2 reactn. (74% yield (101)) (3) (4) (49); from m,m'-diazoaminobenzoic acid (diazoaminobenzene-3,3'-dicarboxylic acid) [Beil. XVI-727] with warm conc. HCl (50) see indic. refs.]

[For form. of \tilde{C} from *m*-chloro-iodobenzene [Beil. V-220, V₂-(167)] by reaction with *n*-butyllithium in ether followed by carbonation with CO₂ (41.5% yield (51)); from *p*-chloronitrobenzene [Beil. V-243, V₁-(129), V₂-(182)] with alc. KCN in s.t. at 200° (52); from 3-chlorophthalic acid (3:4820) or 4-chlorophthalic acid (3:4390) by cat. partial decarboxylation (53); from 3-chlorophthalic acid by mercuration and treatment with HCl (99) see indic. refs.]

Chemical behavior. [\overline{C} (as Na \overline{A}) on reduction in boilg. aq. soln. with Na/Hg yields (36) (54) benzoic acid (1:0715) (for study of reduction of \overline{C} with H₂ + Ni in aq. alk. at ord. temp. see (55)); \overline{C} on electrolytic reduction in alc./H₂SO₄ yields (56) m-chlorobenzyl

alcohol [Beil. VI-444], oil, b.p. 234° (56); note that \bar{C} with Ni/Al alloy (Raney nickel) in aq. alk. soln. at 90° gives (100% yield (106)) benzoic acid (1:0715), m.p. 121°.]

 \bar{C} behaves normally as a monobasic acid: e.g, \bar{C} on titration with standard dil. aq. alk. gives Neut. Eq. 156.5; ionization const. at 25° is 1.55 \times 10⁻⁴ (57), 1.53-1.59 \times 10⁻⁴ (58), 1.506 \times 10⁻⁴ (59) cf. (1) (60). — [For study of acid strength of \bar{C} in MeOH, EtOH, and various other alcs. see (61) (62) (63) (16) (64) (65) (17).]

Salts of inorganic bases. [NH₄ $\bar{\Lambda}$, m.p. 203–204° dec. (39), lfts. from acetone/pet. ether (39), powder from abs. alc. (66). — Hydroxylamine salt, ndls. from xylene, m.p. 144° (72), 145–146° dec. (39). — Na $\bar{\Lambda}$ (67), K $\bar{\Lambda}$ (67) both behave as liquid cryst. on fusion. — Ag $\bar{\Lambda}$, insol. aq. (68) (note that this salt (1 mole) with I₂ (2 equiv.) in dry C₆H₆ refluxed 15–18 hrs. yields (69) phenyl *m*-chlorobenzoate, m.p. 53°, + CO₂ + AgI). — Ca $\bar{\Lambda}$ 2.3H₂O, sol. at 12° in 82 6 pts. aq. (68) (35). — Ba $\bar{\Lambda}$ 2.4H₂O, eas. sol. aq. or alc. (for use in sepn. of \bar{C} from σ -chlorobenzoic acid (3.4150) and ρ -chlorobenzoic acid (3:4940) see (27)). — Cd $\bar{\Lambda}$ 2.2H₂O (71).]

Salts of organic bases. E.g., C with equiv. amt. benzylamine in boilg. EtOAc followed by evapn. of solvent yields (73) benzylammonium m-chlorobenzoate, m.p. 146.8-147.4° u.e., 149 2-149.8° cor. (73), Neut. Eq. 263.6 (note that the m.p. of this salt is only very slightly lower than that of the corresp. salt from o-chlorobenzoic acid (3:4150)). — C similarly treated with a-phenylethylamine yields (73) a-phenylethylammonium m-chlorobenzoate, m.p. 142.0-142.6° u.e., 144 7-145.3° cor. (73), Neut. Eq. 277.6 (note that the m.p. of this salt, although better separated from those of the isomeric acids than the preceding case, is very close to that for the corresp. deriv. of cinnamic acid (1:0735)).

 $\bar{\rm C}$ (1 mole) in alc. mixed with codeine (1 mole), m.p. 155°, in alc. htd. several minutes, solvent evaporated, and resulting syrup recrystallized from aq. yields (74) codeine m-chlorobenzoate, ${\rm C}_{18}{\rm H}_{21}{\rm O}_3{\rm N.\bar{C}}$, m.p. 96° on "Maquenne block"; note that this m.p. although very close to that (99°) of corresp. salt from m-bromobenzoic acid is widely different from the corresp. salts of o-chlorobenzoic acid (3:4150) and p-chlorobenzoic acid (3:4940), which are 134° and 162° respectively. — $\bar{\rm C}$ (1 mole) in alc. (or CHCl₃) with strychnine (1 mole) in alc. bouled for a few minutes then cooled yields (75) strychnine m-chlorobenzoate, ${\rm C}_{21}{\rm H}_{22}{\rm O}_2{\rm N}_2.\bar{\rm C}$, m.p. 185° u.c. on "Maquenne block"; note that this m.p. is somewhat higher than that (170°) of the corresp. salt from o-chlorobenzoic acid (3:4150) and widely different from that (251°) of the corresp. salt of p-chlorobenzoic acid (3:4940).

 \bar{C} with alcohols gives by conventional procedures the corresp esters; for details on methyl m-chlorobenzoate (3:6670) and on ethyl m-chlorobenzoate (3:6770) see these compds. — [For study of rate of esterification of \bar{C} with MeOII (76) or with cyclohexanol (77) see indic. refs.]

 \bar{C} with P_2O_5 in toluene boiled for 4 hrs. (78) or \bar{C} with oxalyl (di)chloride (3:5060) refluxed in C_6H_6 (79) cf. (80) yields m-chlorobenzoic acid anhydride, pl. from C_6H_6 or toluene, ndls. from lt. pet. or alc., m.p. 95.5° (78), 95° (79) (note that \bar{C} (2 moles) with oxalyl (di)bromide refluxed in C_6H_6 similarly gives good yields (80) of the above anhydride but $Na\bar{A}$ with oxalyl dibromide can also be used (80) to prepare m-chlorobenzoyl bromide, oil, b.p. 143-147° at 40 mm. (80)).

 \overline{C} with PCl₅ (31) (68) (3) or with SOCl₂ (81) (82) or with SOCl₂ + pyridine (83) gives (76% yield (31)) m-chlorobenzoyl chloride (3:6590), b.p. 225°.

[\tilde{C} with HN_3 in conc. H_2SO_4 in trichloroethylene (3:5170) soln. at 40° gives (75% yield (107)) m-chloroaniline.]

C fused with KOH, subsequently acidified, yields (84) m-hydroxybenzoic acid (1:0825).

C on nitration with boilg. fumg. HNO₃ for 10 min. (70) or with abs. HNO₃ at 0° or -30° (3) (24) (85) gives a mixt. of two isomeric nitro-m-chlorobenzoic acids; this mixt. consists mainly (92-93% (86) cf. (24)) of 3-chloro-6-nitrobenzoic acid [Beil. IX-401],

cryst. from HNO₃ (D=1.1) (24), ether, C₆H₆, or aq., m.p. 139° (85), 137–138° (70), 136° (3), 135–136° (24), accompanied by a little (7–8% (86)) cf. (24) 3-chloro-2-nitrobenzoic acid [Beil. IX-400], ndls. or tbls. from hot aq., m.p. 235° (70) (85), 233–234° (3) (for details on sepn. of these two isomers see (3) (70) (24) (85)). — Note that the other two possible nitro-m-chlorobenzoic acids are known but are not found in the product from nitration of \bar{C} ; they are 3-chloro-4-nitrobenzoic acid [Beil. IX-404], m.p. 185–186°, and 3-chloro-5-nitrobenzoic acid [Beil. IX-403, IX₁-(165)], m.p. 147°. — [Note also that no dinitro-3-chlorobenzoic acids have ever been reported.]

- Methyl m-chlorobenzoate: b.p. 231°, m.p. 21°. (See 3:6670.)
- Ethyl m-chlorobenzoate: b.p. 245°. (See 3:6770.)
- D p-Nitrobenzyl m-chlorobenzoate: m.p. 107 2° u.c. (87). [From C (as NaA) with p-nitrobenzyl bromide (m.p. 99°) in boilg. dil. alc. (87); note that m.p. of this ester is almost identical with that (106° (88)) of the corresp. ester of o-chlorobenzoic acid (3:4150).]
- D Phenacyl m-chlorobenzoate: m.p. 118° (89), 116.4° (21). [From C (as NaA) with phenacyl bromide (m.p. 50°) in boilg. alc. (98% yield (21)).]
- --- p-Chlorophenacyl m-chlorobenzoate: unreported.
- D p-Bromophenacyl m-chlorobenzoate: m.p. 117.2° (21), 116° (90). [From C (as NaA) with p-bromophenacyl bromide (m.p. 109°) in boilg. alc. (21).]
- --- p-Iodophenacyl m-chlorobenzoate: unreported.
- p-Phenylphenacyl m-chlorobenzoate: m.p. 154° u c. (91). [From C (as NaA) with p-phenylphenacyl bromide (m.p. 126°) in boilg. alc. (91); note that the m.p. of this deriv. is only slightly lower than that (160° u.c. (91)) of the corresp. ester of p-chlorobenzoic acid (3.4940); note also that, since this ester has almost the same m.p. as the original C, care must be taken to show that the supposed ester is insol. in aq. Na₂CO₃ (dif. and sepn. from C); note finally that the m.p. of a mixt. of C with this ester is depressed to 130-132° (91).]
- ⑤ S-(p-Chlorobenzyl)thiuronium m-chlorobenzoate: cryst. from dioxane, m.p. 157° cor. (93). [From NaĀ or KĀ in aq. with 1 equiv. of S-(p-chlorobenzyl)thiuronium chloride, m.p. 197° (10% in alc.) (93); note that the m.p. of this prod. is closely adjacent to that (m.p. 159° cor. (93)) of the corresp. salt of o-chlorobenzoic acid (3:4150), and is also almost identical with that of the original C.]
- S-(p-Bromobenzyl)thiuronium m-chlorobenzoate: m.p. 150° cor. (94). [From NaA or KA in aq. with 1 equiv. of S-(p-bromobenzyl)thiuronium bromide, m.p. 213°, in alc. (94).]
- m-Chlorobenzamide: cryst. from hot aq. or alc., m.p. 135° (100), 134.5° cor. (3), 134° u.c. (95), 132-133° (70). [From o-chlorobenzoyl chloride (3:6590) with conc. aq. NH₄OH (68) (70) or from Č by refluxing with AcOH + (NH₄)₂CO₃ (46-50% yield (100)); note that this amide gives on fusion with HgO a mercuric deriv., m.p. 245° u.c. (95).]
- ① m-Chlorobenzhydrazide: ndls. from aq. or alc., m.p. 158° (96), 157-158° (97). [From ethyl m-chlorobenzoate (3:6770) with hydrazine hydrate in abs. alc. on 8-hr. reflux. (yield: 97% (96), 87% (97)).] [For use of m-chlorobenzhydrazide as general reagt. for identification of aldehydes and ketones see (97).]
- -----N'-(m-Chlorobenzoyl)-N-phenylhydrazide: unreported.

- —— m-Chlorobenzanilide: cryst. from alc., m.p. 122-125° (98). [Prepn. reported but only by indirect means (98).] [Note that the isomeric benz-m-chloroanilide [Beil. XII-605] has m.p. 118°.]
- ---- m-Chlorobenzo-p-toluidide: unreported.
- m-Chlorobenzo- α -naphthalide: unreported.
- ---- m-Chlorobenzo-β-naphthalide: unreported.
- 3:4392 (1) Dippy, Williams, Lewis, J. Chem. Soc. 1935, 343-346. (2) Asinger, Lock, Monatsh. 62, 335 (1933). (3) Montagne, Rec. trav. chim. 19, 51-59 (1900). (4) Koopal, Rec. trav. chim. 34, 144 (1915). (5) Kailan, Antropp, Monatsh. 52, 297, 307-310 (1929). (6) Berger, Rec. trav. chim. 50, 379, 389, 395 (1931). (7) Gluud, Ger. 266,577, Oct. 27, 1913; Cent. 1913, II 1783. (8) Bornwater, Holleman, Rec. trav. chim. 31, 223-225, 230-239, 242-248 (1912). (9) Brooks, Hobbs, J. Am. Chem. Soc. 62, 2851 (1940). (10) Chapas, Compt. rend. 191, 257-259 (1930).
- (11) Sidgwick, Ewbank, J. Chem. Soc. 119, 981, 984, 988 (1921). (12) Sidgwick, J. Chem. Soc. 117, 403-406 (1920). (13) Hope, Riley, J. Chem. Soc. 123, 2479 (1923). (14) Andrews, Lynn, Johnson, J. Am. Chem. Soc. 48, 1282 (1926). (15) Kellas, Z. physik. Chem. 24, 222, 230, 241, 245-246, 249, 251 (1897). (16) Wooten, Hammett, J. Am. Chem. Soc. 57, 2291 (1933). (17) Kuhn, Wassermann, Helv. Chim. Acta 11, 34 (1928). (18) Gruebe, Ann. 138, 200-202 (1866). (19) Johnston, Jones, J. Phys. Chem. 32, 599-601 (1928). (20) Smith, J. Chem. Soc. 1934, 213-218.
- (21) Kelly, Howard, J. Am. Chem. Soc. 54, 4384 (1932).
 (22) Griess, Ann. 117, 13-16 (1861).
 (23) Kolbe, Lautemann, Ann. 115, 194 (1860).
 (24) Holleman, de Bruyn, Rec. trav chim. 19, 197-203 (1900).
 (25) Flaschner, Rankin, Monatsh. 31, 43 (1910).
 (26) Lettré, Barnbeck, Lege, Ber. 69, 1153-1154 (1936).
 (27) Hope, Riley, J. Chem. Soc. 121, 2518-2527 (1922).
 (28) Lettré, Barnbeck, Fuhst, Hardt, Ber. 70, 1411-1412, 1415-1416 (1937).
 (29) Lettré, Lehmann, Ber. 71, 416 (1938).
 (30) Lettré, Ber. 73, 386-390 (1940); C.A. 34, 5831 (1940).
- (31) Novello, Miriam, Sherwin, J. Baol. Chem. 67, 557-558 (1926). (32) Sabalitschka, Dietrich, Desinfektion 11, 67-71, 94-104 (1926), Cent. 1927, I 2670; C.A. 20, 3712 (1926). (33) Goodyear Tire and Rubber Co., French 761,220, March 14, 1934; Cent. 1934, II 854. (34) Graebe, Schultzen, Ann. 142, 346-347 (1867). (35) Bellstein, Schlun, Ann. 133, 243-252 (1865). (36) Otto, Ann. 122, 142, 149-150, 157-158 (1862). (37) Field, Ann. 65, 55 (1848). (38) Stenhouse, Ann. 55, 10-11 (1845). (39) Gluud, Kempf, J. Chem. Soc. 103, 1530-1533 (1913). (40) Lössner, J. prakt. Chem. (2) 13, 427-428 (1876).
- (41) Hübner, Weiss, Ber. 6, 175 (1873). (42) Lossen, Ger. 146,174, Nov. 6, 1903; Cent. 1903, II 1224. (43) Wroblevsky, Ann. 168, 200 (1873). (44) Schrader, Ges. Abhandl. Kenntnis Kohle 4, 310-341 (1920); Cent. 1921, I 537; C.A. 15, 2850-2851 (1921). (45) Bellavita, Gazz. chim. tal. 65, 639, 641 (1935). (46) Heller (to Chem. Fabrik von Heyden), Ger. 639,578, Dec. 8, 1936; Cent. 1937, I 2025; C.A. 31, 3943 (1937). (47) Wynne, J Chem. Soc. 61, 1048-1049 (1892). (48) Korczynski, Faudrich, Compt. rend. 183, 421-423 (1926). (49) Sandmeyer, Ber. 17, 1634-1635 (1884). (50) Griess, Ann. 117, 13-16 (1861).
- (51) Gilman, Langham, Moore, J. Am. Chem. Soc. 62, 2330 (1949). (52) von Richter, Ber. 4, 463 (1871); 8, 1419 (1875). (53) Jaeger (to Selden Co), U.S. 1,953,231 and 1,953,232, April 3, 1934; Cent. 1934, II 669, 1688. (54) Reichenbach, Beilstein, Ann. 132, 311, 321 (1864). (55) Keller, Ber. 54, 2257-2259 (1921). (56) Mettler, Ber. 38, 1749-1750 (1905). (57) Ostwald, Z. physik. Chem. 3, 255 (1889). (58) Smith, Jones, Am. Chem. J. 50, 28 (1913). (59) Saxton, Meier, J. Am. Chem. Soc. 56, 1918-1921 (1934). (60) Osol, Kilpatrick, J. Am. Chem. Soc. 55, 4431-4440 (1933).
- (61) Dippy, J. Chem. Soc. 1941, 550-552. (62) Elliott, Kilpatrick, J. Phys. Chem. 45, 454-465, 466-471, 472-485, 485-492 (1941). (63) Kilpatrick, Mears, J. Am. Chem. Soc. 62, 3047-3051, 3051-3054 (1940). (64) Goodhue, Hixon, J. Am. Chem. Soc. 56, 1329-1333 (1934); 57, 1688-1691 (1935). (65) Bright, Briscoe, J. Phys. Chem. 37, 787-796 (1933). (66) McMaster, Godlove, J. Am. Chem. Soc. 37, 2183-2184 (1915). (67) Vorländer, Huth, Ber. 43, 3129 (1910). (68) Limpricht, von Uslar, Ann. 102, 260-263 (1857). (69) Birckenbach, Meisenheimer, Ber. 69, 723-729 (1936). (70) Hubner, Ann. 222, 91-99 (1883).
- (71) Pfeiffer, Nakatsuka, J. prakt. Chem. (2) 136, 247 (1933). (72) Oesper, Ballard, J. Am. Chem. Soc. 47, 2426 (1925). (73) Buehler, Carson, Edds, J. Am. Chem. Soc. 57, 2181-2182 (1935). (74) Poe, Strong, J. Am. Chem. Soc. 57, 380 (1935). (75) Poe, Suchy, J. Am. Chem. Soc. 56, 1640-1641 (1934). (76) Hartman, Borders, J. Am. Chem. Soc. 59, 2107-2112 (1937). (88) Hartman, Storms, Gassmann, J. Am. Chem. Soc. 61, 2167-2169 (1939). (78) Rule, Patterson, J. Chem. Soc. 125, 2161 (1924). (79) Adams, Wirth, French, J. Am. Chem. Soc. 49, 427 (1918). (80) Adams, Ulich, J. Am. Chem. Soc. 42, 606-607, 609 (1920).

(81) Frankland, Carter, Adams, J. Chem. Soc. 101, 2476-2477 (1912). (82) Bergmann, Bondi, Ber. 64, 1477 (1931). (83) Norris, Bearse, J. Am. Chem. Soc. 62, 953 (1940). (84) Dembey, (85) Holleman, de Bruyn, Rec. trav. chrm. 20, 212-214 (1901). Ann. 148, 222-223 (1868) (86) Holleman, Rec. trav. chim. 29, 394-402 (1910). (87) Kelly, Segura, J. Am. Chem. Soc. 56, 2497 (1934). (88) Reid, J. Am. Chem. Soc. 39, 132 (1917). (89) Chen, Trans. Science Soc. China 7, 73-80 (1931). (90) Chen, Shih, Trans. Science Soc. China 7, 81-87 (1931).

(91) Kelly, Morisani, J. Am. Chem. Soc. 58, 1502-1503 (1936). (92) Donleavy, J. Am. Chem. (93) Dewey, Sperty, J. Am. Chem. Soc. 61, 3251-3252 (1939). Soc. 58, 1004-1005 (1936) (94) Dewey, Shasky, J. Am. Chem. Soc. 63, 3526-3527 (1941). (95) Williams, Rainey, Leopold, J. Am. Chem. Soc. 64, 1738-1739 (1942). (96) Curtius, Foerster, J. prakt Chem. (2) 64, 326-327 (1901). (97) Sah, Wu, Sci Repts. Natl. Tsing-Hua Univ. A-3, 443-449 (1936); Cent. 1936, II 2130. (98) Hantzsch, Ber. 24, 58 (1891). (99) Whitmore, Culhane, J. Am Chem. Soc. 51, 604 (1929). (100) Kao, Ma, Scr. Repts Natl Tsing-Hua Univ. A-1, 21-22 (1931).

(101) Bryd, Roczniki Chem. 7, 436-445 (1927), CA. 22, 2372 (1928). (102) Smith, White, J. Phys. Chem. 33, 1958, 1970 (1929). (103) Quick, Cooper, J. Biol. Chem. 96, 83-101 (1932). (104) Holleman, Vermeulen, de Mooy, Rec. trav chim. 33, 29 30 (1914). (105) Herz, Wittek, Monatsh. 74, 277 (1943). (106) Schwenk, Papa, Whitman, Ginsberg, J. Org. Chem. 9, 1-8 (1944).

(107) Briggs, Lyttleton, J. Chem. Soc. 1943, 422.

3:4395 2-CHLORO-3-HYDROXYBENZOIC ACID

COOH C7H5O3Cl Beil. X - 142 \mathbf{X}_{1} —

M.P. 157.5-158.5° (1) 156.5-157.5° (1) 156-157° (2) (5)156° (3) 155.0-155.5° u.c. (10)

Colorless lfts. from aq. or C_6H_6 . [Ioniz. const. at $25^\circ = 1.40 \times 10^{-3}$ (5).]

For prepn. of C from 2-chloro-3-hydroxybenzaldehyde (3:4085) with 5-6 pts. 50% KOH at 60-70° (Cannizzaro reactn.) (96% yield) see (3); from ethyl 2-chloro-3-hydroxybenzoate (see below) by hydrolysis with 35% KOH see (1) (2) cf. (4); for formn. from m-hydroxybenzoic acid (1:0825) with Cl₂ in McOH (6) (44% yield (10)) or AcOH (1) (together with some of the isomeric 6-chloro-3-hydroxybenzoic acid (3:4720)) see indic. refs.; for prepn. of C from 2-amino-3-hydroxybenzoic acid (1) via diazotization and use of Cu₂Cl₂ reactn see (1).]

Salts: AgA, cryst. ppt. (2).

C in aq. soln. gives with FeCl₃ a violet-red color.

[C with formalin (1:0145) + conc. HCl + HCl gas at room temp, gives (87% yield (10)) 7-chloro-6-hydroxyphthalide, m.p. 290° cor. (10)]

- Methyl 2-chloro-3-hydroxybenzoate: pr. with 1 H₂O from dil. alc., m.p. 70-71° (2); anhydrous form, m.p. 62-65° (2). [From \bar{C} in MeOH with H_2SO_4 (2)] — [This ester with MeI + MeOH/KOH in s.t. at 130° for several hours gives methyl 2-chloro-3-methoxybenzoate, anhydrous ndls. from dil. alc., m.p. 41-42° (2).]
- Ethyl 2-chloro-3-hydroxybenzoate: white ndls. with 1 H₂O from dil. alc., m.p. 58° (2); above m.p. loses aq. giving viscous oil (2). [From ethyl m-hydroxybenzoate (1:1471) with SO₂Cl₂ (together with the isomeric ethyl 6-chloro-3-hydroxybenzoate (2) (4)).] — [This anhydrous ester with AcCl yields ethyl 2-chloro-3-acetoxybenzoate, ndls. from dil. alc., m.p. 48-49° (2).]
- 2-Chloro-3-methoxybenzoic acid: colorless ndls. from aq., m.p. 161.5° (7), 160° (8) (9). [Prepd. indirectly from 2-chloro-3-methoxybenzaldehyde by oxidn, with KMnO₄ (7) (8).]

—— 2-Chloro-3-acetoxybenzoic acid: cryst. from aq. or C_6H_6 , m.p. 152.5-153° u.c. (10). [From $\tilde{C} + Ac_2O + K_2CO_3$ (10).]

3:4395 (1) Beyer, Rec. trav. chim. 40, 626-628 (1921). (2) Mazzara, Gazz. chim. ital. 29, I 380-383 (1899). (3) Lock, Monatsh. 55, 310-311 (1930). (4) Mazzara, Bertozzi, Gazz. chim. ital. 30, II 87-88 (1900). (5) Coppadoro, Gazz. chim. ital. 32, I 546 (1902). (6) Plazek, Roczniki Chem. 10, 761-776 (1930); Cent. 1931, I 1428, C.A. 25, 1504 (1931). (7) Hodgson, Rosenberg, J. Chem. Soc. 1930, 17. (8) Hodgson, Beard, J. Chem. Soc. 1926, 150. (9) Gibson, J. Chem. Soc. 1926, 1428. (10) Buehler, Harris, Shacklett, Block, J. Am. Chem. Soc. 198, 577 (1946).

3:4400 3,5-DICHLORO-4-HYDROXYBENZ-ALDEHYDE

Colorless odorless ndls. from dil. alc. or from CHCl₃; fairly eas. sol. alc., ether, AcOH; more dif. sol. C₆H₆, lgr., CHCl₃.

[For prepn. of \tilde{C} from p-hydroxybenzaldehyde (1:0060) in 5 pts. AcOH at 100° (2) (4) or in CHCl₃ with cooling (1) with Cl₂ see indic. refs.; from corresp. methyl ether (3,5-dichloro-4-methoxybenzaldehyde) with boilg cone HI see (3)

 \bar{C} in N KOH with H_2O_2 yields (4) 2,6-dichlorohydroguinone (3:4600)

[The methyl ether of \bar{C} (see above) has been obtd indirectly (3) from p-methoxybenzaldehyde (p-anisaldehyde) (1:0240) by chlorination with large excess (9 moles) SO₂Cl₂; bright red cryst. from alc., m.p. 61.5° (3); on oxidin. with CrO₃ this prod. gives (80% yield (3)) 3,5-dichloro-p-methoxybenzoic acid [Beil. X-177], m.p. 202.0-202.5° (3)]

- ③ 3,5-Dichloro-4-hydroxybenzaldoxime: colorless ndls. from dil. alc., m.p. 185° (2).
 [From C̄ in moderately conc. NaOH (3 moles) with NH₂OH.HCl (1½ moles), subsequently acidified with AcOH (2)] [This oxime on boilg, with Ac₂O for 2 hrs. yields (2) 3,5-dichloro-4-acetoxybenzonitrile, colorless cryst. from dil. alc., m.p. 93° (2).]
- ⊕ 3,5-Dichloro-4-hydroxybenzaldehyde semicarbazone: greenish yel. ndls. from AcOH, m.p. 236-237° cor. dec (1). [From C in hot AcOH (50 pts.) by addn. of conc. aq. soln. of semicarbazide hydrochloride, followed by ½ hr. htg. (1).]

3:4400 (1) Biltz, Ber. **37**, 4033-4034 (1904). (2) von Auwers, Reis, Ber. **29**, 2356-2358 (1896). (3) Durrans, J. Chem. Soc. **123**, 1426 (1923). (4) Dakin, Am. Chem. J. **42**, 490-491 (1909).

3:4410 cis-1,2,3,4,5,6-HEXACHLORO-CYCLOHEXANE

(a-Benzenehexachloride)

[See also β -benzenehexachloride (3:4990).]

Nine stereoisomeric configurations of benzenehexachloride are possible (cf. (4)) and four are known; \bar{C} (contrary to earlier opinion (5)) is now thought (but not unequivocally proved) to have the crs configuration; the β -isomer has been shown to have the trans configuration; the configurations of the γ -isomer, m.p. 112-113° (2), and the δ -isomer, m.p. 129-132° (2), are unknown.

 \bar{C} cryst. from 80% AcOH (3) or from alc. — \bar{C} is volatile with steam (dif. and separation from β -isomer). — \bar{C} is insol. aq. but sol. in 22.8 pts. CHCl₃ at 15.25°; in 15.4 pts. C₆H₆ at 18.25° (5). — \bar{C} forms with the β -isomer a eutectic (m.p. 155.5°) contg. 79.7% \bar{C} (2).

[For manuf. of ordinary benzenehexachloride (mixt. of stereoisomers) from C_6H_6 (1:7400) + Cl_2 in pres. of light (6) (7) (8), X-radiation (9), or conc. H_2SO_4 (10) see indic. refs.; for study of prepn. of \bar{C} (together with other stereoisomers) from C_6H_6 with Cl_2 in pres. of 1% aq. NaOH see (3) (2) (28), in gas phase (11) (12), in pres. of ethylene in the dark (13), in pres. of NCl₃ in the dark (14) or in light (15), in pres. of light (16) (17) (18) (19) (20).] [For use of \bar{C} as insecticide see (27); note, however, that insecticidal props. are thought to be due to γ -isomer (29).]

C on htg above its m.p. loses HCl and yields (3) (21) 1,2,4-trichlorobenzene (3:6420).

C on htg. with aq. in s.t. at 200° (19), on boilg. with MeOH/KOH (2), EtOH/KOH (2) (3) (19) (20) (22), alc. KCN (19), or pyridine (2), or on htg. with quinoline at 105–110° (2) yields mainly 1,2,4-trichlorobenzene (3:6420) together with other prods.; e.g., C on boilg. with excess 10% alc. KOH for ½ hr. (2) or C boiled with 10 pts. pyridine for 1 hr. (2) gives (yield: 75–86% (2)) 1,2,4-trichlorobenzene (3:6420).

C reacts very vigorously with boilg. aniline (19), but the prods. have not been detd.

[\bar{C} stood in s.t. with 3 pts. liq. Cl₂ for 11 days yields (23) α -nonachlorocyclohexane, cryst. from alc., m.p. 95-96° (23) (24).]

C in alc. boiled with Zn dust yields (25) benzene (1:7400).

Č is very inert to most other reagents: e.g., Č can be recrystallized unchanged from fumg. HNO₃ (3), is unattacked by fumg. H₂SO₄ (19), is unattacked by C₁O₃ (3), is only slightly affected by aq. KMnO₄ even on boilg. (3), and is unaffected by conc. aq. NH₄OH (3), boilg. alc. AgNO₃ (3), or AgOAc (26).

3:4410 (1) van de Vloed, Bull. soc. chim. Belg. 48, 255-256 (1938). (2) van der Linden, Ber. 45, 231-247 (1912). (3) Matthews, J. Chem. Soc. 59, 165-172 (1891). (4) Williams, Fogelberg, J. Am. Chem. Soc. 53, 2103 (1931). (5) Friedel, Bull. soc. chim. (3) 5, 130-138 (1891). (6) Hardie (to Imperial Chem. Ind., Ltd.), U.S. 2,218,148, Oct. 15, 1940; C.A. 35, 1071 (1941). (7) Imperial Chem. Ind., Ltd., Grant, Brit. 504,569, April 26, 1939; Cent. 1939, II 1775; C.A. 33, 7822 (1939). (8) Stephenson, Curtis, Brit. 447,058, May 7, 1936; Cent. 1936, II 3360, C.A. 30, 6766 (1936). (9) Loiseau, French, 565,356, Jan. 25, 1924; Cent. 1925, II 1227. (10) Battegay, French 641,102, July 28, 1928; Cent. 1928, II 1718.

(11) Lane, Noyes, J. Am. Chem. Soc. 54, 161-169 (1932). (12) Smith, Noyes, Hart, J. Am. Chem. Soc. 55, 4444-4459 (1933). (13) Stewart, Hanson, J. Am. Chem. Soc. 53, 1121-1128 (1931). (14) Coleman, Noyes, J. Am. Chem. Soc. 43, 2216 (1921). (15) Hentschel, Ber. 36, 1436 (1897). (16) Faraday, Ann. chim. (2) 30, 274 (1825). (17) Mitscherlich, Ann. Physik 35, 370-374 (1835). (18) Leeds, Everhart, J. Am. Chem. Soc. 2, 206 (1880). (19) Meunier, Ann. chim. (6) 10, 223-269 (1887). (20) Lesimple, Ann. 137, 122-124 (1866).

(21) Tei, Komatsu, Mem. Coll. Sci. Kyoto Imp. Univ. 10-A, 325-330 (1927); Cent. 1928, I 2370; C.A. 22, 1086 (1928). (22) Jungfleisch, Ann. chim. (4) 15, 270 (1868). (23) van der Linden, Rec. trav. chim. 57, 218-221 (1933). (24) Willgerott, J. prakt. Chem. (2) 35, 416 (1887). (25) Zinin, Zeit. für Chemie 1871, 284. (26) Griffin, Nelson, J. Am. Chem. Soc. 37, 1554 (1915). (27) Bender (to Great Western Electrochem. Co.), U.S. 2,010,841, Aug. 13, 1935; Cent. 1936, I 1112. (28) Klingstedt, Wiese, Rüdback, Acta Acad. Aboensis Math. et Phys. 4, No. 2, 1-36 (1927). (29) Taylor, Nature 155, 393-394 (1945).

3:4420 4,8-DICHLORONAPHTHOL-2

M.P. 158-159° (1).

Colorless ndls. from alc. — sol. in NaOH.

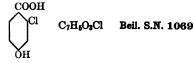
[For prepn. from 4,8-dichloronaphthylamine-2 via diazo reaction see (1).]

[For use in prepn. of azo dyestuffs see (2).]

Č on suitable methylation yields methyl ether, viz., methyl 2,4-dichloro-β-naphthyl ether, colorless ndls., m.p. 93° (1).

3:4420 (1) Friedlander, Karamessinis, Schenk, Ber. 55, 48-49 (1922). (2) Herzberg, Wunderlich (to I.G.), Ger. 459,989, May 18, 1928; Cent. 1928, II 395.

3:4430 2-CHLORO-4-HYDROXYBENZOIC ACID



M.P. 159° (1)

Colorless ndls. from aq.

[For prepn. of \tilde{C} from 2-chloro-4-methoxybenzoic acid (see below) by cleavage with conc. HI (D=1.7) see [1].]

[The corresp methyl ether, viz., 2-chloro-4-methoxybenzoic acid (2-chloro-p-anisic acid), mp 208° (2) (3), has been obtd. indirectly from 2-chloro-4-methoxybenzaldehyde [Beil VIII-81] (2) or from 2-chloro-4-methoxytoluene [Beil. VI-402] (3) by KMnO₄ oxidn. (2) (3) |

3:4430 (1) Hodgson, Jenkinson, J. Chem. Soc. 1927, 1742. (2) Tiemann, Ber. 24, 712 (1891). (3) Ullmann, Wagner, Ann. 355, 368 (1907).

3:4435 3-CHLORO-2-METHYLBENZOIC ACID

COOH CH₃ C₈H₇O₂Cl Beil. IX - 467 IX₁—

M.P. 159° (1)

156° (2) 154° (3)

Colorless ndls. from alc.; eas. sol alc.

[For prepn. of \bar{C} from 3-chloro-2-methylbenzonitrile, m.p. 19° (1), by refluxing with 20% aq. KOH for 5 hrs. (98% yield) see (1); from 3-chloro-1,2-dimethylbenzone (3:8645) on oxidn. with boilg. dil. HNO₃ (D=1.20) see (3); from 2-methylbenzoic acid (o-toluic acid) (1:0690) in CHCl₃ in pres of Fe with Cl₂ (4) or in AcOH with Cl₂ (2) see indic. refs.] Salts: Ca \bar{A}_2 .2H₂O, spar. sol. hot aq. (3).

C on oxidn. with KMnO₄ gives (3) 3-chlorophthalic acid (3:4820)

3:4435 (1) Noelting, Ber. 37, 1025-1026 (1904). (2) Claus, Bayer, Ann. 274, 310-311 (1893). (3) Krüger, Ber. 18, 1758 (1885). (4) Claus, Stapelberg, Ann. 274, 311 (1893).

3:4444 3,5,6-TRICHLORO-2-HYDROXYHYDROQUINONE

M.P. 160° (1)

Ndls. from C_6H_6 . — \tilde{C} cryst. from C_6H_6 or AcOH in solvated form. \tilde{C} is eas. sol. alc., ether; spar. sol. pet. ether.

[For prepn. of \bar{C} from 3,5,6-trichloro-2-hydroxybenzoquinone-1,4 [Beil. VIII-238] by reduction with aq. SO_2 see (1).]

 \bar{C} dis. in aq. yielding colorless soln. which on htg. develops violet color; \bar{C} with aq. alk. gives deep green color changing to brown (1).

- ---- 3,5,6-Trichloro-2-hydroxyhydroquinone trimethyl ether: unreported.
- ---- 3,5,6-Trichloro-2-hydroxyhydroquinone triethyl ether: unreported.
- 3,5,6-Trichloro-2-hydroxyhydroquinone triacetate: ndls from $\lg r./C_6H_6$, m.p. 171° (1). [From \bar{C} with $Ac_2O + NaOAc$ on htg. (1).]

3:4444 (1) Zincke, Schaum, Ber. 27, 557-558 (1894).

M.P. 160°? (1) B.P. 268-269° at 734 mm. (1)

White extraordinarily pliable (2) crystals, difficult to filter with suction (because of their high vapor pressure (3)) and best purified by fractional distn (3) or slow sublimation in vac (2). — Very sol. in alc., ether, or lgr. (1).

[For prepn. of $\bar{\mathbf{C}}$ (100% yield (3)) from 1,1,1,2,2,3,3-heptachloropropane (3:0200) by conversion with MeOH/KOH by loss of HCl to 1,1,1,2,3,3-hexachloropropenc-2 (3:6370) and subsequent treatment with Cl₂ below 50° in sunlight see (3) (2) [For formn from 1,2,3-trichloropropane (3:5840) or from isobutyl chloride (3:7135) with excess ICl₃ at 200° see (1).]

Č on htg. at 300° (1) or on htg. with AlCl₃ (2) splits quantitatively (2) into CCl₄ (3:5100) + tetrachloroethylene (3:5460).

[For fluorination of \bar{C} see (3) (4); for use of \bar{C} + Zn for production of smoke see (5) (6).]

3:4450 (1) Krafft, Merz, Ber. 8, 1296-1302 (1875). (2) Prins, J. prakt. Chem. (2) 89, 416-417 (1914). (3) Henne, Ladd, J. Am. Chem. Soc. 60, 2494 (1938). (4) Henne (to Frigidaire Corp), Brit. 378,324, Aug. 11, 1932; French 730,370, Aug. 11, 1932, Cent. 1933, II 1583, C. A. 27, 3947 (1933). (5) Métivier, Chimie & industrie, Spec. No. 179 (March. 1932); C.A. 26, 3628 (1932). (6) Métivier, French. 649,853, Dec. 28, 1928, Cent. 1931, I 3424.

$C_6H_2O_2Cl_2$ 3:4470 2,5-DICHLOROBENZOQUINONE-1,4 Beil. VII - 632 (p-Dichlorobenzoquinone) VII₁-(346) M.P. 161-162° (1) 160.4-161.4° (2) 161° u.c. (3) 161° (4) (17) (28) 159° (5) (10)158.5° (6) 158-161° (7)

[See also 2,5-dichlorohydroquinone (3:4690).]

Dark yellow cryst. from alc. or C₆H₆; insol. aq.; alm. insol. cold dil. alc., eas. sol. boilg. abs. alc.; fairly eas. sol. other or CHCl₃. — Volatile with steam; sublimes in vacuum.

[For prepn. of C from 2,5-dichlorohydroquinone (3:4690) by oxidn. with K₂Cr₂O₇ or

 $Na_2Cr_2O_7$ + dil. H_2SO_4 (2) (4) (6) (8) (9) or with conc HNO₃ at ord. temp. (5) see indic. refs.; from 2,5-dichlorohydroquinone dimethyl ether with fumg. HNO₃ in the cold see (1); from 2-chlorobenzoquinone-1,4 (3:1100) via conversion with HCl to 2,5-dichlorohydroquinone (3:4690) and subsequent oxidn. of latter see (5) (17); from 2,5-dichloroaniline [Beil. XII-625, XII₁-(311)] with CrO_3 (5) or from 2,5-dichloro-p-phenylenediamine [Beil. XIII-118] with CrO_3 (10) or $K_2Cr_2O_7$ + dil. H_2SO_4 (28) see indic. refs.; for formn. of \bar{C} from benzoquinone-1,4 (1:9025) in CCl_4 with ICl on gentle warmg. see (3); from benzene with ClO_2 see (11); from copper salt of quinic acid [Beil. X-535, X_1 -(270)] by oxidn. with MnO_2 + NaCl + H_2SO_4 see (12)]

[For study of oxidn -reductin potential of system $\bar{C}+2.5$ -dichlorohydroquinone (3:4690) see (6) (13) (14).] — [For use as vulcanization accelerator see (15); for use in prepn. of eurhodol dyes see (16); for study of bactericidal actn. see (18).]

 $[\bar{C} \text{ is sol. in conc. } H_2SO_4 \text{ with greenish-yellow color, in dimethylaniline with deep blue color (19); <math>\bar{C} \text{ is sol. in dil. } aq. \text{ alk. } \text{with brown color and decomposition (11) (12).}]$

[\bar{C} with KCN in 85% MeOH gives (20) a ruby-red soln. with red fluorescence; \bar{C} with diphenylketene in ether + pet. eth. gives a compound, m.p. 180-192° dec. (21).]

Č in aq reduces with SO₂ (12) to 2,5-dichlorohydroquinone (3:4690) q.v. (note that the intermediate quinhydrone, dark violet pr. or greenish-black ndls. with 2 H₂O (12), crystal water lost over H₂SO₄ or on warming giving yellow anhydrous form, m.p. 140−145° (22), is known); however, Č in dil aq. NaOH (under N₂) treated with SO₂ is in part reduced to 2,5-dichlorohydroquinone (3:4690) and in part sulfonated to mono- and disulfonic acids of Č (23).

[\bar{C} in CHCl₃ at low temps, does not react with Cl₂; at ord, temps, however, yields tetrachlorobenzoquinone-1,4 (chloranil) (3:4978) (24). — \bar{C} in AcOH at 70–80° with 2 moles Br₂ gives (alm quant. yield (4)) (25) (9) 2,5-dichloro-3,6-dibromobenzoquinone-1,4 [Beil. VII-642], golden-brown tbls. from C₆H₆, m p. 292° (4).]

[Č with conc. HCl gives on boilg. (5) 2,3,5-trichlorobenzoquinone-1,4 (3:4672), but some tetrachlorobenzoquinone (chloranil) (3:4978) is also formed.]

 \bar{C} (1 pt.) in $\Lambda c_2 O$ (5 pts.) + AcOH (5 pts.) loses color on boilg. with Zn dust (1) and yields (by reductive acylation) 2,5-dichlorohydroquinone diacetate, cryst. from alc, m.p. 141° (1).

Č (1 pt) in hot AcOH (40 pts.) + conc. HCl (0 4-0.5 pt) treated with aniline (0.4-0.5 pt.) yields mainly (26) 2,5-dichloro-3-anilinobenzoquinone-1,4 [Beil. XIV-137], blue lfts., m.p. 180° (26), and 2,5-dichlorohydroquinone (3:4690) accompanied by small amts. of 2,5-dichloro-3,6-dianilinobenzoquinone-1,4 (see below); Č htd. with excess aniline yields (26) 2,5-dichloro-3,6-dianilinobenzoquinone-1,4 [Beil. XIV-144], yel.-br. tbls. from C₆H₆, m.p. 290° (26), and 2,5-dichlorohydroquinone (3:4690)

 $|\bar{C}|$ in C_6H_6 + alc. warmed with slightly more than 1 mole $NH_2OH.HCl$ yields (8) (27) 2,5-dichlorobenzoquinone-1,4 monoxime (2,5-dichloro-4-nitrosophenol) [Beil. VII-633], pale yel. cryst from C_6H_6 , m.p. 155–160° (8) (purified by conv. with Ac_2O + NaOAc to its acetate, yel. pr from C_6H_6 , m.p. 149° (8), and subsequent hydrolysis with NaOH) — \bar{C} in alc. with excess $NH_2OH.HCl$ yields (27) 2,5-dichlorobenzoquinone-1,4 dioxime, grayish yel. cryst. from C_6H_6 , m.p. not stated (27).]

3:4470 (1) Kohn, Gurewitsch, Monatsh. 56, 135–136 (1930). (2) Hammick, Hampson, Jenkins, J. Chem. Soc. 1938, 1264. (3) Jackson, Bolton, J. Am. Chem. Soc. 36, 1484 (1914). (4) Ling, J. Chem. Soc. 61, 558–559, 563–566, 572–576 (1892). (5) Levy, Schultz, Ann. 210, 150–153 (1881). (6) Conant, Fieser, J. Am. Chem. Soc. 45, 2205–2206 (1923). (7) Pfeiffer, Ann. 412, 292–293 (1916). (8) Kehrmann, Grab, Ann. 303, 12–14 (1898). (9) Hantzsch, Schniter, Ber. 20, 2279–2282 (1887). (10) Mohlau, Ber. 19, 2010 (1886).

(11) Carius, Ann. 143, 316 (1867). (12) Stadeler, Ann. 69, 309-312 (1849). (13) Hunter, Kvalnes, J. Am. Chem. Soc. 54, 2874-2875, 2878 (1932). (14) Kvalnes, J. Am. Chem. Soc. 56,

667-670 (1934). (15) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; Cent. 1933, I 3133. (16) Herzberg, Hoppe (to A.G.F.A.) Ger. 368,171, Feb. 3, 1923; Cent. 1923, II 1187. (17) Den Hollander, Rec. trav. chim. 39, 482 (1920). (18) Morgan, Cooper, J. Soc. Chem. Ind. 43-T, 352-354 (1924). (19) Pfeiffer, Böttler, Ber. 51, 1828-1829 (1918). (20) Richter, Ber. 44, 3472 (1911).

(21) Staudinger, Bereza, Ann. 380, 261-262 (1911). (22) Ling, Baker, J. Chem. Soc. 63, 1319-1321 (1893). (23) Dodgson, J. Chem. Soc. 1930, 2498-2502. (24) Oliveri-Tortorici, Gazz. chim. ital. 27, II 585-586 (1897). (25) Levy, Ber. 18, 2367-2368 (1885). (26) Niemeyer, Ann. 238, 329-334 (1885). (27) Kehrmann, Ber. 21, 3319 (1888). (28) Nason, J. Am. Chem. Soc. 40, 1605 (1918).

[See also 2-chloroanthraquinone (3:4922).]

Yellow ndls. from C_6H_6 , toluene, or alc.; eas. sol. C_6H_6 , toluene, AcOH, nitrobenzene, or AmOH on htg.; spar. sol. alc. or lgr.

[For f.p /compn. data and diagram of system $\tilde{C}+2$ -chloroanthraquinone (3:4922) (eutectic, m.p. 143.9–144.2°, contg about 25% \tilde{C}) see (14).]

[For use in coloring oils, fats, and waxes see (19); \tilde{C} is very widely used as intermed. in prepn. of many dyestuffs, but no general summary can be given here although selected examples occur in the following text.]

[For prepn. of \bar{C} from potassium salt of anthraquinonesulfonic acid-1 [Beil. XI-335, XI₁-(81)] by htg. with strong HCl + NaClO₃ (yields: 97–98% (3), 95% (4)) at 100° (3) (4) (10) (6) (8) (for use of this method in detn. of mixt. of anthraquinone- α - and β -sulfonic acids or their salts by f.p./compn. curve of resultant mixt. of \bar{C} + 2-chloroanthraquinone (3:4922) see (4)) or by actn. of Cl₂ at 100° (20) see indic. refs.; from anthraquinonesulfonic acid-1 (9) or its Na salt (15) in dil. HCl on exposure to light see indic. refs.; from anthraquinonecarboxylic acid-1 with HCl + KClO₃ in s.t. at 200° for 12 hrs. see (22); from Na salt of anthracenesulfonic acid-1 [Beil. XI-194, XI₁-(44)] with HCl + NaClO₃ at 100° see (21); from 1-chloroanthraquinonesulfonic acid-5 by electrolysis of alk. soln. see (23); from K salt of anthraquinonesulfonic acid-1 (see above) (24) or from anthraquinonesulfonyl chloride-1 (5) by htg. in s.t. with SOCl₂, or from 1-anthraquinonylarsinic acid by 10 hrs. reflux with SOCl₂ (67), see indic. refs.]

[For prepn. of \bar{C} from 2-benzoyl-3- (or 6)-chlorobenzoic acid by ring closure with conc. H_2SO_4 see (7) (25).]

[For prepn. of C from 1-aminoanthraquinone (see below) via diazotization and use of Cu₂Cl₂ reactn. see (26); from 1-nitroanthraquinone [Beil. VII-791, VII₁-(415)] with Cl₂ in trichlorobenzene soln. at 160-165° see (27); from 1-hydroxyanthraquinone [Beil. VIII-338, VIII₂-(650)] with PCl₅ in boilg. nitrobenzene see (28).]

[\bar{C} on htg. with conc. H₂SO₄ at 200-205° for 9 hrs. rearr. (29) to 2-chloroanthraquinone (3:4922).]

[C on reductn. with Zn dust + conc. aq. NH₄OH under reflux yields (30) 1-chloroanthracene [Beil. V₁-(324)], colorless lfts. from AcOH, m.p. 81-82° (2), 79° (30). — C on reductn. with hydrazine hydrate in MeOH/KOH at 10 atm. and 135° for 1½ hrs. in pres. of Pd/CaCO₃ followed by access of air to the prod. gives (87% yield (31)) anthraquinone (1:9095). — C on reductn. with Al powder + conc. H₂SO₄ (32) (33) (6) (34) yields 1-chloroanthrone-9, yel. ndls. from CHCl₃ + lt. pet., m.p. 118° (32), 114° (6); C on reductn. with Sn + HCl in AcOH contg. PtCl₄, however, gives the isomeric 4-chloroanthrone-9, yel. ndls. from CHCl₃ + lt. pet., m.p. 118° (32) (note that although these two isomeric chloroanthrones have the same m.p. yet each depresses the m.p. of the other (32) and the earlier prod. of m.p. 106° (33) may have been a mixture). — For studies of oxidn.-reductn. potential of C see (12) (17).]

[C with MeOH/KOH at 80° yields (35) 1-methoxyanthraquinone [Beil. VIII-339, VIII₁-(651)], m.p. 169.5° — C with 2-hydroxyanthraquinone + NaOAc + Cu powder in boilg. nitrobenzene gives (36) 1,2'-dianthraquinonyl ether [Beil. VIII-343], but m.p. is not reported. — C with K xanthate + Cu powder boiled for 24 hrs. in AmOH or C with alk. trithiocarbonate in boilg. nitrobenzene (40) gives (64% yield (37)) di-(1-anthraquinonyl) sulfide, red pr. from pyridine, m.p. 321.5° (37) (for disulfide see below). — C with thiosalicylic acid (2-mercaptobenzone acid) + solid KOH htd. in AmOH at 150° for 7 hrs. gives (96% yield (38)) S-(1-anthraquinonyl)thiosalicylic acid [Beil. X₁-(55)], or.-yel. tbls. from alc., m.p. 261° cor. (38); this prod. on htg. with PCl₅ in nitrobenzene gives (98% yield (38)) 3,4-phthalylthioxanthone [Beil. XVII₁-(290)], or.-red lfts., m.p. 346° cor. (38).]

[\bar{C} with NaOH + glycerol htd. at 190° is claimed (39) to yield anthraquinone (1:9095). — \bar{C} on boilg. with aq. alc. Na₂S (41) or Na₂S_x (42) yields 1-mercaptoanthraquinone [Beil. VIII₁-(652)], yel. ndls. from AeOH, m.p. 187° (41); this prod. on oxidn. by air (43) or with K₃Fe(CN)₆ (44) or FeCl₃ (45) readily yields di-(1,1'-dianthraquinonyl) disulfide, m.p. 359° (45), also obtd. from \bar{C} with Na₂S + S in boilg. alc. (46) (43) (42) or from \bar{C} + K thiobenzoate in boilg. AmOH (80% yield (48)). — \bar{C} with K₂Se in dil. alc. at 80° gives (47) 1-selenomercaptoanthraquinone, or.-red lfts. from AeOH, m.p. 212°, and also di-(1-anthraquinonyl) diselenide.]

[C with conc. aq. NH₄OH in pres of Cu salts under press. at elevated temp. gives (49) (50) (57) in alm. quant. yield 1-aminoanthraquinone [Beil. XIV-177, XIV₁-(436)], red ndls., m.p. 242°. — Countless other analogous combinations of C with prim. and sec. amines cannot be included here; however, note that C with 1-aminoanthraquinone (above) + NaOAc + CuCl₂ htd. in nitrobenzene yields (52) cf. (61) di-(1-anthraquinonyl)amine [Beil. XIV-180, XIV₁-(439)], the prototype of a large group of dyes and dye intermediates (for amplification of this topic see (53)). — C with hydrazine hydrate + pyridine refluxed for ½ hr. gives (76% yield (54)) 1-hydrazinoanthraquinone [Beil. XV₁-(199)], dark br. lfts. from xylene, m p. 208.5° cor. (54). — For reactn. of C with NH₂OH.HCl in s.t. at 180° see (1).]

[For condens. of \bar{C} with p-aminoazobenzene (54) or with morpholine (60) and use of prods. as dyes for cellulose acetate see indic refs.; for condens. of \bar{C} with phthalonitrile in pres. of AlCl₃ for prepn. of dyestuffs see (55).]

[C with Cu powder at 290-300° or in boilg. nitrobenzene for 3 hrs. gives (75% yield (56)) bis-1,1'-anthraquinonyl [Beil. VII-903, VII₁-(494)], yel. or yel.-br. cryst. from nitrobenzene, m.p. 435° u.c. on Maquenne block (56); note, however, that in the pres. of NaOAc anthraquinone (1:9095) results (56). — C with 4 moles C₆H₆MgBr in boilg. ether for 4 hrs. gives (51% yield (58)) (57) 1-chloro-9,10-diphenylanthracene, yel. powder from AcOH, m.p.

185° (57), 180-182° (58); a mixt. of this prod. with corresp. prod. (m.p. 193°) from 2-chloroanthraquinone (3:4922) has m.p. 152-160° (58).]

[For formn. of addn. cpds. of \bar{C} with SbCl₅ in CHCl₃ see (16) (18); for formn. of 1-anthra-quinonylpyridinium chloride from \bar{C} + AlCl₃ in pyridine see (59).]

[C on mononitration by soln. in 10 wt. pts. cone. H₂SO₄ and addn. of HNO₃/H₂SO₄ as directed (61) (62) gives (30% yield (61)) 1-chloro-4-nitroanthraquinone [Beil. VII-792, VII₁-(415)], cryst. from AcOH, m.p. 260-261° (63), 259° (61); note that 1-chloro-2-nitroanthraquinone (prepared by indirect means) has m.p. 257-258° (63). — For study of kinetics of nitration of C see (64).]

 $|\bar{C}|$ on monosulfonation, e.g., with fumg. H_2SO_4 (20% SO_3) at 160° for 4 hrs. (65) (66), yields a mixt. of about equal parts of two monosulfonic acids eas. separable via their sodium salts; viz, 1-chloroanthraquinonesulfonic acid-6 (Na salt less sol. boilg. aq, corresp. sulfonyl chloride, pale yel. pr. from lgr., m.p. 207–208° dec.) and 1-chloroanthraquinonesulfonic acid-7 (Na salt more sol. boilg. aq, corresp. sulfonyl chloride, lemon-yel. pl. from C_6H_6 , m.p. 200–201° dec.); the m.p. of mixts. of the two sulfonyl chlorides is depressed below 180° (65). — \bar{C} on sulfonation in the pres. of Hg salts but otherwise as above yields, however, a different result as the principal prod. is 1-chloroanthraquinonesulfonic acid-5 (corresp. sulfonyl chloride, yel. pl. from toluene, m.p. 243–244° dec. (65) (66)), accompanied by 1-chloroanthraquinonedisulfonic acid-4,5.

3:4480 (1) French, Achenbach, Ber. 43, 3255-3256 (1910). (2) Schilling, Ber. 46, 1066-1069 (1913) (3) Scott, Allen, Org. Syntheses, Coll. Vol. 2 (1st ed.), 128-130 (1943). 18, 15-16 (1938).
 4) Ullmann, Ochsner, Ann. 381, 2-6 (1911) (5) Ullmann, Kertes, Ber 52, 547 (1919). (6) Maki, J. Soc Chem. Ind. Japan, Suppl. binding, 38, 630-636 (1935); Cent. 1936, II 468. (7) Dougherty, Gleason, J. Am. Chem. Soc. 52, 1025 (1930). (8) Schwenk, Wildmann, Z angew. Chem. 45, 19 (1932). (9) Eckert, Ber. 66, 1691 (1927). (10) Meyer, Compt. rend. 184, 610 (1927).

Keimatsu, Hirano, Tanabe, J. Pharm. Soc. Japan 49, 531-541 (1929); Cent. 1929, 11
 1536-1537; C.A. 23, 4696-4697 (1929). (12) Conant, Fieser, J. Am. Chem. Soc. 46, 1873, 1875 (1924). (13) Maki, Nagai, J. Soc. Chem. Ind. Japan, Suppl. bind. 38-B, 487-493 (1935); Cent. 1936, I 4905. (14) Coppens, Rec. trav. chim 44, 911-916 (1925). (15) Eckert, Ber. 58, 318 (1925). (16) Brass, Tengler, Ber. 64, 1660 (1931). (17) Baker, Adkins, J. Am. Chem. Soc 62, 3306 (1940). (18) Brass, Eichler, Ber. 67, 783 (1934). (19) du Pont, Brit. 432,867, Sept. 5, 1935; Cent. 1935, II 3996. (20) Bayer and Co., Ger. 205,195, Dec. 28, 1908; Cent. 1909, I 414.

(21) B.A.S.F., Ger. 228,876, Nov. 25, 1910; Cent. 1911, I 102. (22) Day, J. Chem. Soc. 1939, 318. (23) British Dyestuffs Corp. & Hailwood, Brit. 273,043, July 21, 1927, French 626,669, Sept. 16, 1927; Cent. 1928, II 2286. (21) M L.B., Ger. 267,544, Nov. 20, 1913, Cent. 1914, I 89. (25) Imperial Chem. Ind. Ltd. and Loveluck, Thomson & Thomas, Brit. 356,728, Oct. 8, 1931; French 718,333, Jan. 23, 1932. (26) Bayer and Co., Ger. 131,538, May 23, 1902; Cent. 1902, I 1342. (27) B.A.S.F., Ger. 252,578, Oct. 23, 1912; Cent. 1912, II 1708. (28) A.G.F.A., Ger. 290,879, March 21, 1916; Cent. 1916, I 686. (29) Atack, Clough, Brit. 169,732, Nov. 3, 1921; Cent. 1922, IV 377. (30) Fischer, Ziegler, J. prakt. Chem. (2) 86, 293 294 (1912).

Busch, Weber, Zink, J. prakt. Chem. (2) 155, 167 (1940).
 Barnett, Matthews, J. Chem. Soc. 123, 2552-2553 (1923).
 Bayer and Co., Ger. 229,316, Doc. 13, 1910; Cent. 1911, I 180.
 Chem. Soc. 1928, 2805.
 Buyer and Co., Ger. 229,316, Doc. 13, 1910; Cent. 1911, I 180.
 M.L.B., Ger. 216,268, Nov. 11, 1909, Cent. 1909, I 2104.
 Perkin, Sewell, J. Chem. Soc. 123, 3039-3040 (1923).
 Ullmann, Knecht, Ber. 44, 3126-3127 (1911); Ger. 238,983, Oct. 7, 1911; Cent. 1911, II 1289.
 Suppl. binding, 41, 193-195 (1938); Cent. 1939, I 1360; C.A. 32, 7447 (1938).
 Bayer and Co., Ger. 272,298, March 26, 1914; Cent. 1914, I 1387-1388.

(41) Bayer and Co., Ger. 206,536, Feb. 4, 1909; Cent. 1909, I 1059.
(42) Bayer and Co., Ger. 204,772, Dec. 3, 1908; Cent. 1909, I 601.
(43) Fries, Schurmann, Ber. 52, 2176-2177 (1919).
(44) Gattermann, Ann. 393, 137-138 (1911).
(45) Ullmann, Esser, Ber. 49, 2164 (1916).
(46) Fries, Ber. 45, 2967, Note (1912).
(47) Bayer and Co., Ger. 264,941, Sept. 25, 1913; Cent. 1913, II 1351.
(48) Ullmann, Junghans, Ann. 399, 352 (1913).
(49) Thomas, Davies, & Scottish Dyes, Ltd., Brit. 173,006, Jan. 19, 1922; Cent. 1922, IV 948.
(50) Williams (to Dow Chem. Co.), U.S. 1,775,360, Sept. 9, 1930; Cent. 1931, II 1195.

(51) Groggins, U.S. 1,892,302, Dec. 27, 1932; Cent. 1933, II 1764; C.A. 27, 1893 (1933); U.S.

1,923,618, Aug. 22, 1933; Cent. 1933, II 2894; C.A. 27, 5339 (1933). (52) Bayer and Co., Ger. 162,824; Oct. 4, 1905; Cent. 1905, II 1206. (53) Houben, Fischer "Das Anthracene und die Anthraquinone," published by G. Thieme, Lepzig, 1929, pp. 463-470. (54) Imperial Chem. Ind., Brit. 478,665, Feb. 17, 1938, Cent. 1938, I 4723, C.A. 32, 5223 (1938). (55) I.G., Brit. 466,194, June 17, 1937; French 813,180; May 27, 1937; Cent. 1937, II 4394. (56) Ullmann, Minaev, Ber. 45, 687, 689-690 (1912). (57) Barnett, Cook, Wiltshire, J. Chem. Soc. 1927, 1728. (58) E. Bergmann, O. Blum-Bergmann, J. Am. Chem. Soc. 59, 1440 (1937). (59) Miegs, Heidenreich (to I G.), Ger. 593,671, March 5, 1934; Cent. 1934, II 848. (60) Imperial Chem. Ind. Ltd., Hailwood, Tatum, Brit. 317,555, Sept. 12, 1929; Cent. 1930, I 2804.

(61) Eckert, Steiner, Monatsh 35, 1131-1132, 1138-1139 (1914). (62) Bayer and Co., Ger. 137,782, Dec. 15, 1902, Cent. 1903, I 108. (63) Kopetschni, Ger. 363,930, Nov. 15, 1922; Cent. 1923, II 1029-1030. (64) Oda, Ueda, Bull. Inst. Phys.-Chem. Research Tokyo 20, 335-342 (1941); C.A. 36, 4814-4815 (1942). (65) Goldberg, J. Chem. Soc 1931, 1773-1774, 1779-1780. (66) Thorpe, Goldberg, Brit. 373,127, June 16, 1932; Cent. 1933, II 1765-1766. (67) Steinkopf,

Schmidt, Ber. 61, 677 (1928).

3:4485 2,3,5-TRICHLOROBENZOIC Cl
$$C_7H_3O_2Cl_3$$
 Beil. IX - 345 ACID COOH IX₁—

M.P. 163° (1) 162° (2) (3)

Ndls. from hot aq. (2). — Not volatile with steam. — Very spar. sol. cold aq. but sol.

[For prepn. of C from 2,3,5-trichlorotoluene (3.0610) by oxidin with 20% HNO₃ in s.t. at 140° see (2); from 2,3,5-trichlorobenzaldehyde (3:1060) by oxidn, with KMnO₄ sec (3); for prepn. from correspondtrile by hydrolysis sec (1)]

C on soln in warm fumg. HNO₃ readily yields a mononitro cpd., 2,3,5-trichloro-xnitrobenzoic acid, cryst from alc, mp. 158° (1)

C with excess PCl₅ yields (1) 2,3,5-trichlorobenzoyl chloride, cryst. from EtOAc, m.p. 36° (1).

- Methyl 2,3,5-trichlorobenzoate: unrecorded.
- --- Ethyl 2,3,5-trichlorobenzoate: oil. [From \bar{C} + alc. + HCl (1).]
- (D) 2,3,5-Trichlorobenzamide: from 2,3,5-trichlorobenzoyl chloride + (NH₄)₂CO₃; ndls. from dil. AcOH, m p. 204-205° (1)
- ---- 2.3.5-Trichlorobenzanilide: unrecorded.

3:4485 (1) Matthews, J. Chem. Soc. 79, 43-49 (1901) (2) Cohen, Dakin, J. Chem. Soc. 81. 1331 (1902). (3) Hodgson, Beard, J. Chem. Soc. 1927, 2382.

C₁₀H₅O₂Cl Beil. S.N. 674 3:4492 5-CHLORONAPHTHOQUINONE-1,4

M.P. 163° (1)

Yellow ndls. from alc. or lgr. — Sublimes undecomposed. — Fairly eas. sol. AcOH or lgr.; moderately sol. alc.; spar. sol. aq.

[For prepn. of C from 5-chloro-1,4-diaminonaphthalene (5-chloronaphthylenediamine-1,2) by oxidn. of its hydrochloride with FeCl₃ see (1).]

[C with aniline (no details) gives (1) 2(3?)-anilino-5-chloronapthoquinone-1,4, red

bronzy ndls. from AcOH, m.p. 219° (1); note also that Č with aniline boiled for 1 hr. gives (1) a halogen-free cpd., dark violet cryst. from alc., m.p. 140°, but its structure has not been determined.]

3:4492 (1) Fries, Köhler, Ber. 57, 504-505 (1924).

 $(\alpha,\alpha,\alpha',\alpha'$ -Tetrachlorobibenzyl; tolane tetrachloride)

Colorless cryst from AcOH, pet. ether, C_6H_6 , or toluene. — Eas. sol. boilg. C_6H_6 ; moderately sol. hot but spar. sol. cold pet. ether; spar. sol. alc. or ether.

Č with trans-tolane dichloride (3:4210) forms an isomorphous mixt. (8) formerly erroneously regarded as an individual cpd. designated as "ditolane hexachloride."

PREPARATION OF C

From Dinuclear Initial Materials

[For prepn. of \bar{C} from benzil (1:9015) with excess PCl₅ (32% yield (10)) in s.t. at 200° for 6-7 hrs. (5), or from ms-dichlorodesoxybenzoin ("chlorobenzil") [Beil. VII-436, VII₁-(234)] with PCl₅ in s.t. at 200° (11) in POCl₃ soln. (100% yield (12)) cf. (5), see indic. refs.; from diphenylacetylene (tolane) [Beil. V-656, V₁-(319), V₂-(568)] in CHCl₃ at 0° (13) or from either cis-(3:1380) or trans-(3:4210) tolane dichloride (9) with Cl₂ see indic. refs.]

From Mononuclear Initial Materials

From benzotrichloride. [For prepn. of \bar{C} from benzotrichloride (3:6540) by reduction in alc. with H_2 + colloidal Pd (75% yield (4)) or H_2 + Pd/BaCO₃ (14) in alc.-alkali, or by htg. with Cu powder at 100° (6) or in C₆H₆ under reflux for 4 hrs. (30-36% yield (5)) (1) cf. (10), see indic. refs.; for formn. of \bar{C} from benzotrichloride (3:6540) with excess dilute (0.2 N) MeMgCl in ether (7), with EtMgBr (3) or C₆H₆MgBr (3), or by pyrolysis over hot Pt (15), or by htg. with Ni in atm. of CO₂ (16) see indic. refs.]

CHEMICAL BEHAVIOR OF C

[\bar{C} on reduction with conc. HI + P (1) or with H₂ in alc.-alk. + Pd/CaCO₃ (14) gives bibenzyl (1:7149), m.p. 52°.]

[\tilde{C} on removal of two adjacent chlorine atoms with Fe powder in boilg. AcOH (12) cf. (5), with Cu powder at 160° (6), with excess conc. (2 N) MeMgCl in ether refluxed 4 hrs. (7), with H₂ + hydrazine hydrate in MeOH/KOH 1½ hrs. at b.p. (17), or with Zn dust in boilg. alc. (18) (5) (2) (10) gives either or both trans- (3:4210) and cis- (3:1380) tolane dichlorides; note that use of insufficient Zn gives (8) cf. (5) (10) the cis-tolane dichloride (3:1380) + an isomorphous mixt. of \tilde{C} + trans-tolane dichloride (3:4210).]

- [$\bar{\mathbf{C}}$ with Na/Hg in alc. gives (11) diphenylacetylene (tolane) (see ref. above), some stilbene (1:7250) and bibenzyl (1:7149) also being formed (2). $\bar{\mathbf{C}}$ on htg. with Zn dust gives (2) stilbene (1:7250).]
- [\bar{C} is very resistant to hydrolysis and is unattacked by H_2O , alc., or AcOH in s.t. at 200° (2); note, however, that \bar{C} with AcOH in s.t. at 230–250° or with H_2SO_4 at 165° is claimed (2) to give benzil (1:9015).]
- [\bar{C} is very resistant to action of boilg. HNO₃ (2); note, however, that p,p'-dinitrotolane dichloride, m.p. 264–265° dec., has been prepd. indirectly (19) (from p-nitrobenzal(di)-chloride with acetone + KOH).]
- [C with anhydrous HF at 100° yields (20) 1,2-difluoro-1,2-diphenylethylene, m.p. 122-123° (20); however, C with HF in pres. of HgO gives (20) 1,2-dichloro-1,2-difluoro-1,2-diphenylethane, m.p. 128-130° (20).]
- 3:4496 (1) Hanhart, Ber. 15, 901 (1882). (2) Liebermann, Homeyer, Ber. 12, 1971–1973 (1879).
 (3) Sanna, Rend. seiminar faculta sci. univ. Caglian 5, 76–81 (1935), Cent. 1937, II 2345; C.A. 33, 5833 (1939). (4) Borsche, Heimbürger, Ber. 48, 458 (1915). (5) Blank, Ann. 248, 21–25, 33–34 (1888). (6) Onufrowicz, Ber. 17, 833–835 (1884). (7) Fuson, Ross, J. Am. Chem. Soc. 55, 722–723 (1933). (8) Marckwald, Karczag, Ber. 40, 2994–2996 (1907). (9) Davidson, J. Am. Chem. Soc. 40, 399 (1918). (10) Eiloart, Am. Chem. J. 12, 231–232 (1890).
- (11) Zinin, Compt. rend. 67, 720 (1868); Ann. 149, 375 (1869). (12) Lachowicz, Ber. 17, 1164-1165 (1884). (13) Redsko, J. Russ. Phys.-Chem. Soc. 21, 426 (1889); Ber. 22, Referate 760 (1889). (14) Busch, Stove, Ber. 49, 1067-1068 (1916). (15) Loeb, Ber. 36, 3060-3061 (1903). (16) Korczynski, Reinholz, Schmidt, Roczniki Chem. 9, 731-740 (1929); C.A. 24, 1858 (1930). (17) Busch, Weber, J. prakt Chem. (2) 146, 51-52 (1936). (18) Zinin, Ber. 4, 289 (1871). (19) Olivier, Weber, Rec. trav. chim. 53, 889-890 (1934). (20) Balon, Tinker (to du Pont Go.), U.S. 2,238,242, April 15, 1941; Cent. 1942, I 2328; [C.A. 35, 4779 (1941)].

CHAPTER XI

DIVISION A. SOLIDS

(3:4500-3:4999)

3:4500 2,3,6-TRICHLOROBENZOIC
$$Cl$$
 $COOH$ $C_7H_3O_2Cl_3$ Beil. IX - 345 IX₁—

M.P. 163-164° (1) 163-165° (2)

Cryst. from aq. (1).

[For prepn. of C from 2,3,6-trichlorotoluene (3:0625) by oxidn, with HNO₃ see (1) (2).] No further data on this compd. are recorded

3:4500 (1) Cohen, Dakin, J. Chem. Soc. 81, 1332 (1902). (2) Feldman, Kopeliowitsch, Arch. Pharm. 273, 494 (1935).

M.P. 164° (1) 160° (2) 159-160° (3)159°

162°

(2)

Colorless cryst. (from alc. (1)) with camphoraceous odor. — Readily sublimes in open tubes on htg; eas sol. alc. ether

[For prepn. of C from tetramethylethylene glycol (pinacol) (1 5805) with fumg. HCl (4) or with PCl₃ (5) see (4) (5); for formn. from 2,3-dimethylbutane (di-isopropyl) (1:8515) with Cl_2 in pres. of I_2 see (4) (6)]

C with alc. KOH in s.t. at 130-140° gives (4) mainly 2,3-dimethylbutadiene-1,3 (1:8050), b.p. 68.7° (accompanied by unsatd. ethers, b.p. 136-146°) (4). [For study of behavior of C with aq. alc. NaOH see (3).

3:4520 (1) Kahovec, Wagner, Z. physik. Chem. **B-47**, 53 (1940). (2) Schorlemmer, Ann. **144**, 186–187 (1867). (3) Tishchenko, J. Gen. Chem. (U.S.S.R.) **9**, 1380–1388 (1939); C.A. **34**, 1611 (1940). (4) Kondakow, J. prakt. Chem. (2) 62, 169-174 (1900). (5) Couturier, Ann. chim. (6) 26, 443-444 (1892). (6) Silva, Ber. 6, 36 (1873).

Long ndls. from hot aq. (4); cryst. from C₆H₆ + pet. eth. — Eas. sol. alc., ether, or CHCl₃ (5).

[For prepn. of \bar{C} from 2,4,6-trichloroaniline [Beil. XII-627] via conversion by diazo reactn. to 2,4,6-trichlorobenzonitrile, m.p. 77.5° (1), 75° (6), thence to 2,4,6-trichlorobenzamide (see below) and hydrolysis of latter see (1) (4) (5) (2) (12), for prepn. of \bar{C} from 2,4,6-trichlorotoluene (3:0380) by oxidn. with HNO₃ see (3).]

C on soln. in 5 pts. conc. HNO₃ yields (1) 2,4,6-trichloro-3-nitrobenzoic acid [Beil. IX-405], cryst. from CHCl₃, m p. 169 2° (1).

 \bar{C} with PCl₅ (5) (73% yield (2)) or with SOCl₂ + pyridine (7) gives 2,4,6-trichlorobenzoyl chloride, b.p. 272° (5), 107-107.5° at 6 mm. (2), 120.1-120.4° at 3 mm. (7). — This acid chloride is very stable to aq (5) and is alleged to give no ester with MeOH (5). [Note, however, that with EtOH reactn is 99% complete in 1 min (7).] [For study of reactn. of 2,4,6-trichlorobenzoyl chloride with MeMgCl (8) or MeMgBr (12) giving (50% yield (2)) di-(2,4,6-trichlorobenzoyl)methane, m.p. 160-161°, see (8), with MeMgBr giving 2,4,6-trichloroacetophenone, m.p. 51° (8) (14), see (8); with C_0H_6 + AlCl₃ yielding 2,4,6-trichlorobenzophenone, m.p. 103 5°, see (9)]

- Methyl 2,4,6-trichlorobenzoate: unrecorded. $[\bar{C} + MeOH + HC]$ yields no ester (4) (10)]
- Ethyl 2,4,6-trichlorobenzoate: unrecorded. [\bar{C} + EtOH + HCl yields no ester (5)]
- ② 2,4,6-Trichlorobenzamide: m p. 181° (1), 177° (6). [This amide has not been recorded as prepd. from the acid chloride + NH₃; it has been obtd. only by partial hydrolysis (11) (6) (1) of 2,4,6-trichlorobenzonitrile (see above)] [The amide itself is only slowly hydrolyzed to C by 75% H₂SO₄ at 160° (6), but for conversion to C via HNO₂ see (11) (1) (2).]
- 2,4,6-Trichlorobenzanilide: from 2,4,6-trichlorobenzoyl chloride + aniline (12), ndls., m.p. 197° (12).
- 3:4545 (1) Montagne, Rec. trav. chim. 21, 383-388 (1902). (2) Fuson, Bertetti, Ross, J. Am. Chem. Soc. 54, 4381-4382 (1932). (3) Cohen, Dakin, J. Chem. Soc. 81, 1336 (1902). (4) Meyer, Sudborough, Ber. 27, 3151-3152 (1894). (5) Sudborough, J. Chem. Soc. 65, 1030 (1894). (6) Sudborough, Jackson, Lloyd, J. Chem. Soc. 71, 231-232 (1897). (7) Norris, Ware, J. Am. Chem. Soc. 61, 1418-1420 (1939). (8) Ross, Fuson, J. Am. Chem. Soc. 59, 1508-1510 (1937). (9) Montagne, Rec. trav. chim. 26, 279-280 (1907). (10) Meyer, Ber. 28, 1259 (1895).
- (11) Sudborough, J. Chem. Soc. 67, 602 (1895)
 (12) Chapman, J. Chem. Soc. 1927, 1749.
 (13) Fuson, Van Campen, Wolf, J. Am. Chem. Soc. 60, 2269-2270 (1938).
 (14) Lock, Böck, Bor. 70, 925 (1937).

Cryst. from aq., alc. (3), C_6H_6 or $C_6H_6 + \lg r$.—Sublimes undecomposed in ndls. (9) or lfts. (10) — Eas. sol. in boilg. aq. or org. solv. (10).

[For prepn. of \bar{C} from 2,4-dichlorotoluene (3:6290) by oxidn. with dil. HNO₃ at 140° (9) (7) (8) or with KMnO₄ (70% yield (1)) or by electrolytic oxidn. (65% yield (3)) see indic. refs.; from 2,4-dichlorobenzaldehyde (3:1800) via Cannizzaro reactn. see (5); from 2,4-dichloroaniline [Beil. VII-621] via conversion to and hydrolysis of 2,4-dichlorobenzoni-

trile see (4) (5); from 2,4-dichlorobenzotrichloride with 95% H_2SO_4 see (5) (11) (12); for still other misc. methods see Beil. IX-342 + IX₁-(141).]

 \bar{C} warmed at 100° with a mixt. of fumg. HNO₃ (D=1.52) + conc. H₂SO₄ as directed (13) yields 2,4-dichloro-3,5-dinitrobenzoic acid, pr. from dilute alc., m.p. 210-211° (13), together with a trace of 2,4-dichloro-1,3-dinitrobenzene, m.p. 103°, insol. in Na₂CO₃. [A mononitrated \bar{C} , viz., 2,4-dichloro-5-nitrobenzoic acid, cryst. from 30% AcOH, m.p. 161-163° (11), 162° (18), and 2,4-dichloro-6-nitrobenzoic acid, cryst. from C₆H₆, m.p. 189-190° (19), have been prepd. indirectly.]

C with PCl₅ (14) or SOCl₂ (15) (3) yields 2,4-dichlorobenzoyl chloride, b.p. 150° at 3-4 mm. (14), 152-155° at 30 mm. (16), 91.9-92.5° at 1 mm. (15). [For conv. of this acid chloride to 2,4,2',4'-tetrachlorodibenzoyl peroxide see (3).]

- Methyl 2,4-dichlorobenzoate: oil, b.p. 132° at 15 mm., $D_{20}^{20} = 1.572$ (21). [From \tilde{C} by conv. to Na \tilde{A} and htg. with MeI in MeOH for 20 hrs. (73% yield (21))].
- Ethyl 2,4-dichlorobenzoate: constants unrecorded. [For study of rate of hydrolysis see (17).]
- 2,4-Dichlorobenzamide: unrecorded.
- . 2,4-Dichlorobenzanilide: unrecorded.

3:4569 (1) Bornwater, Holleman, Rec. trav. chim. 31, 226-230 (1912). (2) Lock, Bock, Ber. 76, 923 (1937). (3) Fichter, Adler, Hclv. Chim. Acta 9, 286-287 (1926). (4) Gomberg, Cone, Ann. 370, 183 (1909). (5) van der Lande, Rec. trav. chim. 51, 103 (1932). (6) Gassmann, Hartmann, J. Am. Chem. Soc. 63, 2394 (1941). (7) Wynne, J. Chem. Soc. 1936, 703. (8) Cohen, Dakin, J. Chem. Soc. 79, 1129 (1901). (9) Lellmann, Klotz, Ann. 231, 315-316 (1885). (10) Krauss, Ber. 37, 221 (1904).

(11) Villiger, Ber. 61, 2598 (1928). (12) Ger. 234,290, May 4, 1911; Cent. 1911, I 1567. (13) Borsche, Bahr, Ann. 402, 90-91 (1914). (14) Cohen, Briggs, J. Chem. Soc. 83, 1213-1214 (1903). (15) Norris, Ware, J. Am. Chem. Soc. 61, 1418 (1939). (16) B.A.S.F. Ger. 331,696, Jan. 10, 1921 [C.A. 15, 2102 (1921)]. (17) Blakey, McCombie, Sudborough, J. Chem. Soc. 1926, 2863-2868. (18) Grimm, Günther, Tittus, Z. physik. Chem. B-14, 184 (1931). (19) Ruggli, Zaeslin, Helv. Chim. Acta 19, 439 (1936). (20) Roberts, Turner, J. Chem. Soc. 1927, 1846.

(21) Samant, Ber. 75, 1011 (1942).

3:4580 3,5-DICHLOROPHTHALIC ACID

СООН

Beil. IX - 817 IX₁—

M.P. 164° (1) 164° dec. (2)

[See also 3,5-dichlorophthalic anhydride (3:2375).]

Colorless ndls. or tbls. from aq. HCl; readily sol. in cold alc., ether, or acetone, but spar. sol. in C_6H_6 or CHCl₃ even on boilg.

[For prepn. of \bar{C} from 3,5-dichlorophthalic anhydride (3:2375) on boilg. with aq. see (1) (2); from aq. soln. of NH₄H \bar{A} by passing in HCl gas see (1) (2); from 3,5-dichloro-1,2-dimethylbenzene [Beil. V-364] (itself obtd. in good yield from dimethyldihydroresorcinol ("methone") (1:0768) with PCl₅ in CHCl₃ (2) (3)) by oxidn. with dil. HNO₃ in s.t. at 190-200° see (2).]

Salts. $NH_4H\bar{A}$, spar. sol. aq., eas. prepd. by mixing aq. solns. of $(NH_4)_2\bar{A} + \bar{C}$; $Ag_2\bar{A}$, white curdy ppt. from warm aq. soln. of $(NH_4)_2\bar{A}$ by addn. of aq. Ag_3NO_3 .

Esters. Dimethyl 3-chlorophthalate and methyl hydrogen 3-chlorophthalate are unreported: diethyl 3-chlorophthalate (from Ag₂A with EtI in dry ether) is oil, b.p. 312-313° at 760 mm. (2); ethyl hydrogen phthalate is unreported.

Č on htg. alone (1) or with AcCl (2) yields 3,5-dichlorophthalic anhydride (3:2375), m.p. 89°.

3:4580 (1) Waldmann, Schwenk, Ann. 487, 293 (1931). (2) Crossley, LeSueur, J. Chem. Soc. 81, 1536-1537 (1902). (3) Crossley, LeSueur, J. Chem. Soc. 82, 826-827 (1902).

[See also 2,6-dichlorobenzoquinone-1,4 (3:3750).]

Colorless lfts. from dil. alc.; ndls. from aq. or C6H6. — Sublimes.

[For prepn. of \bar{C} from 2,6-dichlorobenzoquinone-1,4 (3:3750) by reductn. with SO₂ in aq. see (80% yield (5)) (6) (7) (note, however, that the quinone in dil. aq. NaOH under N₂ with SO₂ is in part reduced to \bar{C} and in part sulfonated to mono- and disulfonic acids (8)); from 2,4,6-trichlorophenol (3:1673) in 2 N H-SO₄ on electrolytic oxidn. see (4); from 3,5-dichloro-4-hydroxybenzaldehyde (3:4400) in N KOH with H₂O₂ see (3); from sodium benzoquinone-1,4-sulfonate with conc. HCl above 20° in CO₂ (below 20° chlorohydroquinonesulfonic acid results) see (1) (9).]

[For use of \bar{C} as antioxidant and gum inhibitor in cracked gasoline see (10); for use in aq. petroleum emulsion as insecticidal oil spray see (11); for use as vulcanization accelerator see (18).]

Č on oxidn. with CrO₃ (12) or with excess aq. FeCl₃ on warming (3) yields 2,6-dichlorobenzoquinone-1,4 (3:3750) (the intermediate quinhydrone cpd., brown powder or pr. or dark ndls. (5), m.p. 135° (13), may separate with insufficient oxidant). [For studies on oxidn.-reductn. potential of system: Č + 2,6-dichlorobenzoquinone-1,4 (3:3750) see under latter.]

 $[\bar{C}$ in conc. H_2SO_4 with chloral hydrate (3:1270) (2 moles) gives (64% yield (14)) 5,7-dichloro-6-hydroxy-2,4-bis-(trichloromethyl)benzdioxin-1,3, colorless pl. from boilg. alc., CHCl₃, C_6H_6 , or pet. eth., m.p. $114-115^\circ$ (14).

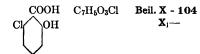
- —— 2,6-Dichlorohydroquinone diacetate: ndls. and pr. from aq. alc., m.p. 98° (2). 85-86° on rap. htg., 111-113° on slow htg. (15), 75.5° (7), 66.5° (16). (The reasons for these divergences appear never to have been explained.) [From C with Ac₂O (16) (15).]
- **D 2,6-Dichlorohydroquinone dibenzoate:** colorless ndls. from alc., m.p. 105° (16). [From $\tilde{\mathbf{C}}$ on htg. with BzCl (16).]
- D 2,6-Dichlorohydroquinone dimethyl ether: m.p. not reported. [From C in dil. aq. alk. with Me₂SO₄ (17); this prod. with 3-4 pts. cold fumg. HNO₃ nitrates yielding (17) 2,6-dichloro-3,5-dinitrohydroquinone dimethyl ether, colorless cryst. from alc., m.p. 121-123° (17).]

3:4600 (1) Seyewetz, Compt. rend. 156, 902 (1913). (2) Kehrmann, Tiesler, J. prakt. Chem. (2)-40, 481 (1889). (3) Dakin, Am. Chem. J. 42, 491 (1909). (4) Fichter, Stocker, Ber. 47, 2016 (1914). (5) Conant, Fieser, J. Am. Chem. Soc. 45, 2202-2204 (1923). (6) Faust, Ann. 149, 155 (1869). (7) van Erp, Ber. 58, 665 (1925). (8) Dodgson, J. Chem. Soc. 1930, 2498-2502. (9) Seyewetz, Paris, Bull. soc. chim. (4) 13, 489-490 (1913). (10) Clarke, Towne (to Texas Co.), U.S. 2,023,871, Dec. 10, 1935; Cent. 1936, I 2671; C.A. 30, 951 (1936).

(11) Yates (to Shell Development Co), U.S 1,778,240, Oct. 14, 1930; Cent. 1931, I 2799; C.A. 24, 5928 (1930). (12) Den Hollander, Rec. trav. chrm. 39, 481-482 (1920) (13) Ling, Baker, J. Chem. Soc. 63, 1321-1322 (1893). (14) Chattaway, Calvet, J. Chem. Soc. 1928, 2915, 2918. (15) Ling, J. Chem. Soc. 61, 560 (1892). (16) Levy, Ber. 16, 1445-1446 (1883). (17) Kohn, Marberger, Monatsh. 45, 654-656 (1924). (18) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; Cent. 1933, I 3134.

3:4610 6-CHLORO-2-HYDROXYBENZOIC ACID

(6-Chlorosalicylic acid)



414

Beil. S.N. 952

M.P. 166° (1)

Colorless adds. from aq., grad. turning red in air. — Sol. in aq. and most org. solvents; not volatile with steam.

[For prepn. of \bar{C} from 6-chloro-2-aminobenzon acid (6-chloroanthranilic acid) [Beil. XIV-366, XIV₁-(548)] by diazotization and boilg. with aq. (*m*-chlorophenol (3:0255) is also formed) see {1}.]

C with FeCl₃ soln. gives violet color.

For NH₄ \bar{A} , K \bar{A} , Ba \bar{A}_2 , Ag \bar{A} , all sol. in aq., see (1).

[The methyl ether of \bar{C} , viz., 6-chloro-2-methoxybenzoic acid, m.p. 141° (2), has been obtd. indirectly from 2-chloro-6-methoxytoluene [Beil. VI-359] by KMnO₄ oxidn. (2)]

[For esterification of C with glycol monoethers and use of prods. as plasticizers see (3).]

3:4610 (1) Cohn, Mitt. Technol. Gewerb -Mus. Wien. 11, 178-182, Cent. 1901, II 925. (2) Ullmann, Panchaud, Ann. 350, 113 (1906) (3) Grether, DuVall (to Dow Chem. Co.), U.S. 2,234,374 March 11, 1941; C.A. 35, 3738 (1941).

3:4612 DI-(p-CHLOROPHENYL)ACETIC ACID

 $\begin{array}{c} \text{Cl} \\ \text{Cl} \\ \text{Cl} \end{array}$

Colorless cryst. from dil. alc. Neut. Eq. = 281.

[For prepn. of Č from 1,1,1-trichloro-2,2-bis-(p-chlorophenyl)ethane ("DDT") (3:3298) by action of excess Ba(OH)₂.8H₂O in ethylene glycol under reflux for 10-12 hrs. (33% yield) see (1); from 1,1-dichloro-2,2-bis-(p-chlorophenyl)ethylene (3:2438) by similar treatment (1) or with alc. KOH in s.t. at 150-160° for 24 hrs. (57% yield (2)) see indic. refs.; for prepn. of Č from chlorobenzene (3:7903) by condensation with glyoxylic acid monohydrate (HO)₂CH.COOH in pres. of conc. + fumg. H₂SO₄ at 20° (18.6% yield) see (1).]

C with KOH in ethylene glycol refluxed 10-12 hrs. loses CO₂ giving alm. 100% yields (1) of 4,4'-dichlorodiphenylmethane (3:1057), m.p. 55°.

Note that \tilde{C} is one of the metabolitic prods. obtd. from the urine after administration of "DDT" (3:3298) to rabbits,

3:4612 (1) White, Sweeney, U.S. Pub. Health Repts. 60, 66-71 (1945). (2) Grummitt, Buck, Jenkins, J. Am. Chem. Soc. 67, 156 (1945).

Colorless ndls. from aq. or alc.

[For prepn. of \tilde{C} from 6-chloro-3-methylacetophenone [Beil. VII-307] by oxidn. with KMnO₄ or dil. HNO₃ see (1); from β -chloroethyl 6-chloro-3-methylphenyl ketone (2) by oxidn. at 100° with mixt. of equal pts. conc. HNO₃ (D=1.42) and water see (2); from β -chlorotoluene (3.8287) in CS₂ with oxalyl (dr)chloride (3:5060) + AlCl₃ for 20 hrs. at room temp. see (3).]

[C with 6 pts SOCI₂ gives (alm. quant. yield (3)) 6-chloro-3-methylbenzoyl chloride, b.p. 165-167° at 85 mm. (3).]

 \bar{C} on oxidn. with KMnO₄ yields (1) (3) 4-chlorobenzenedicarboxylic acid-1,3 (4-chlorosophthalic acid) (3:4980), m.p. 286° u.c. (1).

3:4615 (1) Claus, J. prakt Chem. (2) **46**, 27 (1892). (2) Mayer, Muller, Ber. **60**, 2281 (1927). (3) Scholl, Meyer, Keller, Ann. **513**, 298 (1934).

Ndls. from aq. or dil. alc. — Alm. insol. cold aq., eas. sol. cold abs. alc. (4). — Sublimes in ndls. (4).

[For prepn. of \bar{C} from 1,2,4-trichlorobenzene (3:6420) via nitration, reduction, conversion via diazo reactn. to 2,4,5-trichlorobenzonitrile, m.p. 104° (1), and subsequent indirect hydrolysis see (1); from 2,4,5-trichlorotoluene (3:2100) by oxidn. with HNO₃ (4) (6) or CrO₃ (5) see (4) (5) (6), from 2,4,5-benzotrichloride via htg. with aq. in s.t. at 260° see (3); from 3,4-dichlorobenzoic acid (3.4925) + Ca(OCl)₂ see (3); from HNO₃ oxidn. of certain fractions of chlorinated isopropylbenzene (cumene) see (2).]

For salts, viz., $NH_4\bar{A}$, $Ca\bar{A}_2.2H_2O$; $Sr\bar{A}_2.4H_2O$; $Ba\bar{A}_2.7H_2O$, see (3).

 \bar{C} on nitration with hot mixt. of equal vols. conc. HNO₃ + conc. H₂SO₄ yields (3) 2,4,5-trichloro-x-nitrobenzoic acid, ndls. from aq., m.p. 220° (3).

Č with PCl₅ (3) or SOCl₂ (1) yields 2,4,5-trichlorobenzoyl chloride, b.p. 272° sl. dec. (3), 125° at 2 mm. (1); m.p. abt. 28° (1), 41° (3).

- ---- Methyl 2,4,5-trichlorobenzoate: unrecorded.
- Ethyl 2.4.5-trichlorobenzoate: from \overline{C} + EtOH + HCl (3): m.p. 65° (1) (3).
- D 2,4,5-Trichlorobenzamide: from 2,4,5-trichlorobenzoyl chloride + cold conc. NH₄OH (3), ndls. from C₆H₆, m.p. 167.5° (3), 168° (1). [For conversion of this amide to C via HNO₂ see (1).]

3:4630 (1) Baker, Tweed, J. Chem. Soc. 1941, 800. (2) Qvist, Salo, Acta Acad. Aboensis Math. et Phys. 8, No. 4, 30 pp. (1934); Cent. 1934, II 594-595; 1936, I 538-540; C.A. 29, 6884 (1935).
 (3) Beilstein, Kuhlberg, Ann. 152, 237-240 (1869). (4) Cohen, Dakin, J. Chem. Soc. 81, 1335 (1902). (5) Jannasch, Ann. 142, 301-302 (1867). (6) Feldman, Kopeliowitsch, Arch. Pharm. 273, 494 (1935).

3:4650 2,3-DICHLOROBENZOIC ACID

M.P. 168.3° cor. (1) 166° (2) 164° (3) 163° (4)

Cryst. from C₆H₆ or from 30% AcOH (1).

[For prepn. of \bar{C} from 2,3-dichlorotoluene (3:6345) with alk. KMnO₄ (1) (2) or with dil. HNO₃ in s.t. at 140° (2) (4) see (1) (2) (4); from benzoic acid (1:0715) by chlorination with KClO₃ + HCl (3) (6) or with Ca(OCl)₂ (7) see (5) (6) (7).]

For f.p./compn. data on mixts. of C with 2,5-dichlorobenzoic acid (3:4340), m.p. 154.4°, see (1).

C on htg. with lime yields (6) o-dichlorobenzene (3:6055).

 \bar{C} is unaffected by conc. H₂SO₄ at 300° (6) and scarcely affected by htg. with fumg. HNO₃ (10). — However, \bar{C} dislvd. in bolg. non-fumg. HNO₃ and treated as directed (10) with conc. H₂SO₄ yields 2,3-dichloro-x-nitrobenzoic acid, m.p. 214-215° u.c. (10).

Č with PCl₅ yields (8) 2,3-dichlorobenzoyl chloride, b.p. 140° at 14 mm. (8). [This acid chloride is formed during chlorination of benzoyl chloride in presence of FeCl₃ where it constitutes 23% of the dichlorinated fraction (8).]

- --- Methyl 2.3-dichlorobenzoate: unrecorded.
- Ethyl 2,3-dichlorobenzoate: m.p. unrecorded. [For study of velocity of hydrolysis see (9).]
- 2.3-Dichlorobenzamide: unrecorded.
- 2,3-Dichlorobenzanilide: unrecorded.

3:4650 (1) Hope, Riley, J. Chem. Soc. 123, 2470-2480 (1923). (2) Seelig, Ann. 237, 162 (1887).
 (3) Wynne, Greeves, Proc. Chem. Soc. 11, 151 (1895). (4) Cohen, Dakin, J. Chem. Soc. 79, 1128 (1901). (5) Claus, Ber. 6, 721-723 (1873). (6) Claus, Bucher, Ber. 20, 1621-1627 (1887).
 (7) Claus, Ber. 8, 948-950 (1875). (8) Cohen, Briggs, J. Chem. Soc. 83, 1214 (1903). (9) Blakey, McCombie, Scarborough, J. Chem. Soc. 1926, 2863-2868. (10) Claus, Bucher, Ber. 20, 1624 (1887).

3:4670 5-CHLORO-2-METHYLBENZOIC ACID

M.P. 168.5–169.5° (1) 168° (2)

Colorless ndls. from alc.

Note that the materials of m.p. 130° (3) and 137° (4) formerly supposed to have been \tilde{C} are now believed (1) to have been mixtures of \tilde{C} with the isomeric 4-chloro-2-methylbenzoic acid, m.p. 170° (3:4700).

[For prepn. of C from 5-chloro-2-methylaniline [Beil. XII-835, XII₁-(384)] via conv. to 5-chloro-2-methylbenzonitrile (1) (2), ndls. from pet. ether, m.p. 48° (2), 45-46° (1), and saponification of the latter with 70% H₂SO₄ (2) see indic. refs.]

[\bar{C} yields (no details) an acid chloride which with $C_6H_6+AlCl_3$ in CS_2 gives (2) 5-chloro-2-methylbenzophenone, m.p. 41° (2), b.p. 191° at 12 mm. (2).]

C on oxidn. with KMnO₄ yields (1) 4-chlorophthalic acid (3:4390), m.p. 151° (1).

- ---- Methyl 5-chloro-2-methylbenzoate: unreported.
- Ethyl 5-chloro-2-methylbenzoate: b.p. unreported, $D_4^{20} = 1.1628$ (1), $n_{\rm He}^{20.0} = 1.52483$ (1).
- ---- 5-Chloro-2-methyl benzamide: unreported.

3:4670 (1) von Auwers, Harres, Z. physik. Chem. A-143, 16-18 (1929). (2) de Diesbach, Dobbelmann, Helv. Chim. Acta 14, 375 (1931). (3) Claus, Bayer, Ann. 274, 308-309 (1893). (4) Claus, Stapelberg, Ann. 274, 311 (1893).

3:4672 2,3,5-TRICHLOROBENZO-QUINONE-1,4

Yellow lfts. from alcohol; reddish yel. lfts. from CHCl₃/lgr. — Insol. cold aq.; spar. sol. cold alc.; eas. sol. hot alc. or ether. — \tilde{C} is sublimable [for study of sublimation press see (8).]

[For studies of heat of formation see (9); for studies of heat of combustion see (10) (11).] [For studies of bactericidal actn. of \bar{C} see (12); for patent on use of \bar{C} as vulcanization accelerator see (13)]

PREPARATION OF C

From 2,3,5-trichlorohydroquinone. [For prepn. of C from 2,3,4-trichlorohydroquinone (3:4052) by oxidn., e.g., with CrO₃ at 0° (10), conc. HNO₃ (14) (5) see indic. refs.]

From phenol or chlorinated phenols. [For prepn of \bar{C} from phenol (1:1420) via sulfonation followed by oxidn. with KClO₃ + HCl see (3) (15) cf. (22); note that by this method both \bar{C} and 2,3,5,6-tetrachlorobenzoquinone-1,4 ("chloranil") (3:4978) are produced; for sepn. of \bar{C} from latter see (5) (16)]

[For prepn. of \bar{C} from 2,3,5-trichlorophenol (3:1340) or from 2,3,6-trichlorophenol (3:1160) with fumg. HNO₃ on protracted htg. (17), or from 2,4,6-trichlorophenol (3:1673) with mixt. of conc. HNO₃ + conc. HCl boiled for a few minutes (2), or from 2,3,4,6-tetrachlorophenol (3:1687) by oxidn. with 5 wt. pts. fumg. HNO₃ (70% yield (1)), see indic. refs.]

From amines, aminophenols, etc. [For form. of \bar{C} from aniline during electrolytic oxidn. in HCl soln. see (18); from p-aminophenol hydrochloride with Ca(OCl)₂ soln. see (19); from 2,3,5-trichloro-4-aminophenol hydrochloride by action of Br₂ (20) or NaQBr

(30); from benzal p-anisidine or benzal p-phenetidine by treatment with ter-AmOCl (3:9287) followed by subsequent oxidn. with $K_2Cr_2O_7/H_2SO_4$ see (4).]

From various derivs. of $\bar{\mathbf{C}}$ by hydrolysis. [For form. of $\bar{\mathbf{C}}$ from various imide derivs. of $\bar{\mathbf{C}}$ by acid hydrolysis, e.g., from the corresp. $N-(\rho$ -chlorophenyl)mide [Beil. XII-611] (21), N-(2,4,6-trichlorophenyl)imide [Beil. XII-628] (22) (7), or N-(2,4-dinitrophenyl)-imide [Beil. XII-754] (23), see indic. refs.]

From miscellaneous sources. [For formn. of \bar{C} from C_6H_6 (1:7400) by oxidn. with $CrO_2Cl_2/AcOH$ (24), from copper salt of quinic acid [Bell. X-535, X_1 -(270)] by oxidn. with $MnO_2/NaCl/H_2SO_4$ (14), or from benzoquinone-1,4 (1:9025) with Cl_2 (25) see indic. refs.]

CHEMICAL BEHAVIOR OF C

Reduction. \bar{C} with aq. SO₂ (5) (14) (15) (16), or \bar{C} in other soln, with aq. SO₂ (1) reduces to 2,3,5-trichlorohydroquinone (3:4052). [Note that this reaction is used (16) to separate \bar{C} from 2,3,5,6-tetrachlorobenzoquinone-1,4 ("chloranil") (3:4978) since the latter is but slowly reduced by aq. SO₂] [For studies of oxidin-reduction potential of system \bar{C} + 2,3,5-trichlorohydroquinone (3:4052) see (6) (26) (27).]

Oxidation. \bar{C} with strong HNO₃ on digestion is degraded with forms, of trichloronitromethane ("chloropierin") + CO₂ (15).

Chlorination. [\bar{C} with Cl_2 reacts only very slowly; however, \bar{C} with $Cl_2 + I_2 + aq.$ (15), or \bar{C} with $Cl_2 + HCl$ (28), gives 2,3,5,6-tetrachloro-benzoquinone-1,4 ("chloranil") (3:4978).]

Reaction with HCl. \tilde{C} with conc. HCl on protracted boilg. (29) (3), or \tilde{C} with fumg. HCl in s.t. at 130° (30), gives 2,3,5,6-tetrachlorohydroquinone (3:4941).

Behavior of C with other inorganic reactants. With aq. alkali. [C with dil. aq. KOH turns green and then dis. to a red-brown soln. from which upon acidification is pptd. (5) 2,5-dichloro-3,6-dihyroxybenzoquinone-1,4 ("chloroanilic acid") (3:4970).]

With aq. K_2SO_3 . [\bar{C} dis. in warm aq. K_2SO_3 or KHSO₃ and on cooling ppts. (31) the potassium salt of 2,3,5-trichlorohydroquinonesulfonic acid-6 [Beil. XI-300]; the mother liquor conts. a cpd. which on boilg. with KOH gives (31) the salt of 2,5-dihydroxybenzo-quinone-1,4-disulfonic acid-3,6 [Beil. XI-353].]

With NH₃. [C with alc. NII₃ leacts vigorously yielding (3) a dark soln. from which can be obtd. in small amt. 3,6-dichloro-2,5-diaminobenzoquinone-1,4 ("chloranilamide") [Beil. XIV-144].]

With PCl_5 . [\bar{C} with PCl_5 + $POCl_3$ in s.t. at 180-200° gives (5) hexachlorobenzene (3:4949).]

Behavior of C with organic reactants. With phenol. C with K phenolate (2 moles) at 100° for 20 min. gives (32) 3-chloro-2,5-diphenoxybenzoquinone-1,4, or. tbls. from alc., m.p. 169-170° (32).

With 2,3,5-trichlorohydroquinone. $\ddot{\mathbf{C}}$ (1 mole) with 2,3,5-trichlorohydroquinone (1 mole) (3:4052) in CHCl₃ soln. gives on evaph. (6) (33) the corresp. quinhydrone, green-black cryst., m.p. 114-115° (6), 103° (33).

With acetyl chloride. C with AcCl in s.t. at 160-180° gives (5) 2,3,5,6-tetrachlorohydro-quinone diacetate (cf. 3:4941).

With aniline. [\tilde{C} (1 mole) with aniline hydrochloride (1 mole) in AcOH on boilg. and subsequent partial evapn. (34) cf. (35) gives (66.5% yield (34)) 2,3,5-trichloro-6-anilino-benzoquinone-1,4 [Beil. XIV-137], blue lfts. from hot alc., but without def. m.p. (35).— \tilde{C} with aniline (excess) in alc. (30) (35) or AcOH (35) gives, however, 2,5-dichloro-3,6-dianilinobenzoquinone-1,4 [Beil. XIV-144, XIV₁-(421)], yel.-brown metallic lfts. from C_6H_6 , m.p. 290° (35), 285-290° (30).]

With triphenylphosphine. \bar{C} with 20% soln. of $(C_6H_5)_3P$ in CHCl₃ gives (36) wine-red color; note, however, that a very similar behavior is shown by 2,3,5,6-tetrachlorobenzo-quinone-1,4 ("chloranil").

- 3:4672 (1) Biltz, Giese, Ber. 37, 4016-4017 (1904). (2) Leger, Bull. soc. chim. (4) 3, 581-582 (1908). (3) Knapp, Schultz, Ann. 210, 174-176, 180-181 (1881). (4) Musante, Fusco, Gazz. chim. utal. 66, 647-648 (1936). (5) Graebe, Ann. 146, 22-30 (1868). (6) Conant, Fieser, J. Am. Chem. Soc. 45, 2206-2207 (1923). (7) Bradfield, Cooper, Orton, J. Chem. Soc. 1927, 2858-2859. (8) A. S. Coolidge, M. S. Coolidge, J. Am. Chem. Soc. 49, 101-104 (1927). (9) Sjoström, Svensk Kem. Tid. 48, 121-124 (1936), Cent. 1937, I 58, C.A. 30, 6634 (1936). (10) Valeur, Ann. chim. (7) 21, 496-497 (1900).
- (11) Swietoslawski, Starczewska, J. chim. phys. 22, 399-401 (1925). (12) Morgan, Cooper, J. Soc. Chem Ind. 43-T, 352-354 (1924) (13) Fisher (to Naugatuck Chem. Co) French 740,978, Feb. 3, 1933; Cent. 1933 I 3134, C A. 27, 2845 (1933). (14) Stadeler, Ann. 69, 301, 322 (1849). (15) Stonhouse, Ann. 8uppl. 6, 209-212, 216-219 (1868). (16) Graebe, Ann. 263, 28-30 (1891). (17) Lampert, J. prakt Chem. (2) 33, 382-383 (1886) (18) Erdelyi, Ber. 63, 1201-1202 (1930). (19) Schmitt, Andresen, J. prakt. Chem. (2) 23, 436-437 (1881). (20) Schmitt, Andresen, J. prakt. Chem. (2) 24, 429, 434 (1881).
- (21) Jacobson, Cent 1898, II 36. (22) Orton, Smith, J. Chem. Soc. 87, 395-396 (1905). (23) Réverdin, Crepieux, Ber. 36, 3268 (1903). (24) Carstanjen, Ber. 2, 633 (1869). (25) Woskressenski, J. prakt. Chem. (1) 18, 420 (1839). (26) Conant, J. Am. Chem. Soc. 49, 293-297 (1927). (27) Kvulnes, J. Am. Chem. Soc. 56, 667-670 (1934). (28) Schuloff, Austrian 127,813, April 25, 1932, Cent. 1932, II 924, C.A. 26, 4348 (1932). (29) Levy, Schultz, Ann. 210, 154 (1881) (30) Andresen, J. prakt. Chem. (2) 28, 422-427 (1883).
- (31) Graebe, Ann **146**, 55-59 (1868). (32) Jackson, Grindley, Am. Chem. J. **17**, 653-654 (1895). (33) Ling, Baker, J. Chem. Soc. **63**, 1322-1323 (1893). (34) Brass, Papp, Ber. **53**, 458 (1920). (35) Niemeyer, Ann. **228**, 337-338 (1885). (36) Schonberg, Ismail, J. Chem. Soc. **1940**, 1374-1378.

COOH

3:4675 3-CHLORO-4-HYDROXYBENZOIC C₇H₅O₃Cl Beil. X - 175 ACID Cl Cl X₁— M.P. 169-170° (1) (2) 169° (3) 165-166° (4) 164-165° (5) 164° (6)

Colorless ndls. from aq.; spar. sol. cold but eas. sol. hot aq.; eas. sol. alc., ether; very eas. sol. acetone; spar. sol. C₆H₆, CHCl₃, lgr. — Sublimes undecomposed. [For study of ioniz. const. at 25° see (9).]

[For prepn. of \bar{C} from p-hydroxybenzoic acid (1:0840) with aq. HCl + 30% H₂O₂ (60–90% yield (6)) or in Na₂CO₃ soln. with Cl₂ (100% yield NaĀ (7)), or in AcOH with KClO₃ + HCl (8), or with SbCl₅ on warming (1), see indic. refs.; from 3-amino-4-hydroxybenzoic acid [Beil. XIV-597] via diazotization and use of Cu₂Cl₂ reactn. see (4); from o-chlorophenol (3:5980) in CCl₄ with alc. alk. in s.t. at 125–130° see (5); from methyl 3-chloro-4-hydroxybenzoate (see below) by hydrol. with 40% KOH see (2); from 3-chloro-4-hydroxybenzonitrile (3) via hydrol. with acid see (5).]

C in aq. soln. gives with FeCl₃ a brown ppt. (1).

[C with PCl₅ (2 moles) followed by treatment of the intermediate acid chloride with aq. yields (1) 3,4-dichlorobenzoic acid (3:4925); C on warming with SbCl₅ (2 moles) yields (1) 3,5-dichloro-4-hydroxybenzoic acid (3:4950).]

[For studies of bactericidal actn. of C or its derivatives see (10) (11) (12) (13) (14).]

- 3:4675-3:4680 DIVISION A 420
 - Methyl 3-chloro-4-hydroxybenzoate: ndls. from dil. alc. or lgr., m.p. 107° (2), 106–107° (4). [From C in MeOH with H₂SO₄ (4) or from methyl p-hydroxybenzoate (1:1549) with SO₂Cl₂ (2).] [For reactn. of this prod. with acetobromglucose see (10); for studies of bactericidal power see (11).]

Ethyl 3-chloro-4-hydroxybenzoate: ndls. from dil. alc., m.p. 77-78° (2). [From ethyl p-hydroxybenzoate (1:1534) with SO₂Cl₂ (2); for use as disinfectant see (14).]

- —— 3-Chloro-4-methoxybenzoic acid (3-chloroanisic acid): scales from dil. AcOH, m.p. 214-215° (16), 213° (4) (15), 212-214° (17). [Prepd. indirectly from 3-chloro-4-methoxybenzamide with HNO₂ (15), from 3-chloro-4-methoxytoluene by oxidn. with CrO₃/AcOH (16) or alk. KMnO₄ (17).]
- 3:4675 (1) Lössner, J. prakt. Chem. (2) 13, 432-435 (1876). (2) Mazzara, Gazz. chim. ital. 29, I 385-387 (1899). (3) Biltz, Ber. 37, 4035-4036 (1904). (4) von Auwers, Ber. 30, 1473-1474 (1897). (5) Hasse, Ber. 10, 2192-2194 (1877). (6) Leulier, Pinet, Bull. soc. chim. (4) 41, 1364-1365 (1927). (7) Tishchenko, J. Russ. Phys.-Chem. Soc. 60, 153-162 (1928); Cent. 1928, II 768; C.A. 22, 3397 (1928). (8) Chem. Fabrik von Heyden, Ger. 69,116; Friedländer 3, 847. (9) Coppadoro, Gazz. chim. ital. 32, I 554 (1902). (10) Sabalitschka, Arch. Pharm. 267, 675-685 (1929).

(11) Sabalitschka, Dietrich, Böhn, Pharm. Ztg. 71, 834-836 (1926); Cent. 1926, II 1959; C.A. 20, 3060 (1926). (12) Sabalitschka, Dietrich, Desinfektion 11, 67-71, 94-104 (1926); Cent. 1927, I 2670-2671; C.A. 20, 3712. (13) Sabalitschka, Apoth. Ztg. 43, 670-673 (1928); Cent. 1928, II 271. (14) Sabalitschka, Bohn, Ger. 592,826, Sept. 11, 1930; Cent. 1934, I 3369. (15) Gattermann, Ber. 32, 1118, 1121 (1899). (16) Schall, Dralle, Ber. 17, 2529 (1884). (17) Peratoner, Vitale, Gazz. chim. ital. 28, I 217 (1898).

3:4680 8-CHLORONAPHTHOIC ACID-1

 $\begin{array}{c|c} \text{Cl} & \text{COOH} \\ \hline & & \text{C}_{11}\text{H}_7\text{O}_2\text{Cl} & \text{Beil. IX - 651} \\ \hline & & \text{IX}_{1^-}(276) \end{array}$

M.P. 171-171.5° (1) 170-170.5° (1) 169-170° (2) 168-169° (3) 167-168° (3) 167° (4) (5)

Cryst. from C₆H₆ (2), scales from alc. (4). — Subl. in ndls. (4).

[For prepn. of \bar{C} from naphthalic acid (1:0890) via conv. with Hg(OAc)₂ to anhydro-8-hydroxymercuri-1-naphthoic acid and subsequent reactn. with Cl₂ in AcOH see (1) (3) (6) (7) cf. (8); from 8-aminonaphthoic acid-1 [Beil. XIV-534, XIV₁-(623)] via diazotization and reactn. with CuCN see (4); from α -naphthoic acid (1:0785) with Cl₂ in AcOH contg. I₂ see (4); from 8-nitronaphthoic acid-1 [Beil. IX-653] (3) with SOCl₂ in C₆H₆ (some dichloronaphthostyril also being formed) see (3); from 8-chloro-1-naphthonitrile (see below) by hydrolysis see (9); from 8-chloro-1-naphthoamide (see below) by hydrolysis with AcOH/H₂SO₄ + NaNO₂ see (5) (2).]

 \tilde{C} with Cl₂ in AcOH contg. I₂ yields (4) (1) 5,8-dichloronaphthoic acid-1 [Beil. IX-651], scales from alc., m.p. 186-187° (4) (1).

C with PCl₅ yields (5) 8-chloro-1-naphthoyl chloride (props. not reported).

Č with cold red fumg. HNO₃ yields (10) (11) 8-chloro-5-nitronaphthoic acid-1, lfts. or ndls. from alc., m.p. 227° (10), 225-226° (11). [This prod. with Cu bronze in boilg. toluene for 3 hrs. yields (11) 5-nitronaphthoic acid-1 [Beil. IX-652], m.p. 241-242°.

Salts. CaA₂.2H₂O; ndls. sol. in 42 pts. cold aq. (4).

- Methyl 8-chloro-1-naphthoate: oil, b.p. 188-189° at 16.2 mm. (2). [From C with ethereal diazomethane (2).]
- —— 8-Chloro-1-naphthonitrile: ndls. from MeOH, m.p. 150-151° (9), 145-146° (2), b.p. 200° at 18 mm. (9), 242-244° at 15.5 mm. (?) (2). [From 8-chloronaphthylamine-1 [Beil. XII-1256] via diazotization and reactn. with CuCN (yields: 57% (5), 22% (2)) (9).]
- ---- 8-Chloro-1-naphthoamide: ndls. from alc., m.p. 203.5° (5). [From the nitrile (above) by hydrolysis with AcOH/H₂SO₄ (5).]
- 3:4680 (1) Whitmore, Fox, J. Am. Chem. Soc. 51, 3363-3367 (1929). (2) Bergmann, Hirshberg, J. Chem. Soc. 1936, 334. (3) Rule, Barnett, J. Chem. Soc. 1932, 175-179. (4) Eckstrand, J. prakt. Chem. (2) 38, 150-151 (1888). (5) Kalb, Ber. 47, 1726-1728 (1914). (6) Corbellini, Barbari, Giorn. chim. ind. applicata 15, 335-337 (1933); Cent. 1933, II 2818; C.A. 27, 5737 (1933). (7) Corbellini, Ital. 332,963, May 19, 1934; Cent. 1937, I 2460 (8) Leuck, Perkins, Whitmore, J. Am. Chem. Soc. 51, 1831-1836 (1929). (9) Meisenheimer, Beisswenger, Ber. 65, 32-42 (1932). (10) Eckstrand, J. prakt. Chem. (2) 38, 253-254 (1888).
 - (11) Rule, Pursell, Brown, J. Chem. Soc. 1934, 168-171.

3:4690 2,5-DICHLOROHYDROQUINONE (p-Dichlorohydroquinone) CI Cl C6H4O2Cl2 Beil. VI - 850 VI₁— VI₂-(845)

M.P. 172° (1) (2) 170° (3) 166° (4)

[See also 2,5-dichlorobenzoquinone-1,4 (3:4470).]

Colorless ndls. from boilg. aq., tbls. from C_6H_6 , moclinic pr. from acetone; spar. sol. cold aq., sol. boilg. aq., very eas. sol. alc., ether, or warm AcOH. — Sublimes in ndls.

[For prepn. of \bar{C} from 2,5-dichlorobenzoquinone-1,4 (3:4470) by reductn. with SO₂ see (5); from chlorobenzoquinone-1,4 (3:1100) with hot conc. HCl (83% yield (6)) (4) or in CHCl₃ with HCl gas (4) see indic. refs.; from hydroquinone (1:1590) with HCl + KClO₃ (2) (7), in AcOH or better CHCl₃ with Cl₂ (poor yield together with 2,3-isomer) (6), or in MeOH with Cl₂ (8) see indic. refs.; from chlorohydroquinone (3:3130) with HCl + KClO₃ (68% yield) see (9); from 2,5-dichloro-p-aminophenol (10) by diazotization in H₂SO₄ + ZnSO₄ soln. and hydrolysis of the diazonium salt (10).]

[For use of \bar{C} as an antioxidant and gum inhibitor in cracked gasoline see (11); for use in aq. petroleum emulsion as insecticidal oil spray see (12); for use as vulcanization accelerator see (19).]

 \tilde{C} on oxidn. with $K_2Cr_2O_7$ or $Na_2Cr_2O_7 + dil$. H_2SO_4 (7) (2) (9) (13) (14) or even with conc. HNO₃ at ord. temp. (4) yields 2,5-dichlorobenzoquinone-1,4 (3:4470) q.v. — [For studies of oxidn.-reductn. potential of system \tilde{C} + corresp. quinone see (9) (15) (16).]

- **D 2,5-Dichlorohydroquinone diacetate:** colorless ndls. from dil. alc., m.p. 141° (4) (17). [From \bar{C} with Ac₂O (4) or from 2,5-dichlorobenzoquinone-1,4 (3:4470) in Ac₂O + AcOH with Zn dust (17).]
- **② 2,5-Dichlorohydroquinone dibenzoate:** colorless wooly ndls. from CS₂, m.p. 185° (4). [From \bar{C} on refluxing with BzCl (4).]
- 2,5-Dichlorohydroquinone dimethyl ether: colorless ndls., m.p. 126° u.c. (17), 125-127° (6), b.p. 261-263° u.c. at 744 mm. (16). [From \(\tilde{C}\) in dil. aq. NaOH on shaking with Me₂SO₄ (63% yield (6)), or from hydroquinone dimethyl ether in AcOH with Cl₂ (17) (18).] [This prod. with fumg. HNO₃ in cold does not nitrate but oxidizes to 2.5-dichlorobenzoquinone-1,4 (3:4470) (17).]

3:4690 (1) Krafft, Ber. 10, 800 (1877). (2) Ling, J. Chem. Soc. 61, 558 (1892). (3) Fels, Z. Krist. 37, 481 (1903). (4) Levy, Schultz, Ann. 210, 148-150 (1881). (5) Stadler, Ann. 69, 312-318 (1849). (6) Eckert, Endler, J. prakt. Chem. (2) 104, 83-84 (1922). (7) Hammick, Hampson, Jenkins, J. Chem. Soc. 1938, 1264. (8) Plazek, Rocznki Chem. 10, 761-776 (1930), Cent. 1931, I 1428; C.A. 25, 1504 (1931). (9) Conant, Fieser, J. Am. Chem. Soc. 45, 2205-2206 (1923). (10) Skraup, Steinruck (to Rheinische Kamfer-Fabrik), Ger. 431,513, July 10, 1926; Cent. 1926, II 1462.

(11) Clarke, Towne (to Texas Co), U.S. 2,023,871, Dec. 10, 1935; Cent. 1936, I 2671; C.A. 30, 851 (1936). (12) Yates (to Shell Development Co), U.S. 1,778,240, Oct 14, 1930; Cent. 1931, 1 2799; C.A. 24, 5928 (1930). (13) Kehrmann, Grab, Ann. 303, 12-14 (1898). (14) Hantzsch, Schniter, Ber. 20, 2279-2282 (1887). (15) Hunter, Kvalnes, J. Am. Chem. Soc. 54, 2874-2875, 2878 (1932). (16) Kvalnes, J. An. Chem. Soc. 56, 667-670 (1934). (17) Kohn, Gurewitsch, Monatsh. 56, 135-136 (1930). (18) Habermann, Ber. 11, 1034-1035 (1878). (19) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933, Cent. 1933, II 3134

Colorless ndls. from aq. alc., dil. AcOH or C_6H_6 ; eas. sol. hot aq.; eas. volatile with steam. [For prepn. of \bar{C} from 4-chloro-1,2-dimethylbenzene (3:8675) by oxidn. with boilg. dil. HNO₃ (D=1.20) (7) or with 20 pts. dil. HNO₃ (D=1.10) in s.t. at 160° for 5-6 hrs. (8) (by this method \bar{C} is always accompanied by the isomeric 5-chloro-2-methylbenzoic acid (3:4670) separable by its less sol. calcium salt (1) (8) (7)) see indic. refs.; from 4-chloro-2-methylbenzaldehyde [Beil. VII-296] by air oxidn. see (4); from chloromethyl 4-chloro-2-methylphenyl ketone (4-chloro-2-methylphenacyl chloride) [Beil. VII-306] by oxidn. with KMnO₄ see (2); from β -chloro-2-methyl 4-chloro-2-methylphenyl ketone (5) by oxidn. at 100° with mixt. of equal pts. conc. HNO₃ and aq. see (5); from 4-chloro-2-methylbiphenyl (3) by oxidn. with $CrO_3/AcOH$ (8% yield) see (3); from 1-methyl-1-(trichloromethyl)cyclohexadiene-2,5-one-4 [Beil. VII-149] by treatment with PCl₅ giving 4-chloro-2-methylbenzotrichloride, followed by alk. hydrolysis of the latter, see (9); from 4-chloro-2-methylbenzonitrile, m.p. 67° (1) (10), by boilg. for 16 hrs. with 8% aq. KOH sec (1) (10).]

 \bar{C} on oxidn. with alk. KMnO₄ (7) or with 10-20 pts. dil. HNO₃ (D=1.13) in s.t. at 180-200° for 5 hrs. (1) yields 4-chlorophthalic acid (3:4390).

Č fused with KOH yields (7) 4-hydroxy-2-methylbenzoic acid [Beil. X-215], m.p. 172-173° (7).

Salts. NH₄ \bar{A} , cas. sol. aq.; K \bar{A} .H₂O, very eas. sol. aq.; Ca \bar{A}_2 .3H₂O more sol. in aq. than corresp. salt of 5-chloro-2-methylbenzoic acid (3:4670); Ba \bar{A}_2 .4H₂O, more eas. sol. aq. than calcium salt (for details see (1)).

- --- Methyl 4-chloro-2-methylbenzoate: unrecorded.
- Ethyl 4-chloro-2-methylbenzoate: oil, b.p. 258° (1), $D_4^{20} = 1.1626$ (10), $n_{\rm He}^{20} = 1.52705$ (10). [From $\bar{\rm C}$ in EtOH with HCl gas (1) or from the amide (see below) with ethyl nitrite in s.t. at 140° for 4-5 hrs. (1).]
- —— 4-Chloro-2-methylbenzamide: colorless ndls. from hot aq., from alc. or ether, m.p. 183° (1). [Obtd. indirectly by partial sapon. of corresp. nitrile (above) (1).]
- 3:4700 (1) Claus, Stapelberg, Ann 274, 287-291 (1893).
 (2) Kunckell, Ber. 41, 2648 (1908).
 (3) Huntress, Seikel, J. Am Chem Soc. 61, 820 (1939).
 (4) von Auwers, Keil, Ber. 38, 1696 (1905).
 (5) Mayer, Muller, Ber. 60, 2281 (1927).
 (6) Mayer, Albert, Schon, Ber. 65, 1295-1299 (1932).
 (7) Kruger, Ber. 18, 1757 (1885).
 (8) Claus, Bayer, Ann. 274, 308 (1893).
 (9) von Auwers, Julicher, Ber. 55, 2167-2168, 2179-2180 (1922).
 (10) von Auwers, Harres, Z. physik. Chem. A-143, 15-16, 18 (1929).

M.P. 172° (1) B.P. 180° at 26 mm. (1) 174° (2)

[See also naphthalene tetrachloride (3:4750)]

Cryst, from AcOH.

[For prepn. of $\bar{\mathbb{C}}$ from 1,2,3,4-tetrahydronaphthalene (tetralin) (1:7550) with $\mathbb{C}l_2$ in pres. of \mathbb{I}_2 (15% yield (2)) at 15° in diffuse daylight see (1) (2); for forms, in small amt. from tetralin during prepn. of 7-chloro-1,2,3,4-tetrahydronaphthalene (β -chlorotetralin) with $\mathbb{C}l_2$ in pres. of \mathbb{I}_2 at 10° see (1).]

 \bar{C} with $2Br_2$ in boilg. CS_2 yields (1) 1,2-dibromo-5,6,7,8-tetrachloronaphthalene [Beil. V_2 -(388)], m.p. 142° (1), which with alc. (?) NaOEt gives (alm. quant. yield (1)) 1,2,3,4-tetrachloronaphthalene [Beil. V_2 -(446)], m.p. 198°.

3:4703 (1) von Braun, Ber. 56, 2337 (1923). (2) Wynne, J. Chem. Soc. 1946, 61.

3:4704 3-CHLORONAPHTHOQUINONE-1,2 (3-Chloro-β-naphthoquinone) Cl C₁₀H₅O₂Cl Beil. VII-72C

M.P. 172° (1) (2) (3)

Red ndls. from CHCl3. — Sol. hot alc., AcOH, C6H6, CHCl3.

[For prepn. of \bar{C} from β-naphthol (1:1540) by conversion with Cl₂ in AcOH (2) to 1,1,3,4-tetrachloro-2-keto-1,2,3,4-tetrahydronaphthalene [Beil. VII-371] (lfts. of monohydrate from aq., m.p. 90-91°; anhydrous lfts. or ndls. from hot lgr., m.p. 101-103°)

followed by treatment with aq. Na₂CO₃ (2) (3) (overall yield of \bar{C} is 56% (4)). — For prepn. of \bar{C} from naphthoquinone-1,2 (1:9062) with Cl₂ in AcOH (1) (5), or from 1,3-dichloronaphthol-2 (3:1990) by oxidn. with conc. HNO₃ in AcOH (3), see indic. refs.]

C on reduction with SO₂ in AcOH gives (1) 3-chloro-1,2-dihydroxynaphthalene [Beil.

VI-975], colorless ndls., m.p. 116-117° (1).

[Č on oxidn. with aq. Ca(OCl)₂ undergoes rupture of the quinoid ring and a subsequent series of changes (5) resulting in formation of (phthalidyl-3)-dichloroacetic acid [Beil. XVIII-419], this. of monohydrate from aq., anhydrous ndls. from C₆H₆, m.p. 157°, accompanied by some 2,2-dichloroindandione-1,3 [Beil. VII-696, VII₁-(375)], m.p. 124-125°.]

[C although insol. in aq. Na₂CO₃ gradually dissolves in dil. aq. alkali with conversion (1) to 3-chloro-2-hydroxy-naphthoquinone-1,4 (3-chloro-4-hydroxynaphthoquinone-1,2) [Beil. VIII-304], yel. ndls. from alc., m.p. 215°.]

[C with alc. NH₃ on htg. gives (1) 3-chloro-2-hydroxynaphthoquinone-1,4-imine-4 (3-chloro-4-aminonaphthoquinone-1,2) [Beil. VIII-305], m.p. abt. 260°.]

[Č with alc. aniline on htg. similarly gives (1) 3-chloro-2-hydroxynaphthoquinone-1,4-anil-4 (3-chloro-4-anilino-naphthoquinone-1,2) [Beil. XII-225], yel. ndls. from AcOH, m.p. 253°.]

Č with 2,3,-dimethylbutadiene-1,3 (1:8050) in spec. purified CHCl₃ in s.t. at 100° in dark for 1 hr. readily forms (70% yield (4)) a Diels-Alder type adduct C₁₆H₁₅O₂Cl, lemonyel. ndls. from ether/pet. ether, m.p. 87-88°; this adduct is unstable even at 10° and in alc. or ether soln. on shaking with air loses HCl and is oxidized (by loss of 2 hydrogen atoms) giving (87% yield (4)) 2,3,-dimethylphenanthraquinone, m.p. 237-238° u.c., 242-243° cor. (4). — For study of reaction of Č with excess 2,3-dimethylbutadiene-1,3 (1:8050) giving 36% yield of a halogen-free prod. of m.p. 135° see (6).

3:4764 (1) Zincke, Ber. **19,** 2497 (1886). (2) Zincke, Kegel, Ber. **21,** 3550-3552 (1888). (3) Zincke, Kegel, Ber. **21,** 3380, 3386 (1888). (4) Fieser, Dunn, J. Am. Chem. Soc. **59,** 1019-1020 (1937). (5) Zincke, Schmidt, Ber. **27,** 737-739 (1894). (6) Fieser, Dunn, J. Am. Chem. Soc. **59,** 1021-1024 (1937). (7) Zincke, Schmunk, Ann. **257,** 140-145 (1890).

3:4705 5-CHLORO-2-HYDROXYBENZOIC COOH $C_7H_5O_3Cl$ Beil. X - 102 X₁-(47) (5-Chlorosalicylic acid)

M.P. [176°	(1)]	M.P. (contd.)	171-172.5°	(10)
173°	(2)		170-171°	(11)
172.5°	(3)		168°	(12) (13)
172-173°	(4)		167.5°	(14) (15) (16)
172°	(5) (6) (7) (8) (9) (22) (27)		167-168°	(17) (18) (19)

Colorless ndls. from aq. or alc.; sol. in 1100 pts. aq. at 20° and in 80 pts. aq. at 100° (17); eas. sol. alc., ether, C_6H_6 , CHCl₃, AcOH; spar. sol. lgr. — Yolatile with steam (12). — Shows sternutatory props.

[For prepn. of \tilde{C} from p-chlorophenol (3:0475) in CCl₄ with aq. NaOH (very small yield (15)) in pres. of Cu (19) or in CCl₄ with alc. KOH in s.t. at 140° for 5-6 hrs. (17) see indic. refs.; from dry sodium p-chlorophenolate with CO₂ at 140-150° under press. see (12) (20); from salicylic acid (1:0780) with Cl₂ in CS₂ (65% yield (38)) (3), in MeOH (21) or EtOH (22) (much 3,5-dichlorosalicylic acid (3:4935) also being formed), in AcOH (85%)

yield (4)) or in nitrobenzene at 50-60° (23), or with $C_6H_5ICl_2$ in suitable solvents (89% yield (2)), or by htg. with $SbCl_5$ (14), or with HCl + 30% H_2O_2 (56-66% yield (6)), see indic. refs.; from mono K salicylate in aq. with Cl_2 (24) or from di-potassium salicylate with KOCl (1) (much 3,5-dichlorosalicylic acid (3:4935) being also formed) see indic. refs.]

[For prepn. of \bar{C} from 5-chloro-2-aminobenzoic acid (5-chloroanthranilic acid) [Beil. XIV-365] with nitrous acid at 50° see (11); from 5-amino-2-hydroxybenzoic acid (5-amino-salicylic acid) [Beil. XIV-579, XIV₁-(650)] via diazotization and use of Cu₂Cl₂ reactn. (62-71% yield (16)) (25) see indic. refs.; from 5-chloro-2-hydroxybenzonitrile [Beil. X-104] by hydrolysis with H₂SO₄ see (13); from ethyl 5-chloro-2-hydroxybenzoate (see below) by hydrolysis with KOH see (7) (25); from 5-chloro-2-methoxybenzoic acid (see below) by cleavage with conc. HI see (10); from chloral-5-chlorosalicylamide (see below) by hydrolysis with 10% NaOH see (26); from 5-chlorosalicylin by oxidn. with K₂Cr₂O₇ + H₂SO₄ (18) or with KMnO₄ followed by acid hydrolysis (9) see indic. refs.; from 6-chloro-2,3-dimethyl-chromone (27), 6-chloro-2,3-diphenylchromone (28), or 7-chloro-1,2,3,4-tetrahydroxanthone (5) by alk. hydrol. see indic. refs.]

[For use of various esters of \bar{C} as mothproofing agents (29), as insecticides (30), or as plasticizers (31) (32) see indic. refs.; for studies of bactericidal power of \bar{C} see (33) (34); for study of fate of \bar{C} in animal body see (35).]

[\bar{C} on electrolytic reduction in aq. alc. H_2SO_4 yields (36) 5-chloro-2-hydroxybenzyl alcohol [Beil. VI-893], m.p. 93° (36); \bar{C} on reductn. with Na/Hg as directed (16) yields 5-chloro-2-hydroxybenzaldchyde (3:2800).]

[Č with PCl₅ (37) in lgr. (38) yields 4-chloro-2-chloroformylphenylphosphoryl dichloride, Cl.CO.C₆H₃Cl.O-P(O)Cl₂ [Beil. X-103], oil, b.p. 183-184° at 13 mm. (38); Č with PCl₃ yields (38) 4-chloro-2-chloroformylphenyl metaphosphite, Cl.CO.C₆H₃Cl.O-P:O [Beil. X-103], m.p. abt. 55-57°, b.p. 155-156° at 14 mm. (38).]

 $[\bar{C} \text{ with ClSO}_3H \text{ at } 50-70^\circ \text{ yields } (39) \text{ 3-chlorosulfonyl-5-chloro-2-hydroxybenzoic acid} [Beil. XI_1-(106)], pr. from <math>\Lambda cOH$, m.p. $206-207^\circ$ (39).]

[C with HNO₃ + conc. H₂SO₄ at 0° (23), or C on warming with fumg. HNO₃ (22), or C in AcOH treated with 5 pts. fumg. HNO₃ in AcOH (40), yields 5-chloro-3-nitrosalicylic acid [Beil. X-120], pale yel. ndls., m.p. 162–163° (22); note that by loss of CO₂ and further nitration 4-chloro-2,6-dinitrophenol [Beil. VI-260, VI₁-(128)], yel. ndls. from aq., m.p. 80° (22), is also formed.]

[\bar{C} in alc. with I_2 + HgO gives (41) 5-chloro-x-iodo-salicylic acid, colorless ndls. from hot dil. alc., m.p. 224° sl. dec. (41); \bar{C} in alk. with I_2/KI yields (25) by loss of CO₂ and further iodination 4-chloro-2,6-diiodophenol [Beil. VI₁-(112)], yellowish ndls. from alc., m.p. 108° (25) (ethyl ether, m.p. 69°, acetate, m.p. 127.5° (25)).]

Č in aq. soln. gives with FeCl₃ a violet coloration.

Salts. LiĀ, 2H₂O (8); NaĀ (8) (12), KĀ (8) all eas. sol. aq.; CaĀ₂.3H₂O (14), BaĀ₂.3H₂O (11) (12) (14) (17) (18) see indic. refs.; PbĀ₂ (11), AgĀ (12) (18), insol. aq.

- Methyl 5-chloro-2-hydroxybenzoate (methyl 5-chlorosalicylate): ndls. from alc., m.p. 50° (1), 48° (7) (12), b.p. 249° sl. dec. (12). [From C in MeOH with HCl gas (12), or from AgA with MeI (1): also from methyl salicylate (1:1750) by chlorination with methyl N.N-dichlorocarbamate in AcOH (44).]
- Ethyl 5-chloro-2-hydroxybenzoate (ethyl 5-chlorosalicylate): ndls. from alc., m.p. 25° (7). [From ethyl salicylate (1:1755) with SO₂Cl₂ (7).]
- 5-Chloro-2-methoxybenzoic acid: ndls. from aq., m.p. 82° (42), 81-82° (10), 80-81°
 (4). [Obtd. indirectly from 2-methoxybenzoic acid (1:0685) in AcOH with Cl₂ (4), or from 5-chloro-2-methoxybenzonitrile by alk. hydrolysis (43).]

- **D** 5-Chloro-2-ethoxybenzoic acid: lfts. from dil. alc., m.p. 118° (7).
- **5-Chloro-2-acetoxybenzoic acid:** cryst. from C₆H₆, m.p. 149° (8), 148° (42), 142° (25). [From $\tilde{\mathbf{C}}$ with AcCl (42),]
- 5-Chloro-2-hydroxybenzamide: Ifts. from alc. or C₆H₆, m.p. 226-227° (26) (13), 223.5-224° (7), 222-223° (8). [From methyl or ethyl 5-chlorosalicylates (above) with alc. NH₃ (7).] [This amide with chloral (3:5210) gives on warming (26) chloral-5-chloro-2-hydroxybenzamide, ndls. from C₆H₆, m.p. 148-149° dec. (26).]
- 3:4705 (1) Lassar-Cohn, Schultze, Ber. 38, 3800 (1905). (2) Neu, Ber. 72, 1511 (1939). (3) Hübner, Brenken, Ber. 6, 174 (1873). (4) Hirwe, Rana, Gavankar, Proc. Indian Acad. Sci. A-8, 211-212 (1938). (5) Hall, Plant, J. Chem. Soc. 1933, 234. (6) Leulier, Punet, Bull. soc. chim. 44, 1363 (1927). (7) Mazzara, Gazz. chim ital. 29, I 340-347 (1899). (8) Smith, Ber. 11, 1226-1227 (1878). (9) van Wawen, Arch. Pharm. 235, 567-568 (1897). (10) Peratoner, Condorelli, Gazz. chim. ital. 28, I 211-212 (1898).

(11) Hübner, Weiss, Ber. 6, 175 (1873). (12) Varnholt, J. prakt. Chem. (2) 36, 19-22 (1887). (13) Biltz, Stepf, Ber. 37, 4026-4027 (1904). (14) Bellstein, Ber. 8, 816 (1875); Ann. 179, 285 Note 2 (1875). (15) Sen, Ray, J. Indian Chem. Soc. 9, 176 (1932). (16) Weil, Traun, Marcel, Ber. 55, 2664-2665 (1922). (17) Hasse, Ber. 10, 2190-2192 (1877). (18) Visser, Arch. Pharm. 235, 549-550 (1897). (19) Zeitner, Landau, Gor. 258,887, April 17, 1913, Cent. 1913, I 1641-1642. (20) Chem. Fabrik von Heyden, Ger. 33,635, May 10, 1885, Freedlander 1, 234 (1877)87).

(21) Plazek, Roczniki Chem 10, 761-776 (1930); Cent. 1931, I 1428, C.A. 25, 1504 (1931). (22) Smith, Peirce, Am. Chem. J. 1, 176-181 (1879/80); Ber 13, 34 36 (1880). (23) B.A.S.F., Ger. 137,118, Nov. 20, 1902, Cent. 1902, HI 1439-1140. (24) Cahours, Ann. chim. (3) 13, 108-111 (1845), Ann. 52, 341-342 (1844). (25) Brennans, Girod, Compt. rend 186, 1553-1555 (1928). (26) Hirwe, Rana, Ber. 72, 1351-1352 (1939). (27) Simonis, Schuhmann, Ber. 50, 1144-1145 (1917). (28) Wittig, Ann. 446, 190 (1925). (29) I G, Brit 274,425, Sept. 7, 1927; French 635,973, March 29, 1928, Cent. 1929, I 434 (30) I.G, French 702,768, April 16, 1931; Cent. 1931, II 3530, Austrian 125,712, Dec. 10, 1931; Cent. 1932, I 2886.

(31) Grether, DuVall (to Dow Chem. Co.), U.S. 2,198,883, April 23, 1940; C.A. 34, 5965 (1940).
(32) Grether, DuVall (to Dow Chem. Co.), U.S. 2,234,374, March 11, 1941, C.A. 35, 3738 (1941).
(33) Delauney, J. pharm. chim. (8) 25, 254-266, 545-560 (1937). (8) 26, 177-216 (1937). Cent. 1938, I 2019.
(34) Rochaix, Pinet, Bull. sci. pharmacol. 34, 486-487 (1927), Cent. 1927, II 2684; C.A. 22, 443 (1928).
(35) Girod, J. pharm. chim. (8) 9, 513-520 (1929); Cent. 1929, II 1815; C.A. 24, 163 (1930).
(36) Mettler, Ber. 39, 2939 (1906).
(37) Akt. Ges. für Anillinfabrikation, Ger. 89,556; Friedlander, 4, 156 (38) Anschutz, Anspach, Ann. 346, 318-323 (1906).
(39) Bayer and Co., Ger. 264,786, Sept. 23, 1913; Cent. 1913, II 1350.
(40) Ref. 38, pp. 338-339.

(41) Smith, Knerr, Am. Chem. J. 8, 95-96 (1886).
(42) Anschutz, Ann. 367, 263 (1999).
(43) Brand, Pabst, J. prakt. Chem. (2) 120, 207-208 (1928).
(44) Bougault, Chabrier, Compt. rend. 213, 400-402 (1941); Chabrier de la Saulniere, Ann. chim. (11) 17, 353-370 (1942); C.A. 38, 3255 (1944).

3:4707 3,5,6-TRICHLORO-2,4-DIMETHYL-PHENOL

(Trichloro-m-4-xylenol)

$$\begin{array}{cccc} \text{OH} & \text{C}_8\text{H}_7\text{OCl}_3 & \textbf{Beil. VI} & -\\ \text{Cl} & & \textbf{VI}_1 -\\ \text{Cl} & & \textbf{VI}_2 - (\textbf{460}) \end{array}$$

M.P. 174° (1)

Pale yellowish ndls.

[For prepn. of C from 3,5,6-trichloro-2,4-dimethylaniline (1) via diazotization and hydrolysis (yield not stated) see (1).]

[For prepn. of basic Hg and Bi derivs. see (1).]

- **3.5,6-Trichloro-2,4-dimethylphenol methyl ether:** m.p. 91.5° (1). [From \bar{C} with $Me_2SO_4 + aq. alk. (1).]$
- 3,5,6-Trichloro-2,4-dimethylphenol ethyl ether: m.p. 53.5° (1).
- 3,5,6-Trichloro-2,4-dimethylphenyl acetate: m.p. 86° (1).
- --- 3,5,6-Trichloro-2,4-dimethylphenyl benzoate: unreported.

3:4707 (1) Bures, Borgmann, Časopis Českoslov. Lékárnictva, 7, 270-280 (1927); Cent. 1928 I 1171, C.A. 22, 4503 (1928).

3:4709 3,4,6-TRICHLORO-2,5- OH
$$C_8H_7OCl_3$$
 Beil. VI — VI₁— VI₂-(467)

M.P. 175° (1)

Pale greenish ndls. from alc, Λ cOH, or pet eth. or by sublimation — Readily sol. in ether, C_6H_6 , or CHCl₃; less sol alc. or other org solvents; insol aq. — Volatile with steam. [For prepn. of \bar{C} from 3,4,6-trichloro-2,5-dimethylaniline (1), via diazotization and hydrolysis (yield not stated), see (1).]

[For conversion of C to basic Hg or Bi derive see (1)]

- (1) 3,4,6-Trichloro-2,5-dimethylphenol methyl ether: yellowish ndls from dil. alc. or pet. ether, m.p. 91° (1) [From C with Me₂SO₄ + hot aq. alk (1).]
- 3,4,6-Trichloro-2,5-dimethylphenol ethyl ether: alm colorless cryst, m.p. 79° (1). [From \ddot{C} with Et_2SO_4 + hot aq. alk. (1).]
- 3,4,6-Trichloro-2,5-dimethylphenyl acetate: pr. from alc. + other, m.p. 103° (1). [From \ddot{C} with $\Lambda c_2 O$ (10 pts.) + trace of $H_2 SO_4$ on htg (1)]
- 3,4,6-Trichloro-2,5-dimethylphenyl benzoate: hexag. pr. from alc. or pet. ether, m.p. 101° (1). [From C with benzoyl chloride + aq alk. (1).]

3:4709 (1) Bures, Rubes, Collectron Czechoslov Chem. Commun. **1**, 648–657 (1929), C.A. **24**, 1851 (1930) also in Časopis Českoslov. Lékárnictva, **8**, 225–231, 258–264 (1928), Cent. **1929**, I 506–507; C.A. **23**, 3674 (1929).

3:4711 $d,l-\alpha,\alpha'$ -DICHLOROSUCCINIC COOH $C_4H_4O_4Cl_2$ Beil. II - 619 II_1 -(267) II_2 -(557) isodichlorosuccinic acid) Cl-C-H

[See also meso-\alpha,\alpha'-dichlorosuccinic acid (3:4930).]

Cryst. from ether + pet. ether. - \bar{C} is much more sol. aq. than its meso stereoisomer; e.g., 100 cc. satd aq. soln of \bar{C} at 0° conts. 64.0 g. \bar{C} (8); \bar{C} is eas. sol ether, less so in alc. [For prepn. of \bar{C} from disodium salt of fumaric acid (1:0895) with Cl₂ in satd. NaCl soln. in dark or diffuse daylight at 5° (yields: 75% (7), 68% (11), 30% (1)) (11) (9) see indic. refs. (note that as a side reactn. some addn. of HOCl also occurs leading to as much as 13% (9) chloromalic acid, and that under some (capricious) circumstances the reactn. yields as much as 80% (9) of the meso stereoisomer (3:4930)); from maleic anhydride (1:0625) in CCl₄ by addn. of Cl₂ in sunlight followed by hydrolysis see (12) (9); from d_1l - d_2 - d_1l -

dichloride [Beil. VII-573] (13) or toluquinone dichloride [Beil. VII-576] (13) by oxidn. with aq. KMnO₄ (or BaMnO₄) at 0° see (3); from $d_1 l_{-\alpha,\alpha'}$ -dichlorosuccinyl (di)chloride (3:0395) by aq. hydrolysis see (14).]

C behaves as a normal dibasic acid: titration with standard dil. aq. alk. gives Neut. Eq. 93.5. — For study of acid strength $(K_1 = 372.0 \times 10^{-4} \text{ at } 16^\circ; K_2 = 18.0 \times 10^{-4} \text{ at}$ 16.7° (8) cf. (15); for study of conductivity see (4).

[Salts (of metals): $(NH_4)_2\bar{A}.2H_2O$ (10), $K_2\bar{A}.H_2O$ (6), $KH\bar{A}.2H_2O$ (6), $CaA.2\frac{1}{2}H_2O$ (10), Ba7.7H₂O (10), CuA.2½H₂O (10), all eas. sol. aq.; SrA.7H₂O (10), sol. in 15 pts. aq.; $Pb\overline{A}.3H_2O$ (10) spar. sol. aq.]

C on boilg, with aq. (12) or with aq. KOH (7) (6) or aq. acid (6) loses 1 HCl yielding chlorofumaric acid (3:4853); for study of rate at 25° see (7) (16).

 $[K_2\bar{A}]$ in aq. soln. maintained at neutrality at 100° yields mainly (6) d_il-tartaric acid (1:0550).1

 \bar{C} with PCl₅ (2 moles) gives (100% yield (14)) $d_i l_i - \alpha_i \alpha'$ -dichlorosuccinvl (di)chloride (3:0395), m.p. 39°.

- Dimethyl $d_{sl}-\alpha_{s}\alpha'$ -dichlorosuccinate: m.p. 43° (see 3:0485).
- Diethyl $d_{l}-\alpha_{l}\alpha'$ -dichlorosuccinate: oil (see 3:9578).
- Acid salt of \bar{C} with $d_i l$ - α -phenylethylamine: pr. from aq., m.p. 149–150°, rap. htg. (6); satd. aq. soln. at 25° conts. 18.67 g./liter (6). [For details of resolution of \bar{C} with opt. act. α -phenylethylamine see (6) (1); note incidentally that, although m.p. of C is 175°, the m.p. of each of the opt. act. stereoisomeric forms is lower, viz., 166-167° dec. (6), 168° (1).]
- 3:4711 (1) Timmermans, van Lancker, Jaffe, Bull. soc. chim. Belg. 48, 39-46, 63 (1939). (2) Kuhn, Zumstein, Ber. 59, 485 (1926). (3) Dimroth, Eber, Wehr, Ann. 446, 136-137, 145-146 (1926). (4) Michael, Bunge, Ber. 41, 2912 (1908). (5) Aminoff, Arkıv Kemi, Mineral., Geol., 7, No. 9, 5 (1918); Cent. 1919, III 319; C.A. 14, 2119 (1920). (6) Holmberg, Arkıv Kemi, Mineral., Geol. 8, No. 2, 33 (1920); Cent. 1921, I 830; C.A. 16, 2116 (1922). (7) Robinson, Lewis, J. Chem. Soc. 1933, 1260-1262. (8) Kuhn, Wagner-Jauregg, Ber. 61, 484, 487-497 (1928). (9) Kuhn, Wagner-Jauregg, Ber. 61, 501, 518-521 (1928). (10) van der Riet, Ann. 280, 219-222 (1894). (11) Terry, Eichelberger, J. Am. Chem. Soc. 47, 1068, 1076-1077 (1925). (12) Michael, Tissot, J. prakt. Chem. (2) 46, 392-393 (1892). (13) Clark, Am. Chem. J. 14, 556-557, 567-568
- (1892). (14) Lutz, J. Am. Chem. Soc. 49, 1110 (1927). (15) Holmberg, J. prakt. Chem. (2) 84, 164-165 (1911). (16) Holmberg, Z. physik. Chem. 79, 165-167 (1912).

3:4713 2,4,6-TRICHLORO-3,5-DIMETHYLPHENOL

(Trichloro-m-5-xylenol)

Beil. S.N. 529

C₈H₇OCl₃

428

M.P. 177-178° 175-177° (2) (4)

Yellow ndls. from lt. pet.

[For prepn. of C from 3,5-dimethylphenol (m-5-xylenol) (1:1455) with Cl₂ in hot CCl₄ (87% yield (1)) or by action of ClSO₃H + conc. HCl + H_2O_2 (2) see indic. refs.: for form. of C from 3,5-dimethylphenol-2,4-bis-(sulfonyl chloride) (2) by preliminary KOH hydrolysis followed by action of conc. $HCl + 30\% H_2O_2$ see (2) cf. (4).

C with fumg. HNO3 is oxidized (64% yield (1)) to 2,6-dichloro-3,5-dimethylbenzoquinone-1.4 (3,5-dichloro-m-xyloquinone), yel. lfts., m.p. 177-178° (1), 178° u.c. (3).

[C with NaNO₂ in AcOH at room temp. gives (48% yield (1)) of a mol. cpd. contg. 2 moles $\ddot{C}+1$ mole of 2,6-dichloro-3,5-dimethylbenzoquinone-1,4 (above), crimson cubes from CCl₄, becoming yellow at 118-119° without melting, but fusing slowly from 133-164° (1).]

3:4713 (1) Raiford, Kaiser, J. Org. Chem. 4, 565, 567 (1939). (2) Katscher, Lehr, Monatsh. 64, 239-240 (1934). (3) Claus, Runschke, J. prakt. Chem. (2) 42, 124 (1890). (4) Lehr, Anilin Farben-Ind. (Russ.) 4, 77-84 (1934); Cent. 1935, I 1365; not in C.A.

M.P. 178° (1)

Ndls. from dil. alc.

[For formn. of \bar{C} (in very small yield) from 5-chloro-1,3-dimethylcyclohexadiene-3,5 (5-chloro-1,2-dihydro-m-xylene) [Beil. V-119, V₁-(64)] by oxidn. with boilg. 30% HNO₃ see (1).]

·Č on oxidn. with KMnO₄ gives (1) 5-chlorobenzenedicarboxylic acid-1,3 (5-chloroisophthalic acid) (3:4960), m.p. 278° (1), together with a little 5-hydroxybenzenedicarboxylic acid-1,3 (5-hydroxyisophthalic acid) [Beil. X-504, X₁-(257)], m.p. 288°.

COOH

3:4715 (1) Klages, Knoevenagel, Ber. 28, 2045-2046 (1895).

3:4720 6-CHLORO-3-HYDROXYBENZOIC Cl C₇H₅O₃Cl Beil. X-143 X₁— M.P. 178-179° (1) 178° (2) (6) 177-178° (3) 176-177° (3) 175° (4) 169-170° (5)

Colorless cryst. from aq. [Ioniz. const. of \bar{C} at $25^{\circ} = 1.40 \times 10^{-3}$ (6)].

[For prepn. of \bar{C} from 6-chloro-3-aminobenzoic acid [Beil. XIV-412, XIV₁-(565)] via diazotization and boilg with aq. (yield: 60–70% (4) 10% (3)) see indic. refs.; from 6-amino-3-hydroxybenzoic acid [Beil. XIV-591] via diazotization and use of Cu₂Cl₂ (?) see (1); from 6-chloro-3-hydroxytoluene (3:1535) via conv. with POCl₃ to 4-chloro-3-methylphenylphosphoric acid, oxidn. with KMnO₄ to 4-chloro-3-carboxyphenylphosphoric acid, and finally acid hydrolysis to \bar{C} see (3); for formn. of \bar{C} from methyl ether of \bar{C} (see below) by cleavage with HI see (5), from ethyl ester of \bar{C} (see below) by hydrolysis with 35% KOH see (2); from m-hydroxybenzoic acid (1:0825) with Cl₂ in MeOH (7) or in AcOH (1) see indic. refs [

- [C on distn. with Ba(OH)₂ yields (5) p-chlorophenol (3:0475).]
- [\bar{C} with cinnamic acid (1:0735) in conc. H_2SO_4 + a few drops fumg. H_2SO_4 (18% SO_3) gives (29% yield (3)) anthracoumarin, golden-yel. ndls. from AcOH or by sublimation, m.p. 274° (3).]
 - Methyl 6-chloro-3-hydroxybenzoate: tbls. from dil. alc., m.p. 100° (2). [From C in MeOH with conc. H₂SO₄ (2).]

- Ethyl 6-chloro-3-hydroxybenzoate: not specifically characterized. [For formn. (together with the isomeric ethyl 2-chloro-3-hydroxybenzoate) from ethyl m-hydroxybenzoate (1:1471) by actn. of SO₂Cl₂ see (2).]
- 6-Chloro-3-methoxybenzoic acid: ndls. from AcOH, m.p. 173.5° (9), 170-171° (2) (8). [Prepd. indirectly from methyl ester (above) with McI + McOH/KOH, followed by hydrolysis with 35% KOH; also from 6-chloro-3-methoxytoluene by oxidn. with KMnO₄ (5), or from 6-chloro-3-methoxybenzaldehyde by oxidn. with alk. KMnO₄ (8).]

3:4720 (1) Beyer, Rec. trav. chim. 40, 628 (1921). (2) Mazzara, Gazz. chim. ital. 29, I 376-379 (1899). (3) Minney, Ripper, Monatsh 42, 76-80 (1921); J. Russ. Phys-Chem. Soc. 54, 673-679 (1922/23); Cent. 1924, I 905. (4) Minney, J. Russ. Phys-Chem. Soc. 58, 113-118 (1926); Cent. 1926, II 2295. (5) Peratoner, Condorell, Gazz. chim. ital. 28, I 214 (1898). (6) Coppadoro, Gazz. chim. ital. 32, I 547 (1902). (7) Plazek, Roczniki Chem. 10, 761-776 (1930); Cent. 1931, I 1428; C.A. 25, 1504 (1931). (8) Hodgson, Beard, J. Chem. Soc. 1926, 154. (9) Gibson, J. Chem. Soc. 1926, 1428.

M.P. 178.6-179.6° (1)

B.P. 192° cor. at 1175 mm. (1)

 \bar{C} can be purified by sublimation or by recrystn. from alc; difficult to separate, however, from 1,2,3-trichloro-2-methylpropane (3:5885), b p 162-163 l° (1). — \bar{C} is easily volatile with steam; cas sol alc or ether.

[For formn of \bar{C} (together with other products) from 1,1,2-trichloro-2-methylpropane (3:5710) or from ter-butyl chloride (3:7045) with Cl_2 see (1); for formn of \bar{C} together with other products) from β,β,β -trichloro-ter-butyl alcohol (" Chloretone") (3:2662) + PCl_5 see (2).]

 $\overline{\mathbf{C}}$ on htg. in s.t with aq. at 180° yields (3) α -chloroisobutyric acid (3:0235).

3:4725 (1) Rogers, Nelson, J. Am. Chem. Soc. **58**, 1027-1029 (1936). (2) Willgerodt, Dürr, Ber. **20**, 539-540 (1887). (3) Willgerodt, Durr, J. prakt. Chem. (2) **39**, 284 (1889).

3:4740 1,1,1,2,3-PENTACHLOROPROPANE H
$$C_3H_3Cl_5$$
 Beil. I-107 (unsym.-Pentachloropropane) $ClCH_2$ — C — CCl_3 I_1 — I_2 —

Colorless ndls. (from hot alc.) with camphoraceous odor. — Sublimes readily. — Insol. aq.; sol. org. solvents. [New comml. prod. (1942) in U.S.A.]

[For prepn. from 1,1,1-trichloropropene-2 (3:5345) by actn. of Cl_2 in diffuse light see (1).]

[For use as plasticizer with cellulose acetate films see (3).]

3:4740 (1) Victoria, Rec. trav. chim. 24, 282 (1905). (2) Henry, Rec. trav. chim. 24, 342 (1905). (3) Spicers, Ltd., Hand, Brit. 279,139, Nov. 17, 1927; French 125,165, Aug. 4, 1927; Cent. 1928, I 770.

M.P. 180-181° (1)

Ndls. from dil. alc. or lt. pet.

[For prepn. of \bar{C} from 5-chloro-2,3-dimethylphenol (5-chloro-o-3-xylenol) (3:2115) with Cl_2 in lt. pet. ether see (1).]

4,5,6-Trichloro-2,3-dimethylphenyl acetate: unreported.
 4,5,6-Trichloro-2,3-dimethylphenyl benzoate: mp. 128-129° (1).

3:4742 (1) Hinkel, Collins, Ayling, J. Chem. Soc. 123, 2971 (1923).

Colorless ndls. from aq. or dil. alc.; 100 pts. aq. at 3.5° dis. 0.8 g. \bar{C} ; eas. sol. alc., AcOH, or CHCl₃. — Volatile with steam; sublimes with slight decompn.

[For prepn. of \bar{C} from o-chlorophenol (3:5980) by treatment of dry sodium salt with CO_2 at 140–150° under press. see (3); from 5-sulfo-2-hydroxybenzoic acid (5-sulfosalicylic acid) [Beil. XI-411, XI₁-(106)] in AcOH with Cl₂ followed by hydrolysis of the resultant 3-chloro-2-hydroxy-5-sulfobenzoic acid with superheated steam (72% yield) see (1); from 6-chlorosalicylamide (see below) by hydrolysis with 10 pts boilg. 10% NaOH for 6 hrs (86% yield) see (1); for formin of \bar{C} from 7-chlorosaccharia (4) by NaOH fusion see (4); for formin from salicylic acid (1.0780) in Na₂CO₃ soln, with Cl₂ (5-chloro-2-hydroxy-benzoic acid (3:4705) is also formed) see (13).]

[For reactn of \bar{C} with methylenedisaheylamide in prepn. of dye intermediates by oxidn. with NaNO₂ see (5)]

[\bar{C} on reductn. with Na/IIg in pres. of H₃BO₃ yields(6) cf. (7) 3-chloro-2-hydroxybenzalde-hyde (3:1010); \bar{C} with ClSO₃II at 50–70° vields (8) 5-chlorosulfonyl-3-chloro-2-hydroxybenzoic acid, cryst. from CHCl₃, m p. 163–164° (8), which with Zn dust in alc. yields (9) 3,3'-dichloro-4,4'-dihydroxy-5,5'-dicarboxydiphenyl disulfide, m.p. 258–259° (9), which in turn with alk. Na₂S₂O₄ undergoes reductive cleavage to 3-chloro-2-hydroxy-5-thiol-benzoic acid (3-chloro-5-thiolsalicyhc acid), m p. 210° (9)]

[C with PCl₅ in low-boilg, pet. ether yields (2) 3-chlorosalicyloyl chloride, ndls. from pet. ether, m.p. 62-63° (2); this prod. on htg. yields (2) a mixt. of 3-chlorosalicylids: C with PCl₃ yields (2) 6-chloro-2-chloroformylphenyl metaphosphite Cl.CO.C₆H₃Cl.O.PO, m.p. abt. 65° (2).]

C in aq. soln. gives with FeCl₃ an intense violet color.

Salts. NaĀ (3), KĀ (1), CaĀ₂.3H₂O (1); BaĀ₂.3H₂O (3), AgĀ (1); for details see indic. refs.

- Methyl 3-chloro-2-hydroxybenzoate (methyl 3-chlorosalicylate): ndls. from MeOH, m.p. 38° (2), b.p. 259-260° sl. dec. (3). [From C in MeOH with HCl gas (3), or from 3-chlorosalicyloyl chloride (above) in MeOH (2).] [For formn. from methyl salicylate (1:1750) with chloropicrin under influence of light see (10) (11).]
- Ethyl 3-chloro-2-hydroxybenzoate (ethyl 3-chlorosalicylate): ndls. from cold alc., m.p. 21° (2), b.p 269-270° (2), 147° at 12 mm. (2). [From 3-chlorosalicyloyl chloride (above) with EtOH (2).]
- © 3-Chloro-2-methoxybenzoic acid: white ndls. from alc., m.p. 120-121° (1). [From \tilde{C} in dil. aq. KOH by shaking with Me₂SO₄ in cold, followed by hydrol. of the intermed. ether-ester with hot aq. KOH and subsequent acidif. (1).] [For nitration with mixt. of HNO₃ (D=1.5) + conc. H₂SO₄ at 20-30° giving (100% yield) 3-chloro-2-methoxy-5-nitrobenzoic acid, m.p. 155.5°, see (14).]
- ③ 3-Chloro-2-hydroxybenzamide (3-chlorosalicylamide): white ndls. from dil. alc., m.p. 174-175° (1). [From methyl 3-chlorosalicylate (above) or from 3-chlorosalicyloyl chloride (above) with conc. aq. NH₄OH in cold (1).]—[This prod. with chloral (3:5210) gives on warming (12) chloral-3-chlorosalicylamide, colorless ndls. from alc., m.p. 159-160° (12) (1), also obtd. from chloral-salicylamide in AcOH with Cl₂ (1).]
- ① 3-Chloro-2-hydroxybenzanilide (3-chlorosalicylanilide): colorless ndls. from alc., m.p. 158.5-159° (2). [From 3-chlorosalicyloyl chloride (above) with 2 moles aniline in ether soln. (2).]
- 3:4745 (1) Hirwe, Rana, Gavankar, Proc. Indian Acad Sci A-8, 208-213 (1938). (2) Anschütz, Anspach, Ann. 346, 312-317 (1906). (3) Varnholt, J. prakt. Chem. (2) 36, 22-24 (1887). (4) Reissert, Cramer, Ber. 61, 2565 (1928). (5) Durand, Huguenin, Brit. 183,123, Sept. 6, 1922; Cent. 1922, IV 1171. (6) Farbenfabriken vorm. F. Bayer & Co., Ger. 228,838, Nov. 22, 1910; Cent. 1911, I 51. (7) Farbenfabriken vorm. F. Bayer & Co., Ger. 216,305, Nov. 9, 1909; Cent. 1909, II 2107. (8) Farbenfabriken vorm. F. Bayer & Co., Ger. 264,786, Sept. 23, 1913; Cent. 1913, II 1350. (9) British Dyestuffs, Ltd., Saunders, Mendoza, Brit. 260,058, Nov. 18, 1926; Cent. 1929, I 149. (10) Piutti, Atti congr. naz. chim. pura applicata 1923, 398, 437-438; Cent. 1924, I 2514.
- (11) Piutti, Badolato, Atti accad. Lincei (5) 33, I 475-479; Cent. 1924, II 1893. (12) Hirwe, Rana, Ber. 72, 1351 (1939). (13) Tischenko, J. Russ. Phys.-Chem. Soc. 60, 153-162 (1928); Cent. 1928, II 768; C.A. 22, 3397 (1928). (14) Davies, Rubenstein, J. Chem. Soc. 123, 2851-2852 (1923).

3:4747 2,5,6-TRICHLORO-3,4-DIMETHYLPHENOL (Trichloro-o-4-xylenol)

$$\begin{array}{c|cccc} OH & & & & \\ Cl & Cl & C_8H_7OCl_3 & & Beil. \ VI - & & & \\ Cl & CH_3 & & & VI_{2^-}(456) \end{array}$$

M.P. 182.5° (1)

Ndls, from pet. ether.

[For prepn. of \bar{C} from 5-chloro-3,4-dimethylphenol (6-chloro-o-4-xylenol) (3:2705) with Cl_2 in CHCl₃ see {1}.]

2,5,6-Trichloro-3,4-dimethylphenyl acetate: unreported.

D 2,5,6-Trichloro-3,4-dimethylphenyl benzoate: m.p. 120° (1)

3:4747 (1) Hinkel, J. Chem. Soc. 125, 1853 (1924).

3:4750 NAPHTHALENE TETRACHLORIDE

(1,2,3,4-Tetrachloro-1,2,3,4-tetrahydronaphthalene; 1,2,3,4-tetrachlorotetralin)

C₁₀H₈Cl₄

Beil. V - 492 V₁---V₂-(386)

[See also 5,6,7,8-tetrachloro-1,2,3,4-tetrahydronaphthalene (3:4703).]

Cryst. from CHCl₃ or ether. — Very spar. sol. boilg alc., somewhat more sol. ether. — For data on crystallographic consts. see (4) (5); for X-ray study of cryst. structure see (6) (7). — For 2.39% soln. of \bar{C} in CHCl₃, D_4^{23} = 1.48466 and n_D^{23} = 1.44883 (8).

[For prepn. of \bar{C} from naphthalene (1:7200) in equal wt. C_6H_6 with 4.3 wt. pts. SO_2Cl_2 refluxed 3 hrs. (15% yield) see (1); with Cl_2 as directed (45% yield (9)) (10) (11) (12); with $KClO_3$ + HCl see (13) (9); with dil. HOCl see (3); note that in all these methods numerous by-products are formed and it cannot be said that the prepn. is very satisfactory.]

Č on vigorous boilg. in small quantities evolves HCl and yields (14) 1,4-dichloronaphthalene (3:1655), m.p. 68°; with larger units numerous other prods. are also formed (14).

 \bar{C} (3 pts.) with aq. (100 pts.) boiled for 48 hrs. (15) gradually dissolves and the soln. after concn. deposits (65% yield (15)) a dichloroglycol ("dichloronaphthydreneglycol") [Beil. VI-971], cryst. from alc., m.p. 155-156° (diacetate, m.p. 130-131°; dibenzoate, m.p. 148-150°) (15).

Č with alc. KOH on boilg. yields (2) (16) (17) (18) (19) (20) mainly 1,3-dichloronaphthalene (3:1310), m.p. 61-62°, accompanied by some 1,4-dichloronaphthalene (3:1655), m.p. 68°, and a little 2,3-dichloronaphthalene (3:3665), m.p. 120°: note that the prod., m.p. 38°, supposed by the earlier workers to have been 1,3-dichloronaphthalene has been shown (19) to consist of a mixt. (possible mol. cpd.) of 1,3-dichloronaphthalene and 1,4-dichloronaphthalene.

 \bar{C} on oxidn. with 8.7 wt. pts. conc. HNO₃ (D=1.45) at 100° under reflux for $\frac{3}{4}$ hr gives (20) 2,3-dichloronaphthoquinone-1,4 (3:4857), m.p. 196° (20); but \bar{C} on oxidn. with boilg. HNO₃ also yields (21) (13) (presumably by further oxidn of the above precursor) phthalic acid (1:0820) and oxalic acid (1:0445).

C on oxidn. with CrO₃/AcOH yields (20) 2,4-dichloronaphthol-1 (3:3250), m.p. 106-107° (20).

[C with moist silver oxide in s t. at 200° yields (19) (9) a chloronaphthol, m.p. 130° (9), 2,3-dichloronaphthalene (3:3665), and other prods. (9).]

[\bar{C} on nitration with HNO₃ (D=1.5) at not above 30-35°, followed by htg. of prod. with MeOH/Na₂CO₃ or MeOH/NaHCO₃ in C₆H₆ at 130-150° (22) or with MeOH/NH₃ at ord. temp. (23), yields 5,8-dichloro-1-nitronaphthalene [Beil. V-556, V₂-(453)], m.p. 94° (22).]

[For conversion of \bar{C} to artificial resins by htg. with metal halides such as AlCl₃ or FeCl₃ (24), or by htg. with naphthalene + a surface cat. such as fuller's earth (25), see indic. refs.]

3:4750 (1) Pongratz, Eichler, Ber. 69, 1295 (1936). (2) Faust, Saame, Ann. 160, 65-66 (1871). (3) Klingstedt, Wiese, Rudbäck, Acta Acad. Aboensis Math. et Phys. 4, No. 2, 1-36 (1927); Cent. 1928, I 504; C.A. 23, 1399 (1929). (4) Hintze, J. prakt. Chem. (2) 8, 253-255 (1873). (5)

Groth, Chem. Krystalog. 5, 368 (1919). (6) Robertson, Proc. Roy. Soc. (London) 118-A, 709-727 (1928). (7) Bragg, Z. Krist. 66, 27-32 (1927). (8) Kanonnikoff, J. prakt. Chem (2) 31, 342-343 (1885). (9) Leeds, Everhart, J. Am. Chem. Soc. 2, 207-209, 210-213 (1880). (10) Laurent, Ann. chim. (2) 52, 275-281 (1833), 59, 201-204 (1835).

(11) Paul, Depoully, Bull. soc chim (2) 4, 10-12 (1865). (12) Schwarzer, Ber. 10, 379 (1877). (13) Fischer, Ber. 11, 735-741, 1411 1412 (1878) (14) Krafft, Becker, Ber. 9, 1088-1090 (1876). (15) Grimaux, Bull soc. chim. (2) 18, 205-212 (1872); Compt. rend. 75, 352-355 (1872). (16) Widman, Ber. 15, 2161-2162 (1882). (17) Cleve, Ber. 23, 954 (1890). (18) Armstrong, Wynne, Chem. News 58, 264-265 (1888). (19) Armstrong, Wynne, Chem. News 61, 273, 284 (1890); Proc. Chem. Soc. (London) 4, 106 (1888). (20) Helbig, Ber. 28, 505-507 (1895).

(21) Laurent, Ann. chim. (2) **74**, 26-27 (1840); Ann. **35**, 292-293 (1840). (22) Matter, Ger. 317,755, Dec. 29, 1919; Cent. **1920**, II 601. (23) Matter, Ger. 348,069, Jan. 28, 1922; Cent. **1922**, IV 45. (24) A.G.F.A., Ger. 332,391, Feb. 2, 1921, Cent. **1921**, II 652, Ger. 334,710, March 17, 1921; Cent. **1921**, II 954. (25) Schering-Kahlbaum, Freund, Jordan, Ger. 461,358, June 20,

1928; Cent. 1929, I 1052, Brit 202,997, Oct. 24, 1924, Cent. 1925, I 1456.

3:4755 2,3,3-TRICHLORO-2-METHYLBUTANE

M.P. 182-183° (1) abt. 170° (2)

[For prepn. of \tilde{C} from 2-chloro-2-methylbutane (3:7220) or from 2,3-dichloro-2-methylbutane (3:7975) with Cl_2 see (2); for formn. from 3-chloro-2-methylbutene-2 (3:7335) + Cl_2 (10% yield together with other prods.) see (1) (an earlier product (3) obtd. by this latter method and to which this structure was assigned was reported as a liquid, b.p. 176°, $D_1^{45} = 1.215$, $n_D^{21} = 1.472$).]

C is not (2) saponified by 20% aq. K₂CO₃.

 $\bar{\mathbf{C}}$ on htg. with 2 moles quinoline at 195–225° gives (60% yield (2)) β -chloroisoprene (3:7290).

3:4755 (1) Tishchenko, J. Gen. Chem. (U S S.R.) **8,** 1232-1246 (1938); Cent. **1939,** II 4223, C.A. **33,** 4190 (1939). (2) Tishchenko, J. Gen. Chem. (U.S S.R.) **6,** 1116-1132 (1936); Cent. **1937,** I 573; C.A. **31,** 1003 (1937). (3) Brochet, Ann. chem. (7) **10,** 385 (1897).

3:4775 3,4-DICHLORONAPHTHO-QUINONE-1,2

Red tbls. or ndls. from AcOH, C_6H_6 or CHCl₃. — Spar. sol. alc., fairly eas. sol. CHCl₃. — Sublimes undecomposed.

[For prepn. of \bar{C} from 1-aminonaphthol-2 hydrochloride [Beil. XIII-676, XIII₁-(274)], in AcOH with Cl₂ (68.5% yield (3)) (2) (4), or from naphthoquinone-1,2 (1:9062) in AcOH with Cl₂ (2), see indic. refs.; for formn. of \bar{C} from 3,4-dichloro-naphthoquinone-1,2-oxime-1 (3,4-dichloro-1-nitroso-naphthol-2) [Beil. VII-721] on oxidn. with conc. HNO₃ in AcOH soln. see (5); from 3,4-dichloro-3-nitro-1,2-dioxonaphthalene tetrahydride-1,2,3,4 [Beil. VII-701] with AcCl in s.t. at 100° see (6).]

Č dis. in cold dil. aq. alk. yielding colorless soln. which upon acidification gives (90% yield (4)) 1,2-dichloro-3-hydroxyındenecarboxylic acid-3 [Beil. X-325], ndls with 1 H₂O (from dil. HCl), m.p. 99–100° (4). [This prod. on oxidn. in dil. aq. or AcOH soln. with CrO₃ gives (34% yield (3)) (2) (4) 1,2-dichloroindene-1-one-3 ("dichloroindene") [Beil. VII-384], gold-yel. ndls. from alc. or AcOH, m p. 89–90°.] [For behavior of C̄ with Ca (OCl₂) soln. see (7).]

Č with alc. NaOEt yields (8) 3-chloro-4-ethoxynaphthoquinone-1,2, [Beil. VIII-299], or.-red ndls. from alc., m.p. 149° (8).

 \bar{C} in hot alc soln. on treatment with alc. NH₃ yields (2) 3-chloro-2-hydroxynaphtho-quinone-1,4-imide-4 (4-amino-3-chloronaphthoquinone-1,2) [Beil VIII-305], m.p. abt. 260° (2).

Č in dil. AcOH with excess SO₂ (2) reduces to 3,4-dichloro-1,2-dihydroxynaphthalene [Beil. VI-975], m.p. 125° (2).

[For cpd. formn. of \bar{C} with SnCl₄ see (9); for reactn. of \bar{C} with 2,3-dimethylbutadiene-1,3 in CHCl₃ see (10)]

3:4775 (1) Zincke, Ann. 257, 146–147 (1890). (2) Zincke, Ber. 19, 2499–2500 (1886). (3) Brass, Mosl, Ber. 59, 1271 (1926). (4) Zincke, Engelhardt, Ann. 283, 347–349 (1894). (5) Zincke, Schmuuk, Ann. 257, 146–147 (1890). (6) Zincke, Scharfenberg, Ann. 268, 303–304 (1892). (7) Zincke, Schmidt, Ber. 27, 744 (1894). (8) Hirsch, Ber. 33, 2414 (1900). (9) Brass, Fengler, Ber. 64, 1663–1664 (1931). (10) Fieser, Dunn, J. Am. Chem. Soc. 59, 1020 (1937).

Ndls. with 3 H₂O, m.p. 75° (1) from alc. or C_6H_6 (2); this trihydrate in vac. over H₂SO₄ loses 2 H₂O, the final H₂O at 110° (2). — \bar{C} is spar. sol in cold aq., C_6H_6 , CHCl₃, CCl₄, or CS₂; eas. sol alc., ether, or hot aq.

[For prepn. of \bar{C} from pyrogallol (1,2,3-trihydroxybenzene) (1:1555) in 60% AcOH with Cl₂ (2), or with SO₂Cl₂ in dry ether (3), see indic. refs.]

[For prepn. of \bar{C} from "leucogallol" [Beil VI-1078] or "mairogallol" [Beil VI-1078] by reduction with Zn dust + dil. H_2SO_4 see (1); from gallie acid (1:0875) in CHCl₃ with Cl₂ see (4).

[C in CCl4 or CHCl3 prev. satd. with Cl2 gives (2) "leucogallol."]

Č in other soln, with aq. Ba(OH)₂ gives deep blue coloration; with aq. Na₂SO₃ a fugitive red coloration (2).

C with aq. FeCl₃ gives (4) a blue coloration.

 \bar{C} with conc. HNO₃ is oxidized and decomposed (2); \bar{C} dis. in cold conc. H₂SO₄ without evoln. of gas but on warming decomposes (2).

C reduces NH₄OH/AgNO₃ (1).

- --- 4,5,6-Trichloropyrogallol triethyl ether: unreported.
- —— 4,5,6-Trichloropyrogallol triacetate: ndls. from dil. AcOH, m.p. 125° (4), 122° (1). [From C on short boilg. with Ac₂O (1) (4).]

436

3:4782 (1) Hantssch, Schniter, Ber. **20,** 2034-2037 (1887). (2) Webster, J. Chem. Soc. **45,** 205-208 (1884). (3) Peratoner, Condorelli, Gazz. chim. ital. **28,** I 225-226 (1898). (4) Bietrix, Bull. soc. chim. (3) **15,** 904-906 (1896). (5) Bartolotti, Gazz. chim. ital. **27,** I 290-291 (1897).

3:4790 2,3,4,5-TETRACHLORO-BENZOIC ACID

M.P. 186° (1)

Ndls. from alc. — Eas. sol. alc., ether; spar sol. aq.

[For prepn. of \tilde{C} from tetrachlorophthalic acid (3:4946) by htg. with 2-3 pts. AcOH in s.t. at 300° for 3-4 hrs. see (1); by htg. with steam + H₂ at 200-400° over decarboxylating cat. see (2).]

 \bar{C} on $\frac{1}{2}$ hr. boilg. with mixt. of 2 pts. HNO₃ (D=1.48) + 1 pt. conc. H₂SO₄ gives (100% yield (1)) 2,3,4,5-tetrachloro-2-nitrobenzoic acid [Beil. IX-405], lfts. from aq., but no m.p. has been reported.

Neither the action (if any) of PCl₅ or SOCl₂ on $\bar{\mathbb{C}}$ nor the expected 2,3,4,5-tetrachlorobenzoyl chloride has been recorded.

- Methyl 2,3,4,5-tetrachlorobenzoate: unrecorded.
- —— Ethyl 2,3,4,5-tetrachlorobenzoate: from \bar{C} + EtOH + HCl gas; ndls. alc., m.p. 34.5° (1).
- ---- 2,3,4,5-Tetrachlorobenzamide: unrecorded.
- --- 2,3,4,5-Tetrachlorobenzanilide: unrecorded.

3:4790 (1) Tust, Ber. **20**, 2439-2431 (1887). (2) Jaeger (to Selden Co.), U.S. 1,953,232, April 3, 1934; Cent. **1934**, II 669; C.A. **28**, 3743 (1934).

3:4810 2,3,4-TRICHLOROBENZOIC ACID

M.P. 186-187° (1)

Ndls. from hot aq. (1). — \bar{C} does not melt under boiling water (1).

[For prepn. from 2,3,4-trichlorotcluene (3:0425) by oxidn. with HNO₃ in s.t. at 150° see (1); from 2,3,4-trichlorobenzaldehyde (3:2445) by oxidn. with KMnO₄ see (2).] [The latter product was probably impure (1).]

No further data on C are recorded.

3:4810 (1) Cohen, Dakin, J. Chem. Soc. 81, 1328 (1902). (2) Seelig, Ann. 237, 150 (1887).

3:4820 3-CHLOROPHTHALIC ACID

M.P. 186-187° (1)

185-187° (2)

186° (3

184° (4) (5)

[See also 3-chlorophthalic anhydride (3:3900).]

Ndls. from aq.; eas. sol. alc.; eas. sol. ether (use in sepn. from phthalic acid (1:0820) (6). — 100 pts. aq. at 14° dis. 2.16 pts. \bar{C} (5). — [For sepn. of \bar{C} from o-chlorobenzoic acid (3:4150) by use of CHCl₃ see (7).]

[For prepn. of \bar{C} from 3-chlorophthalic anhydride (3:3900) by hydrolysis with boilg. dil. HCl see (3) (6); from 1,5-dichloronaphthalene (3:3200) by oxidn. with CrO₃/AcOH see (5); from 5-chloro-1,2,3,4-tetrahydronaphthalene [Beil. V₁-(237)] (1) by oxidn. with KMnO₄ see (1); from 3-chloro-2-methylbenzoic acid (3:4435) by oxidn. with KMnO₄ see (8).]

C on htg. above its m.p. yields (5) (8) 3-chlorophthalic anhydride (3:3900).

[\bar{C} on KOH fusion yields (8) (note rearrangement) 4-hydroxyphthalic acid [Beil. X-499, X_1 -(255)], m.p. 204-205°, with conv. to corresp. anhydride, m.p. 171°.]

 $[\bar{C}$ with steam passed over cat. at 350° loses CO₂ presumably yielding (9) o-chlorobenzoic acid (3:4150) and/or m-chlorobenzoic acid (3:4392).]

[C htd. with Hg(OAc)₂ in AcOH as directed (2) gives anhydro-2-hydroxymercuri-3-chlorobenzoic acid which on htg. with aq. HCl yields m-chlorobenzoic acid (3:4392).]

Salts. Ag₂Ā, ndls. from hot aq. (5); BaĀ, eas. sol. cold aq., but spar. sol. hot aq., on protracted boilg. with aq. gives monohydrate which is insol. cold aq. (8).

Esters. The neutral dimethyl and diethyl esters of \bar{C} are unreported: of the various possible acid esters only ethyl hydrogen 3-chlorophthalate, m.p. 118-119° (1), has been reported.

3:4820 (1) von Braun, Larbig, Kredel, Ber 56, 2337-2338 (1923). (2) Whitmore, Culhane, J. Am. Chem. Soc. 51, 602-605 (1929). (3) Bogert, Boroschek, J. Am. Chem. Soc. 23, 751 (1901). (4) Egerer, Meyer, Monatsh. 34, 81 (1913). (5) Guareschi, Gazz. chim. ital. 17, 120-122 (1887). (6) Smith, J. Chem. Soc. 1933, 1643-1644. (7) Jaeger (to Selden Co.), U.S. 1,685,634, Sept. 25, 1928; Cent. 1929, I 807. (8) Krüger, Ber 18, 1759 (1885). (9) Jaeger (to Selden Co.), U.S. 1,953,231, April 3, 1934; Cent. 1934, II 1688.

[See also 4.5-dichlorophthalic acid (3:4890).]

Tbls. or pr. from hot toluene or from CCl₄; spar. sol. cold but eas. sol. hot C₆H₆ or toluene; very little sol. in CCl₄.

[For prepn. of \bar{C} from 4,5-dichlorophthalic acid (3:4890) by htg. at 200° (4) or by htg. with AcCl (2) see indic. refs.; for formn. of \bar{C} (together with other isomers) from phthalic anhydride (1:0725) with Cl₂ in pres. of Fe or Fe salts at 160-260° (5), or from phthalic anhydride (1:0725) or 3-chlorophthalic anhydride (3:3900) with Cl₂ in fumg. H₂SO₄ in pres. of I₂ (4) (1), see indic. refs.; for formn. of \bar{C} from aq. solns. of alk. salts of phthalic acid (1:0820) with Cl₂ see (2) (6) (7).]

[For sepn. of C from isomeric dichlorophthalic anhydrides by means of salts of corresp.

acids, etc., see (4) (8) (1); by means of differential hydrolysis with H_2SO_4 (prods. with no α chlorine such as \bar{C} require H_2SO_4 of 98-100% concn., those with 1 α chlorine such as 3,4-dichlorophthalic anhydride hydrolyze with 56-95% H_2SO_4 , those with 2 α chlorine atoms such as 3,6-dichloro- or 3,4,5,6-tetrachlorophthalic anhydrides hydrolyze at H_2SO_4 concns. of less than 50%) see (9).]

C dislyd. in abs. alc. yields (4) ethyl hydrogen 4,5-dichlorophthalate, ndls from CHCl₃, m.p. 133-134° (4).

[Č with 1 mole NH₂OH.HCl + Na₂CO₃ in aq. soln as directed (4) yields 4,5-dichlorophthaloylhydroxylamine (N-hydroxy-4,5-dichlorophthalimide) [Beil XXI-504], pr from MeOH, m.p. 195–197° dec (4); this prod. on warming with aq Na₂CO₃ gives 100% yield 4,5-dichloro-2-aminobenzoic acid (4,5-dichloroanthranilic acid) [Beil XIV-368, XIV₁-(549)], m.p. 213–214° (4).]

[$\tilde{\mathbf{C}}$ with steam passed over cat. at 380–420° loses CO₂ presumably yielding (10) 3,4-di-chlorobenzoic acid (3:4925)]

 $\bar{\mathbb{C}}$ with benzene + AlCl₃ (12) or in acetylene tetrachloride (11) gives (98% yield (12)) 4,5-dichloro-2-(o-benzoyl)benzoic acid [Beil. X_1 -(357)], cryst. from C_6H_6 (12) or toluene (11), m.p. 209° (12), 208° (11), which on htg. with 20 pts cone H_2SO_4 at 160° for 1 hr. gives (92% yield (12)) (11) 2,3-dichloroanthraquinone [Beil. VII-788, VII₁-(413)], yellowish ndls. from AcOH, m.p. 267° cor. (12), 265° (11). — $[\bar{\mathbb{C}}$ with o-xylene + AlCl₃ in acetylene tetrachloride gives (80% yield (11)) 4,5-dichloro-2-(3',4'-dimethylbenzoyl)benzoic acid, cryst. from cyclohexane, m.p. 184° (11), which with 10 pts. conc. H_2SO_4 at 100° gives (45% yield (11)) 6,7-dichloro-2,3-dimethylanthraquinone, cryst from xylene, m.p. 305° (11) — $\bar{\mathbb{C}}$ with o-dichlorobenzene (3:6055) + AlCl₃ 4 hrs. at 100° gives (80% yield (11)) 3,4-dichloro-2-(3',4'-dichlorobenzoyl)benzoic acid, cryst. from C_6H_6 , m.p. 183°, which with 12 pts. conc. H_2SO_4 6 hrs. at 100° gives mainly 2,3,6,7-tetrachloroanthraquinone, cryst. from o-dichlorobenzene, m.p. 348° (11) — For analogous reactns of $\bar{\mathbb{C}}$ with naphthalene (13), pyrene (14), or o-chlorotoluene (15) see indic. refs.]

[\bar{C} with hydroquinone (1:1590) + H_3BO_3 htd at 190° and afterward treated with hot conc. H_2SO_4 at 150–165° (16), or \bar{C} with $AlCl_3$ + NaCl htd at 200–220° (17), or \bar{C} with p-chlorophenol (3:0475) htd. with fumg. H_2SO_4 + H_3BO_3 (18) gives (yield: 80% (17), 15% (16)) 6,7-dichloro-1,4-dihydroxyanthraquinone (6,7-dichloroquinizarin) [Beil. VIII-452, VIII₁-(716)], red-br. cryst from xylene, m.p. 295.5° (17), 288° (16), (diacetate, m.p. 125° (16), dimethyl ether, m.p. 168 5° (17))]

[For use of \bar{C} in preparation of pigments of the copper phthalocyanine type see (19)]

 \bar{C} with $(NH_4)_2CO_3$ htd. at 250° for $\frac{1}{2}$ hr (20) yields 4,5-dichlorophthalimide, pl from alc., m.p. 221° (20) (note that behavior of \bar{C} with cone aq. NH_4OH is different yielding (4) 4,5-dichlorophthalamic acid (not specifically characterized) which with alk. NaOCl gives 4,5-dichloro-2-aminobenzoic acid (above)). — [For behavior of \bar{C} with hydrazine hydrate in AcOH yielding corresp. cyclohydrazide see (21)]

Č (1 pt) in boilg. AcOH (6 pts.) treated with and (1 pt.) gives (82% yield (1)) 4,5-dichlorophthalanil (N-phenyl-4,5-dichlorophthalimide) [Beil. XXI₁-(391)], cryst. from AcOH, m.p. 212.5-213° cor. (1).

Č on saponification with standard alkali (Sap. Eq. = 108.5), followed by acidification, yields 4,5-dichlorophthalic acid (3:4890) q.v

3:4830 (1) Pratt, Perkins, J. Am. Chem. Soc. 40, 215-216, 218 (1918). (2) Hinkel, Ayling, Bevan, J. Chem. Soc. 1928, 1876. (3) Ayling, J. Chem. Soc. 1929, 255. (4) Villiger, Ber. 42, 3538-3539, 3546-3549 (1909). (5) Dvornikoff (to Monsanto Chem. Co.), U.S. 2,028,383, Jan. 21, 1936; Cent. 1936, I 2830; C.A. 30, 1394 (1936). (6) Rushchinskii, J. Applied Chem. (U.S.S.R.) 7, 1113-1115 (1934); Cent. 1936, II 2902. (7) Rushchinskii, Russ. 41,515, Feb. 28, 1935; Cent. 1935, II 3704; C.A. 30, 8247 (1936). (8) Hodgson, J. Soc. Dyers Colourust 49, 215 (1933).

(9) Imperial Chem. Ind., Ltd., French 749,954, Aug. 2, 1933, Cent. 1933, II 2748-2749. (10) Jaeger (to Selden Co.), U.S. 1,964,516, June 26, 1934, Cent. 1934, II 3047.

(11) Barnett, Goodway, Watson, Ber. 66, 1878-1879, 1884-1889 (1933). (12) Ullmann, Billig, Ann. 381, 27-28 (1911). (13) Waldmann, J. prakt. Chem. (2) 131, 79 (1931). (14) Verein fur Chem. und Metallurg. Produktion, Czechoslovak. 46,835, Feb. 25, 1934; Cent. 1934, II 518. (15) Keimatsu, Hirano, J. Pharm Soc. Japan 49, 20-26 (1929); Cent. 1929, I 2533. (16) Frey, Ber. 45, 1363-1364 (1912). (17) Waldmann, J. prakt. Chem. (2) 126, 253-254 (1930). (18) Scottish Dyes, Ltd., Bangham, Hooley, Thomas, Birt. 339,589, Jan. 8, 1931; Cent. 1932, I 2095. (19) Imperial Chem Ind., Ltd., French 808,845, Feb. 16, 1937; Brit. 464,126, April 12, 1937; Cent. 1937, II 3820, C A 31, 6255 (1937). (20) Drew, Pearman, J. Chem. Soc. 1937, 590.

(21) Drew, Pearman, J. Chem. Soc. 1937, 32

```
3:4835
          HEXACHLOROETHANE
                                           Cl<sub>3</sub>C-CCl<sub>3</sub>
                                                                   C_2Cl_6
                                                                                Beil. I - 87
           (Perchloroethane)
                                                                                     I_{1}-(26)
                                                                                     I_{2}-(58)
  M.P.
                                       B.P.
                                       185.5° at 776.7 mm. (7)
  189° s.t.
                               (1)
  187-188°
                        (74) (115)
                                               at 760 mm. (18)
  187.71-188.75° cor., s.t. (7)
  187° s.t.
                           (2) (3)
  187°
              (4) (5) (6) (63) (64)
  186.85-187.4° cor., s.t.
                               (7)
  186.8°
                               (8)
  186-187°
                         (9) (133)
  186°
                         (10) (75)
  185-186°
                              (11)
  185°
              (12) (13) (14) (132)
  183-184° s.t.
                              (15)
  183.0-184.0°
                              (16)
  181° s.t.
                              (17)
```

White cryst with camphoraceous odor which readily sublime without melting. — Cryst. from alc, ether, CHCl₃ or CS₂. — \bar{C} is trumorphous: below about 46° cryst \bar{C} is orthorhombic, in range 46–71° cryst \bar{C} is truclinic; about 71° cryst \bar{C} is cubic, at these transition temps volume alterations occur which have sometimes (5) been mistaken for mp.'s. — [For details on trimorphism and these transitions see (19) (8) (20) (21) (25) (26); for influence of high press, see (22) — For crystallographic data see (20) (23) (24); for X-ray crystallog. data see (27) (28)]

 \bar{C} is almost abs. insol aq. and vice versa at ord temp (29); for patents on drying of \bar{C} see (30) (31) — [For studies of vap press. of \bar{C} at various temps, see (13) (4) (7) (32). — For prevention of "caking" of cryst. \bar{C} by addn. of 1-10% paraformaldehyde see (33).]

Cryoscopic const. of \bar{C} , i.e, f.p. lowering per mole solute in 100 g. \bar{C} , is 5.6° (34). [For thermal anal. of binary systems of \bar{C} with naphthalene (1:7200) (8) (34), with phenanthrene (1:7240) (34), or with anthracene (1:7285) (34) see indic. refs.]

USES OF C

 \bar{C} finds many uses in industry, some based on its physical characteristics and some on its chem. behavior. — [E.g., for use of \bar{C} as solvent for prepn. of solid solns. of I_2 for use in place of usual tincture see (35); for use of \bar{C} as means for temporary marking of cloth removable at will by heat (sublimation) see (36).]

[For use of \bar{C} as addition agent to CCl₄ fire extinguishers see (37); as component of certain types of explosives (e.g., 75% nitrostarch + 20% \bar{C} + 5% NaNO₃) see (38); for use of \bar{C} as mothproofing agent see (39) (40) (41) (42); for use of \bar{C} as insecticide and/or fungicide see (43) (44); for use of \bar{C} together with CS₂ (45) or rotenone (46) as insecticides see indic. refs.]

 \tilde{C} is an important component of "HC" smoke candles or grenades used for the production of screening clouds or smokes; a mixture of \tilde{C} with powdered metal (usually Zn) once started undergoes vigorous decomposition yielding ZnCl₂ + C; other materials are usually added to ignite the mixture and to modify the character of the resultant smoke; for further details see (47) (48) (49). — [For use of this type of reactn. in prepn. of activated carbon see (153).]

PHYSIOLOGICAL ASPECTS OF C

[For studies of toxicity of \bar{C} and its ability to penetrate skin see (50) (51) (52) cf. (160); for studies of \bar{C} as anthelmintic see (53) (54); for study of antiseptic power of \bar{C} see (55).]

DETERMINATION OF C

For detn. of \tilde{C} by reactn. with Na + ethanolamine in dioxane followed by detn. of resultant chloride ion see (161).

PREPARATION (OR FORMATION) OF C

 $\bar{\mathbf{C}}$ is a by-product of the tech. prepn. of CCl₄ (5:5100) from CS₂ + Cl₂ (56), of prepn. of CHCl₃ (3:5050) and of CH₂Cl₂ (3:5020) (57), and is found (12) (together with other by-products) in the high-boilg. fractn. ("Tri-Nachlauf") from the prepn. of trichloroethylene (3:5170) from acetylene tetrachloride (3:5750). — For quick prepn of $\bar{\mathbf{C}}$ from CCl₄ (3:5100) refluxed with Al powder (80% yield (14)) or with Al/Hg (65% yield (58)) cf. (96) see indic. refs.; for prepn. of $\bar{\mathbf{C}}$ from ethylene with Cl₂ over activated carbon at 300–350° (90% yield) see (59). — For many other methods of preparation, manufacture, or formation see below.

From various polychloroethanes. From 1,2-dichloroethane (ethylene dichloride) (3:5130). [For prepn. of \bar{C} from ethylene dichloride in vapor phase with $Cl_2 + cat$. (60) (61) or with Cl_2 under press. (62) see indic. refs.; note that ethylene dichloride in liq. phase with Cl_2 gives mainly (61) 1,1,2-trichloroethane (3:5085). — Note also that 1,2-dibromoethane (ethylene dibromide) refluxed with $AlCl_3$ while treated with Cl_2 (63) gives \bar{C} .]

From 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750). [For formn. of C together with other prods. from acetylene tetrachloride over pumice at 700° (64), or with anhydr. FeCl₃ on htg. in s.t. (65), or with Cl₂ (66) in u.v. light at 50-60° (67) or X-radiation (68), or with Cl₂ over activated carbon at 300-400° (69) (70) or at 60-70° (71), or with Cl₂ in pres. of AlCl₃ at 20-100° (71) or at 120° under reflux (80% yield (72)), or with Cl₂ in pres. of Fe at 20-80° (71), or with Cl₂ in CCl₄ soln. (73), or even with aq. bleaching powder (71), see indic. refs. — (Note also that acetylene tetrabromide with AlCl₃ + Cl₂ under reflux yields (63) C̄).]

From pentachloroethane (3.5880). [For formn. of \bar{C} together with other prods. from pentachloroethane with dry $Cl_2 + AlCl_3$ at 70° (74), or with Cl_2 over activated carbon at 300-400° (70), or with Cl_2 in u.v. light (67), or with excess F_2 at 90° for 10 hrs. (16), see indic. refs. — (Note also that pentabromoethane with $SbCl_5$ in s.t. at 160° for 2 hrs. gives (75) \bar{C} .)]

From various polychloroethylenes (or acetylenes). From trichloroethylene (3:5170). [For formn. of \tilde{C} together with other products from trichloroethylene by pyrolysis over

pumice at 700° (64), or with anhydrous FeCl₃ on htg. in s.t. (65), or with Cl₂ over act. carbon at 60-70° (98% yield (70)), see indic. refs.]

From tetrachloroethylene (3:5460). [For prepn. and/or formn. of \bar{C} from tetrachloroethylene with Cl₂ (162) (76) (77) in direct sunlight (78) cf. (79) (80) (106) or in pres. of suitable cat. in dark at 80-100° (81), or in CCl₄ soln. at 22° (82) cf. (73) or in vapor phase at 40° and low press. in light and absence of oxygen (33) see indic. refs. (note that tetrachloroethylene (3:5460) with Cl₂ + light in presence of O₂ undergoes photo-oxidation to trichloroacetyl chloride (3:5420)). — For formn. of \bar{C} from tetrachloroethylene with SO₂Cl₂ in pres. of dibenzoyl peroxide (84), or in small amt. with dibenzoyl peroxide alone (85), or with chlorine monoxide in CCl₄ at -20° (86), see indic. refs.] See also below under formn. of \bar{C} from acetylene.

From dichloroacetylene (3:5010). [For form. of \bar{C} from dichloroacetylene with Cl_2 in CCl_4 soln. see (2).]

From various polychloromethanes. From trichloromethane (chloroform) (3:5050). [For formn. of C together with other prods. from CHCl₃ by pyrolysis at 425° (87), in electric arc (6), by actn. of radium radiation (88), or by actn. of NCl₃ in sunlight (89) see indic. refs.]

From carbon tetrachloride (3.5100). [For formn. of \bar{C} together with other prods. from CCl₄ by pyrolysis at 600–1500° (90) cf. (91) (76), by actn. of electric arc (6), dark electric discharge (92), or radium radiation (88), with hydrogen at 600–650° (93), or with hydrogen over reduced Ni at 270° (94), or from CCl₄ in nitrogen over GeO₂ at 500–865° (95), see indic. refs.]

[For prepn. of \overline{C} from CCl₄ (3:5100) by refluxing with Al powder (80% yield (14)), Al/Hg (65% yield (58)), or Al + AlCl₃ (96), or by htg. with Cu powder in s.t. at 120° (97), amorphous As in s.t. at 160° (98), or molecular Ag in s.t. at 200° (99), see indic. refs.]

From various hydrocarbons. From methane. [For formn. of \tilde{C} together with other prods. from $CH_4 + Cl_2$ in silent elec. discharge see (100).]

From ethane. [For form. of C together with other prods. from ethane with Cl₂ in pres. of activated carbon or other cat. at elev. temp. see (101) (102) (103).]

From ethylene. [For form. of C together with other prods. from ethylene with Cl₂ over act. carbon at 120-125° (104) or at 300-350° (90% yield (59)) cf. (101) (105).]

From acetylene. [For formn. of \bar{C} together with other prods. from acetylene with Cl₂ at 650-1000° as directed (106) or at 700-950° as directed (107), with Cl₂ in an inert gas such as N₂ or HCl over act. carbon at elev. temp. (108), or with S₂Cl₂ in pres. of 1-2% reduced iron (109) (110) see indic. refs. — (Note that by this mode of procedure acetylene tetrachloride (see this heading above) is a probable intermediate.)]

From miscellaneous sources. C has been observed as one of the products of decomposition of many different types of compounds contg. the —CCl₃ group. [For example, for formn. of C (together with other prods.) from iodotrichloromethane on distn. (111), from bromotrichloromethane in ultraviolet light (112), from trichloroacetyl chloride (3:5420) at 600° (113), from trichloroacetyl bromide in s.t. at 400° (113), from trichloroacetyl iodide on distn. at ord. press. (113), from nitrosotrichloromethane with O₂ at 120° (114), or from nitrotrichloromethane (chloropicrin) with HCl gas over pumice at 400° (1) see indic. refs. — For formn. of C together with other prods. from trichloroacetaldehyde (chloral) (3:5210) with Cl₂, Br₂, or I₂ in pres. of AlCl₃ (115), from trichloroacetic acid (3:1150) by pyrolysis over ThO₂, kaolin, or carbon (116), from K trichloroacetate by electrolysis of its soln. in aq. KOAc (15), from ferric trichloroacetate in aq. soln. in light (117) (118) (119), from pentachlorodimethyl ether on htg. with aq. (120), or from trichloromethyl benzoate on htg. (121) see indic. refs.]

The forms. of C has also been observed in connection with certain acid chlorides [e.g.,

for formn. of C from acetyl chloride (3:7065) with excess PCl₅ in s.t. at 180° (122), from pentachloropropionyl chloride (3:0470) with AlCl3 on warming (123), from dichloromalcyl (di)chloride (3:6197) with PCl₅ at 230° for 6 hrs. (124), or from pentachloroethyl chloroformate with AlCl₃ at 100° (125) see indic. refs.]

[For formn. of C from various alkanes with SbCl₅ + I₂ (126), from a mixt. of dichloropropanes or from hexachlorobutadiene (3:6425) with Cl2 at 400° and 30 atm. (127), from an electric arc between carbon electrodes in Cl₂ (128), from n-propyl chloride (3:7040) or isobutyl chloride (3:7135) with excess ICl₃ in s t. at 200° (129), from CaC₂ with gaseous or liq. Cl2 at 20° under press. (10), from various iodochlorides of ethylene on warming (9), from lignin on boilg. with SbCl₅ + I₂ (130), from humic acid with KClO₃ + HCl (131), from β, β' -dichlorodicthyl sulfide ("mustard gas") with dry Cl₂ at 100° (132), or from $\alpha,\alpha,\beta,\beta,\beta,\beta'$ -hexachlorodiethyl sulfide or $\alpha,\alpha,\beta,\beta,\beta,\alpha',\beta'$ -heptachlorodiethyl sulfide with Cl₂ in cold (133) see indic. refs.]

CHEMICAL BEHAVIOR OF C

Pyrolysis. [C passed over porcelain in hot tube gives (78) tetrachloroethylene (3:5460); $\bar{\mathbf{C}}$ (in stream of air) pyrolyzed at 550–600° gives (57) tetrachloroethylene (3.5460) +CCl₄ (3:5100) in conversions of substantially 100% — Note also that C with SbCl₅ above 450° yields almost exclusively (126) CCl₄ (3:5100).]

Reduction. C with granulated Zn in boilg, alc. (134), with Zn + dil. H₂SO₄ at room temp. for several days (100% yield (135)) (136) (76), with $Z_n + aq$. above 80° (137), with H₂ over Ni at 270° (138), or with alc. KSH (139) loses 2 chlorine atoms giving tetrachloroethylene (3:5460) [for other, less direct conversions of C to tetrachloroethylene see latter under preparation; also below.)]

Oxidation. C is oxidized only with considerable difficulty [e.g., for behavior of C over hot CuO see (140); for detn. of chlorine in C by cat. oxidn over Fc₂O₃ (low results) see (141); C with CrO₃/H₂SO₄ is incompletely oxidized (142); C with SO₃ in s.t. at 150° (143) cf. (144) yields trichloroacetyl chloride + S₂O₅Cl₂]

Partial replacement of chlorine by fluorine. [C with F_2 gas over Cu gauze cat. at 125° (145), or with SbF₃Cl₂ htd. under press. (146) (147) (148), or with SbF₃ + Cl₂ + SbCl₃ as directed (149) yields 1,1,2,2-tetrachloro-1,2-difluoromethane, mp. 24-25°, b.p. 92°, accompanied by numerous other partially fluorinated prods |

Behavior with alkalies. [C with solid KOH in s.t. at 210-220° for several days yields (150) KCl + potassium oxalate; C with alc. KOH in s.t. at 100° for a week yields (151) the same prods. accompanied by ethylene and hydrogen; C with N/10 abs EtOH/NaOH at 25° (17), with alc.-free NaOEt in other under press. htd. to 140° (152), yields tetrachloroethylene (3:5460) (for study of kinetics see (17)).]

Behavior with metals. [C with alk. or alk.-earth metals is (like many other polychloro compounds) subject to explosion by mechanical shock; for study of sensitivity of C with Li, Na, K, Mg, Ca, Sr, Ba, Al, or Tl see (154). — C with "molecular" Ag at 280° loses 2 atoms of chlorine yielding (99) tetrachloroethylene (3:5460).]

Behavior with organometallic compounds. [For behavior of C with RMgX compds. see (155) (166); \overline{C} does not (11) react with Hg di-(p-tolyl)

Behavior with NH₃ or organic bases. [C with NH₃ at 700-800° gives up its halogen quant. (157) yielding NH₄Cl. — C with excess phenylhydrazine in xylene soln. on stdg. or on warming is reduced to tetrachloroethylene (3:5460), HCl, C₆H₆, and N₂ also being formed (158) (note that analogous reactns. are also shown by 1,1,2,2-tetrachloroethane (3:5750) and by pentachloroethane (3:5880)). — For kinetics of reactn. of \tilde{C} with pyridine or piperidine see (159).]

- 3:4835 (1) Silberrad, Chem. News 123, 271 (1921). (2) Straus, Kollek, Heyn, Ber. 63, 1875 (1930). (3) Schaum, Naumann, Z. anorg. allgem. Chem. 148, 217 (1925). (4) van der Lee, Z. anorg. allgem. Chem. 223, 213-216 (1935). (5) Leder, J. prakt. Chem. (2) 130, 257-258 (1931). (6) Tarczynski, Z. Elektrochem 22, 253 (1916). (7) Staedel, Ber. 11, 1735-1738 (1878). (8) Parijs, Z. anorg. allgem. Chem. 226, 425-428 (1936). (9) Howell, J. Am. Chem. Soc. 45, 186 (1923). (10) Biesalski, van Eck, Z. angew. Chem. 41, 720 (1928).
- (11) Whitmore, Thurman, J. Am. Chem. Soc. 51, 1497 (1929). (12) Müller, Huther, Ber. 64, 590 (1931). (13) Nelson, Ind. Eng. Chem. 22, 971-972 (1930). (14) Ray, Dutt, J. Indian Chem. Soc. 5, 107-108 (1928). (15) Gibson, Proc. Roy. Soc. Edinburgh 44, 140-145 (1923/4). (16) Miller, J. Am. Chem. Soc. 62, 342 (1940). (17) Taylor, Ward, J. Chem. Soc. 1934, 2003-2010. (18) Locat, Rec. trav. chim. 47, 17 (1928). (19) Wiebenga, Z. anory. allgem. Chem. 225, 38-42 (1935). (20) West, Z. Krist. 88, 195-197 (1934).
- (21) Steinmetz, Z. physik. Chem. 52, 466 (1905).
 (22) Bridgman, Proc. Am. Acad. Arts Sci. 51, 84-90 (1915/16).
 (23) Ress, Zimmermann, Z. Krist. 57, 474, 485 (1923).
 (24) Gossner Z. Krist. 38, 151 (1904).
 (25) Schwartz, Z. Krist. 68, 614 (1896).
 (26) Lehmann, Z. Krist. 6, 584-585 (1882).
 (27) Yardley, Proc. Roy. Soc. London, A-118, 449-463 (1928).
 (28) Hendricks, Chem. Revs. 7, 438 (1930).
 (29) van Arkel, Vles, Rec. trav. chim. 55, 410 (1936).
 (30) Schmidt, Funke (to Chem. Werke Aussig-Falkenau), Ger. 715,068, Dec. 16, 1941, Cent. 1942, I 2584; C.A. 38, 2051 (1944).
- (31) Myers, U.S. 1,966,456, July 17, 1934; Cent. 1935, I 3198, C.A. 28, 5554 (1934). (32) Staedel, Ber. 15, 2563 (1882). (33) Rinegardner (to du Pont Co.), U.S. 2,081,236, May 25, 1937; Cent. 1937, II 3381, C.A. 31, 5112 (1937). (34) Pascal, Compt. rend. 154, 883, 886 (1912). (35) "Chemia" Ungarische Chemische Industrie, A. G. & von Dalmady, Ger. 389,778, Feb. 7, 1924; Austrian 95,732, Jan. 25, 1924, Cent. 1924, I 2801; not in C.A. (36) Kharasch, U.S. 1,761,347, June 3, 1930; Cent. 1930, II 1451; C.A. 24, 3657 (1930). (37) Beythien (to Minimax, A.G.), Ger. 639,395, Dec. 4, 1936; Cent. 1937, I 1990, C.A. 31, 1534 (1937). (38) Snelling (to Trojan Powder Co.), U.S. 1,588,277, June 8, 1926; Cent. 1926, II 1487; C.A. 20, 2751 (1926). (39) Frey, Arb. physiol. angew. Entomol. Berlin-Dahlem 6, 189-197 (1939); Cent. 1939, II 3506; C.A. 33, 9487 (1939). (40) Gassner, Seifensuder Zig., see Cent. 1928, I 2629; not in C.A.
- (41) Chem. Fabrik Griesheim-Elektron, Ger. 353,682, May 22, 1922; Cent. 1922, IV 239; not in C.A. (42) Hase, Desinfektion 8, 1-4 (1923); Cent. 1923, II 1005; not in C.A. (43) Salzbergwerk Neu Stassfurt, French 665,930, Sept. 25, 1929; Cent. 1930, I 1996; C.A. 24, 1458 (1930). (44) B. Grether, G. Grether, W. Grether, Ger. 497,478, May 10, 1930, Cent. 1930, II 1601; C.A. 24, 3577 (1930). (45) Salzbergwerk Neu Stassfurt, Swiss 99,217, May 16, 1923; Cent. 1923, IV 916, not in C.A. (46) Akt. Ges. fur medizinische Prod., Brit. 410,364, June 7, 1934; Cent. 1935, II 3969; C.A. 28, 6260 (1934). (47) Frentiss "Chemicals in War," 1st ed., pp. 245-247 (1937). (48) Walker, Ind. Eng. Chem. 17, 1064 (1925). (49) Metivier, French 613,884, Dec. 1, 1926; Cent. 1927, I 1199; not in C.A.: French 648,853, Dec. 28, 1928, Cent. 1931, I 3424; not in C.A. (50) Schwander, Arch. Gewerbepath. Gewerbehyg. 7, 109-116 (1939); Cent. 1939, II 1331; not in C.A.
- (51) Burgi, Wien. klin. Wochechr. 49, 1545-1548 (1936); Cent. 1937, I 3515; not in C.A. (52) Barsoun, Saad, Quart. J. Pharm. Pharmacol. 7, 205-214 (1934); Cent. 1934, II 2550; C.A. 28, 6194 (1934). (53) Tomb, Helmy, J. Trop. Med. Hyg. 36, 265-270 (1933); Cent. 1934, I 728; not in C.A. (54) Hall, Cram, J. Agr. Research 30, 949-953 (1925); Cent. 1925, II 2176; not in C.A. (55) Joachimoglu, Bwchem. Z. 124, 130-136 (1921); Cent. 1922, I 363; C.A. 16, 946 (1922). (56) Meyer, Ber. 27, 3160-3161 (1894). (57) McBee, Hass, Chao, Welch, Thomas, Ind. Eng. Chem. 33, 176-181 (1941). (58) Hofmann, Sciler, Ber. 38, 3058 (1905). (59) Miller, Ind. Eng. Chem. 17, 1182-1183 (1925). (60) Schrader, Havestadt (to T. Goldschmidt, A. G.), Ger. 712,999, Oct. 2, 1941; Cent. 1942, I 2064; C.A. 37, 4748 (1943).
- (61) Hamei, Bull. Chem. Soc. Japan 9, 542-548 (1934); Cent. 1935, I 2801. (62) I.G., French 837,741, Feb. 20, 1939; Cent. 1939, II 228. (63) Mouneyrat, Bull. soc. chim. (3) 17, 799-801 (1897). (64) Nicodemus, J. prakt. Chem. (2) 83, 315-318 (1911). (65) Erdmann, J. prakt. Chem. (2) 85, 84 (1912). (66) Berthelot, Jungfleisch, Ann. Suppl. 7, 255 (1870). (67) Salzbergwerk Neu Stassfurt, Ger. 248,982, July 6, 1912; Cent. 1912, II 299; C.A. 6, 2824 (1912). (68) Loiseau, French 565,356, Jan. 25, 1924; Cent. 1925, II 1227; not in C.A. (69) Blas, Ceva, Anales fis, quim. 37, 298-315 (1941); C A. 37, 74 (1943). (70) Mkryan, Babayan, Sbornik Trudov Armyanskogo Filiala Akad. Nauk 1940, No. 2, 51-58; C.A. 37, 5694 (1943).
- (71) Kokatnur, J. Am. Chem. Soc. 41, 122-123 (1919).
 (72) Mouneyrat, Bull. soc. chim. (3)
 19, 454-455 (1898).
 (73) Gruner (to Kali-Chemie, A.G.), Ger. 712,478, Oct. 21, 1941; Cent.
 1942, I 1053; C.A. 37, 4407 (1943).
 (74) Mouneyrat, Bull. soc. chim. (3) 17, 797-799 (1897);
 (3) 19, 182-183 (1898).
 (75) Elbs, Newmann, J. prakt. Chem. (2) 58, 254 (1898).
 (76) Weiser, Wightman, J. Phys. Chem. 23, 415-439 (1919).
 (77) Fink, Bonilla, J. Phys. Chem. 37, 1141-

1144 (1933). (78) Faraday, Ann. chim. (2) 18, 53-56 (1821). (79) Fruhwirth (to Donau Chemie, I.G.), Ger. 726,713, Sept. 10, 1942; C.A. 37, 6279 (1943). (80) Rüsberg, Gruner (to Kali-Chemie, A.G.), Ger. 712,784, Oct. 25, 1941; Cent. 1942, I 1053; C.A. 37, 4407 (1943).

(81) Levine, Bond (to du Pont Co.), U.S. 2,037,419, April 14, 1936; Cent. 1936, II 864; C.A. 30, 3837 (1936). (82) Leermakers, Dickinson, J. Am. Chem. Soc. 54, 4648-4657 (1932). (83) Dickinson, Carrico, J. Am. Chem. Soc. 56, 1473-1480 (1934). (84) Kharasch, Brown, J. Am. Chem. Soc. 61, 3433 (1939). (85) Reijnhart, Bösseken, Rec. trav. chm. 46, 75 (1927). (86) Goldschmidt, Schussler, Ber 58, 568, 570 (1925). (87) Herndon, Reid, J. Am. Chem. Soc. 56, 3070, 3073 (1928). (88) Kailan, Monatsh. 38, 541, 551 (1917). (89) Hentschel, Ber. 30, 1437 (1897). (90) Strosacker, Schwegler (to Dow Chem. Co.), U.S. 1,930,350, Oct. 10, 1933; Cent. 1934, I 124; C.A. 28, 180 (1934).

(91) Kolbe, Ann. 54, 147 (1845).
(92) Besson, Fournier, Compt. rend. 150, 1119 (1910).
(93) Schwarz, Pflugmacher, J. prakt. Chem. (2) 158, 2-7 (1941).
(94) Sabatier, Mailhe, Compt. rend. 138, 409 (1904).
(95) Dede, Russ, Ber. 61, 2462 (1928).
(96) Bartlett, U.S. 1,800,371, April 14, 1931; Cent. 1931, II 629; C.A. 25, 3362 (1931).
(97) Radziszowski, Ber. 17, 834 Note (1884).
(98) Auger, Compt. rend. 145, 809 (1907).
(99) Goldschmidt, Ber. 14, 928-929 (1881).

(100) Schleede, Luckow, Ber. 55, 3717 (1922).

(101) Schrader, Havestadt (to T. Goldschmidt, A.G.), Ger. 713,000, Oct. 2, 1941; Cent. 1942, I 2064; C.A. 37, 4748 (1943). (102) Mamedaliev, Efendieva, Azerbaitzhanskoe Neftyanoe Khoz. 1936, No. 7, 60-66; Cent. 1936, II 3745; C.A. 31, 8502 (1937). (103) Jones, Allison, Ind. Eng. Chem. 11, 639-643 (1919). (104) Alexeyevskii, J. Russ. Phys.-Chem. Soc. 55, 401-425 (1924); Cent. 1932, II 642; C.A. 19, 2634 (1925). (105) Askenasy, Heller, Ger. 549,341, April 26, 1932; Cent. 1932, II 287; C.A. 26, 3807 (1932). (106) Fruhwith (to Donau A.G.), Ger. 718,888, July 25, 1942; Cent. 1942, II 2085; C.A. 37, 5082 (1943). (107) Fruhwirth (to Donau A.G.), Ger. 772,463, July 13, 1942; Cent. 1942, II 2086; C.A. 37, 5082 (1943). (108) Hennig (to I.G.), Ger. 712,579, Oct. 22, 1941; Cent. 1942, I 1809; C.A. 37, 4407 (1943). (109) Michel, Z. angew. Chem. 19, 1096-1097 (1906). (110) Salzbergwerk Neu Stassfurt, Ger. 174,068, Sept. 8, 1906; Cent. 1906, II 1297; C.A. 1, 950 (1907).

(111) Besson, Compt. rend. 115, 1079 (1892). (112) Noddack, Z. Elektrochem. 27, 361 (1921). (113) Simons, Sloat, Meunier, J. Am. Chem. Soc. 61, 436 (1939). (114) Prandtl, Sennewald, Ber. 62, 1756, 1764 (1929). (115) Mouneyrat, Bull. soc. chm. (3) 17, 794-797 (1897). (116) Senderens, Compt. rend. 172, 155-156 (1921). (117) Jacger, J. Chem. Soc. 119, 2071 (1921). (118) Jaeger, Berger, Rec. trav. chm. 41, 71-81 (1921). (119) Jaeger, Cent. 1911, II 1851-1852, 1912, I 1817. (120) Rabcewicz-Zubkowski, Chvalınski, Roczniki Chem. 10, 680-689 (1930); Cent. 1931, I 919; C.A. 25, 911-912 (1931).

(121) Gelissen, Ger. 480,362, Aug. 7, 1929, Cent. 1929, II 2831; C.A. 23, 4950 (1929) Dutch 14,663, June 15, 1926, Cent. 1929, II 2831; C.A. 20, 3576 (1926). (122) Hubner, Muller, Zeit. für Chemie 1876, 328. (123) Böeseken, Rec. trav. chim. 32, 12 (1913). (124) Leder, J. prakt. Chem. (2) 130, 278-279 (1931). (125) Müller, Ann. 258, 62-64 (1890). (126) Hartmann, Ber. 24, 1011-1026 (1891). (127) McBee, Hass, Pierson, Ind. Eng. Chem. 33, 181-185 (1941). (128) von Bolton, Z. Elektrochem. 8, 169 (1872). (129) Krafft, Merz, Ber 8, 1296-1302 (1875). (130) Tropsch, Ges. Abhandl. Kenntnis Kohle, 6, 301-302 (1921); Cent. 1923, III 1640; C.A. 18, 2332 (1924).

(131) Tropsch, Schellenberg, Ges. Abhandl. Kenntnis Kohlc, 6, 235-247 (1921); Cent. 1924, I 602; C.A. 18, 2873 (1924). (132) Mann, Pope, J. Chem. Soc. 121, 597 (1922). (133) Phillips, Davies, Mumford, J. Chem. Soc. 1929, 543, 547. (134) Bourgoin, Ann. chim. (5) 6, 142-144 (1875); Bull. soc. chim. (2) 23, 344 (1875). (135) Biltz, Ber. 35, 1529-1530 (1902). (136) Geuther, Ann. 107, 212-213 (1858). (137) Howell & Imp. Chem. Ind., Ltd., Brit. 535,026, April 24, 1941; Cent. 1942, II 2203; C.A. 36, 1336 (1942). (138) Sabatier, Mailhe, Compt. rend. 138, 409 (1904). (139) Regnault, Ann. 33, 324-325 (1840). (140) Biesalski, Z. angew. Chem. 37, 317 (1924).

(141) Heslinga, Rec. trav. chim. 43, 182 (1924). (142) Guyot, Simon, Compt. rend. 170, 736 (1920). (143) Prudhomme, Ann. 156, 342-343 (1870). (144) Armstrong, J. prakt, Chem. (2) 1, 251-252 (1870). (145) Miller, Calfee, Bigelow, J. Am. Chem. Soc. 59, 198-199 (1937). (146) Booth, Mong, Burchfield, Ind. Eng. Chem. 24, 328-331 (1932). (147) Locke, Brode, Henne, J. Am. Chem. Soc. 56, 1726-1728 (1934). (148) Henne (to General Motors Corp.), U.S. 1,978,840, Oct. 30, 1934; Cent. 1935, I 1934; C.A. 29, 178 (1935). (149) Henne (to Frigidaire Corp.), Brit. 378,324, Sept. 1, 1932; Cent. 1933, II 1583; C.A. 27, 3947 (1933): French 730,370, Aug. 11, 1932; Cent. 1933, II 1583; C.A. 27, 304 (1933). (150) Geuther, Ann. 111, 174-175 (1859). (151) Berthelot, Ann. 109, 120-121 (1859). (152) Geuther, Brockhoff, J. prakt. Chem. (2)

(151) Berthelot, Ann. 109, 120-121 (1859).
(152) Geuther, Brockhoff, J. prakt. Chem. (2)
7, 107-111 (1873).
(153) de Gibon, French 802,765, Sept. 15, 1936; Cent. 1937, I 1990; C.A. 31, 1968 (1937).
(154) Lenz, Metz, Z. ges. Schiess- u. Sprengstoffw. 27, 294 (1932); Cent. 1933.

I 1716. (155) Korshak, J. Gen. Chem. (U.S.S.R.) 9, 1153-1154 (1939); C.A. 34, 1303 (1940).
(156) Binaghi, Gazz. chim. ital. 57, 674-675 (1927); Cent. 1928, I 908; C.A. 22, 573 (1928). (157)
Heslinga, Rec. trav. chim. 43, 178-179 (1924). (158) Gowing-Scopes, Analyst, 39, 385-386 (1914).
(159) Tronow, J. Russ. Phys.-Chem. Soc. 58, 1278-1301 (1926); Cent. 1927, II 1145; not in C.A.
(160) von Oettingen, J. Ind. Hyg. Toxicol. 19, 405 (1937).

(161) Rauscher, Ind. Eng. Chem., Anal. Ed. 9, 296-299 (1937). (162) Schott, Schumacher,

Z. physik. Chem. B-49, 107-125 (1941), C.A. 38, 3551 (1944).

3:4840 3,5-DICHLOROBENZOIC ACID
$$C_7H_4O_2Cl_2$$
 Beil. IX - 344 IX₁-(141)

Ndls. from alc. — Sublimes (10). — Very eas. sol. alc., spar. sol. aq. or lgr.

[For prepn. from 3,5-dichlorotoluene (3:6310) by oxidn. with dil. HNO₃ at 150–170° see (8) (7); from 3,5-dichlorobenzaldehyde (3:1475) by oxidn. with KMnO₄ (74% yield) see (3); from 3,5-dichlorobiphenyl (3:0360) by oxidn. with CrO₃ + AcOH see (9): for prepn. from 3,5-diamnobenzoic ac. via diazo reactn see (1); from 4-amino-3,5-dichlorobenzoic ac. via diazo reactn. see (2); from 3,5-dichloroaniline via conv. to acid hydrolysis of the nitrile see (10); for prepn. from 5-nitro-3-sulfobenzoic acid via PCl₅ and subsequent boilg. with alk. see (11)

 \bar{C} added to 8 pts. fumg. HNO₃ (D=1.48), stood 2-3 hrs. at 70°, cooled, ppts. 75% yield 2-nitro-3,5-dichlorobenzoic ac., ndls. from dil. alc, m.p. 194° cor. (5). [This prod. depresses m.p. of \bar{C} (5).]

C with PCl₅ yields (12) 3,5-dichlorobenzoyl chloride, b.p. 135-137° at 25 mm. (12).

- --- Methyl 3,5-dichlorobenzoate: m.p. 58° (13).
- Ethyl 3,5-dichlorobenzoate: m.p. unrecorded. [For study of velocity of hydrolysis see (14).]
- --- 3.5-Dichlorobenzamide: unrecorded.
- --- 3.5-Dichlorobenzanilide: ndls. from dil. alc., m.p. 148° (15).

3:4840 (1) Bornwater, Holleman, Rec. trav. chim 31, 229 (1912). (2) Elion, Rec. trav. chim. 42, 178 (1923). (3) Asinger, Lock, Monatsh. 62, 346 (1933). (4) Lock, Bock, Ber. 70, 923 (1937). (5) Asinger, Monatsh. 63, 390-391 (1933/34). (6) Gassmann, Hartmann, J. Am. Chem. Soc. 63, 2393-2395 (1941). (7) Cohen, Dakin, J. Chem. Soc. 79, 1112, 1134 (1901). (8) Lellmann, Klotz, Ann. 231, 324 (1885). (9) Hinkel, Hey, J. Chem. Soc. 1928, 2789. (10) Claus, Stavenhagen, Ann. 269, 225 (1892).

Franchimont, Rec. trav. chim. 29, 376 (1910). (12) Cohen, Briggs, J. Chem. Soc. 83, 1214 (1903). (13) Müller, Tietz, Ber. 74, 807-824 (1941); C.A. 35, 7953 (1941). (14) Blakey, McCombie, Scarborough, J. Chem. Soc. 1926, 2863-2868. (15) Waters, J. Chem. Soc. 1929, 2108.

3:4845 6-CHLORONAPHTHOIC ACID-1

COOH C₁₁H₇O₂Cl Beil. S.N. 951

M.P. 189° cor. (4) 188-189° (1) (2) Cryst. from C6H6 or 95% alc.

[For formn. of \bar{C} from furoic acid (1:0475) + chlorobenzene (3:7903) + AlCl₃ (18% yield (2)) (3) or from methyl furoate (1:3452) + chlorobenzene (3:7903) + AlCl₃ (yield 39% (1)) see indic. refs.]

C on decarboxylation by htg. in quinoline at 225° in pres. of copper chromite cat. for 4 hrs. yields (2) 2-chloronaphthalene (3:1285), m.p. 58-59° (2).

- Methyl 6-chloro-1-naphthoate: b p. 165-170° at 2 mm. (1). [From methyl furoate (1:3452) + chlorobenzene (3:7903) + AlCl₃ (15% yield (1)).]
- Ethyl 6-chloro-1-naphthoate: unreported.
- D p-Bromophenacyl 6-chloro-1-naphthoate: mp. 142-143° cor. (4).

3:4845 (1) Price, Huber, J. Am. Chem. Soc. 64, 2139 (1942). (2) Price, Chapin, Goldman, Krebs, Shafer, J. Am. Chem. Soc. 63, 1857, 1861 (1941). (3) McCorkle, Turck, Proc. Iowa Acad. Sci. 43, 205-206 (1936), Cent. 1938, II 1950, C.A. 32, 4161 (1938). (4) Horn, Warren, J. Chem. Soc. 1946, 144.

3:4850 PENTACHLOROPHENOL

Cryst. from alc. as monohydrate, $\bar{C}.H_2O$, m.p. 174°; anhydrous ndls from C_6H_6 ; sublimes in long ndls. — Very insol. aq. (17), very eas. sol. alc., ether; mod. sol. C_6H_6 ; spar. sol. cold lgr.; for quant data on solubility in 15 solvents at 7 temps. from 0° to 60° see (1) (17). — Odor pronounced only on htg; dust of \bar{C} causes sneezing — Slightly volatile with steam.

[For general review see (1), for use as wood preservative see (17) (19); for studies on toxicity see (20) (21); for fate of \bar{C} in organism see (22)]

[For prepn. see Beil. VI-194, VI₁-(104); for comml prepn. from hexachlorobenzene (3:4939) + NaOH + MeOH see (12) cf. (23); from chlorination of phenol or polychlorophenols in pres. of AlCl₃ see (13), from "hexachlorophenol" (3:3180) by reduction with SO₂ in alc see (18).]

 \bar{C} is acidic and in alc. soln. titrates quant. using thymol-blue (Neut. Eq. = 266.5) (1). [For dissoc. const. see (2).] — \bar{C} is insol. in NH₄OH (1) but slowly dis. in cold Na₂CO₃ soln. (8). — \bar{C} in alk. soln. does not couple with diazonium salts. [For spectrophotometric detn. see (11).]

Salts. See Beil. VI-194. Na\(\bar{A}\), ndls. (from acctone + lgr), spar sol. aq. (3), Na\(\bar{A}\). H₂O, loses aq. at 110°, sol. aq., alc., ether. [For comml. application as preservative see (1) (14).] — Ag\(\bar{A}\), yel. ppt. turning orange on drying. — Heavy metal salts insol. aq. and often colored (1).

 \tilde{C} in alk. shaken with $(CH_3)_2SO_4$ (6), or \tilde{C} treated with diazomethane (6), or \tilde{C} htd. in MeOH with $CH_3I + KOH$ (15), yields its methyl ether, pentachloroanisole, ndls. from alc., m.p. 108° (6), 106.5° (6).

Dentachlorophenyl acetate: from \tilde{C} on htg. with Ac₂O + NaOAc (15) or from \tilde{C} in CS₂ + AcCl + AlCl₃ (16); ndls. from alc., m.p. 149.5-150 5° (16), 147-148° (15). [This prod. is very resistant to saponification (16).]

- D Pentachlorophenyl benzoate: from C + BzCl by warming in pyridine (3); ndls. from alc., m.p. 164-165° (3), 159-160° (15), 159° (10). [Very resistant to saponification (16).]
- 3:4850 (1) Carswell, Nason, Ind. Eng. Chem. 30, 622-626 (1938). (2) Tiessens, Rec. trav. chim. 50, 116, 120 (1931). (3) Biltz, Giese, Ber 37, 4018-4020 (1904). (4) Fels, Z Krist. 32, 369 (1900). (5) Fichter, Glantzstein, Ber. 49, 2481 (1916). (6) Pollak, Gebauer-Fülnegg, Monatsh. 47, 116-117 (1926). (7) Hugounenq, Ann. chim. (6) 20, 545 (1890). (8) Merz, Weith, Ber. 5, 459 (1872). (9) Zincke, Broeg, Ann. 363, 238 (1908). (10) Brazier, McCombie, J. Chem. Soc. 101, 976-977 (1912).
- (11) Deichmann, Schafer, Ind. Eng. Chem., Anal Ed. 14, 310-312 (1942). (12) Smith, Livak (to Dow Chem. Co), U.S. 2,107,650, Feb. 8, 1938; Cent. 1938, I 3821; CA. 32, 2548 (1938). (13) Stoesser (to Dow Chem. Co.), U.S. 2,131,259, Sept. 27, 1938, Cent. 1938, II 4312; C.A. 32, 9102 (1938). (14) Carswell (to Monsanto Chem. Co.), U.S. 2,157,113, May 9, 1939; Cent. 1939, II 2720. (15) Weber, Wolff, Bcr. 18, 336 (1885). (16) Barral, Bull soc chm (3) 13, 342-343 (1895) (17) Carswell, Hatheld, Ind. Eng. Chem. 31, 1431-1435 (1939). (18) Britton, Alquist (to Dow Chem. Co.), U.S. 2,176,417, Oct. 17, 1939; C.A. 34, 1038 (1940). (19) Hatfield, Proc. Am. Wood Preserving Assoc 1944, 4765, C.A. 39, 2631 (1945). (20) Goodinght, Ind. Eng. Chem. 34, 868-872 (1942)
- (21) Deichmann, Machle, Kitamiller, Thomas, J. Pharmacol. 76, 104-117 (1942); C.A. 37, 461 (1943). (22) Machle, Deichmann, Thomas, J. Ind. Hyg. Toxicol. 25, 192-194 (1943). (23) Troitskii, Voronina, Ory. Chem. Ind. (U.S.S.R.) 7, 240-241 (1940); C.A. 35, 3989 (1941).

3:4853 CHLOROFUMARIC ACID Cl—C—COOH C₄H₃O₄Cl Beil. II - 744 Π_{1-} (302) Π_{2-} (640)

M.P.	193°	(1)	
	192°	(2)	(3) (4)
	191.5-192.5° cor. (5)		
	191.5°	(6)	
	191-192°	(22)	
	191°	(8)	(10) (19)
	190–191°		(12)
	189°	(11)	
	188-189°	(14)	

[See also chloromaleic acid (3:3432).]

Tbls from AcOH. — \tilde{C} is very cas sol aq., alc. or ether; spar. sol. C_6H_6 or lgr. — \tilde{C} sublimes without forming anhydride

[For prepn of $\bar{\rm C}$ from chloromaleic acid (3.3432) by repeated evapn, with cone. HCl see (5) (2); from $d_i l_i - \alpha_i \alpha'_i$ -dichlorosuccime acid (3:4711) on boilg, with aq (7), or with aq. KOH (8) (9) or aq acid (9) see indic 1efs; from $meso_i - \alpha_i \alpha'_i$ -dichlorosuccinic acid (3:4930) with aq. KOH at 0° see (7) (8) (9) (note that from this source action of acid yields (9) both $\bar{\rm C}$ and chloromaleic acid (3:3432)); from diethyl $d_i l_i - \alpha_i \alpha'_i$ -dichlorosuccinate (3:9578) on hydrolysis with boilg. 30% H₂SO₄ see (1); from diethyl chlorofumarate (3:6864) by evapn, with 1°1 HCl see (6); from chlorofumaro(di)nitrile (b.p. 172° at 74 mm., 64.0–64.2° at 10 mm., $D_i^{20} = 1.2499$, $n_i^{20} = 1.49571$ (22)), by hydrol. see (22).]

[For formn. of $\bar{\rm C}$ from diethyl oxaloacetate [Beil. III-782, III₁-(273), III₂-(479)] by actn. of PCl₅ followed by alc. KOH see (11); from acetylenedicarboxyhc acid [Beil. II-801, II₁-(317), II₂-(670)] with conc. HCl on stdg. 10 days at room temp. see (12) cf. (13); from 3-chlorofuroic acid [Beil. XVIII-282] on oxidn. with dil. HNO₃ or from 3,5-dichlorofuroic acid [Beil. XVIII-283] or 4,5-dichlorofuroic acid [Beil. XVIII-283] on oxidn. with Br₂/aq. see (14).]

 $\ddot{\mathbf{C}}$ on gentle boilg. largely decomposes into $\mathbf{CO}+\mathbf{CO_2}+\mathbf{HCl}$ (5); but $\ddot{\mathbf{C}}$ on vigorous boilg. splits off aq. and isomerizes (or vice versa) yielding (5) chloromaleic anhydride (3:0280). — $\ddot{\mathbf{C}}$ with $\mathbf{P_2O_5}$ (6) (15), or with $\mathbf{POCl_3}$ (16) or with \mathbf{AcCl} (5), gives on distn. chloromaleic anhydride (3:0280). — $\ddot{\mathbf{C}}$ (1 mole) with chlorofumaryl (di)chloride (3:6105) (1 mole) at 125° for 1 hr. also yields (17) chloromaleic anhydride (3:0280).

 $[\bar{C} \text{ (as } K_2\bar{A}) \text{ in aq. soln. with Na/Hg is dehalogenated and reduced yielding (18) succinic acid (1:0530).]}$

Č readily reduces aq. KMnO₄.

[\bar{C} in aq. soln on protracted treatment with Cl₂ gives (19) β,β,β -trichloro- α,α -dihydroxy-propionic acid ("trichloropyruvic acid hydrate") [Beil. III-623, III₂-(408)], ndls. from CHCl₃, m.p. 102° (19). — \bar{C} does not (5) add Br₂ even at 100° (dif. from chloromaleic acid (3:3432)).]

Č behaves normally as a dibasic acid: e.g., titration with standard dil. aq. alk. gives Neut. Eq. 75.3; for study of electrometric titration see (2).

[Salts. (NH₄)₂Ā, eas. sol. aq. (5), but spar. sol. MeOH, EtOH, and insol. in ether, acetone, AcOEt, CHCl₃, or C₆H₆ (20) see indic. refs. — KHĀ, much less sol. than corresp. prod. from chloromaleic acid, e.g., 100 g. of its satd. soln. at 15° conts. 3.843 g. KHĀ (5). — Ag₂Ā (10) (12). — BaĀ.3H₂O, fairly sol. aq. (10). — PbĀ.2H₂O (13).]

[Č on stdg. at ord. temp. with slight excess 0.76 N aq. KOH gives chlorine ion about 40 times as fast (12) as the isomeric chloromaleic acid (3:3432).]

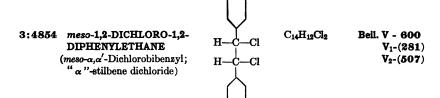
The acid (di)chloride corresp. to C, viz., chlorofumaryl (di)chloride (3:6105), has been reported only by indirect means.

- Dimethyl chlorofumarate: oil (see 3:6582).
- —— Diethyl chlorofumarate: oil (see 3:6864).
- **bis-(p-Nitrobenzyl)** chlorofumarate: m.p. 138.5° (21). [From Na₂\bar{A} with p-nitrobenzyl bromide in 63% ale. refluxed 2 hrs. (21).]
- Chloromaleanii [N-phenyl-chloromaleinimide]: ndls. from boilg. alc., m.p. 170° (17). [From aniline salt of \bar{C} on htg. for a few minutes at 170°-180°; note that during the process isomerization occurs and therefore that the prod. is the same as similarly obtd. from chloromaleic acid (3:3432) q.v.]
- © Chlorofumaro-bis-(p-bromoanilide): faintly yel. ndls. from boilg. alc., m.p. 236° (17). [From chlorofumaryl (di)chloride (3:6105) with p-bromoaniline (4 moles) in dry ether; note that crude prod. is also accompanied by a little N-(p-bromophenyl)-chloromaleinimide, m.p. 190° (17).]

3:4853 (1) Patterson, Todd, J. Chem. Soc. 1929, 1769, 1770. (2) Ashton, Partington, Trans. Faraday Soc. 30, 602, 605-606, 608 (1934). (3) Langseth, Z. physik. Chem. 118, 54 (1925). (4) Stelling, Z. physik. Chem. B-24, 410, 424 (1934). (5) Perkin, J. Chem. Soc. 53, 697-700, 703-705 (1888). (6) von Auwers, Harres, Ber. 62, 1685-1687 (1929). (7) Michael, Tissot, J. prakt. Chem. (2) 46, 393-395 (1892). (8) Robinson, Lewis, J. Chem. Soc. 1933, 1260. (9) Holmberg, Arkiv Kemi, Mineral., Geol. 8, No. 2, 33 (1920); Cent. 1921, I 830; C.A. 16, 2116 (1922). (10) Kauder, J. prakt. Chem. (2) 31, 29-32 (1885).

(11) Nef. Ann. 276, 223-226 (1893). (12) Michael, J. prakt. Chem. (2) 52, 306-308, 321-322 (1895). (13) Bandrowski, Ber. 15, 2695 (1882). (14) Hill, Jackson, Am. Chem. J. 12, 36, 50, 115 (1890). (15) Walden, Ber. 30, 2885-2886 (1897). (16) Thomas-Mamert, Bull soc. chim. (3) 13, 847 (1895). (17) Chattaway, Parkes, J. Chem. Soc. 125, 466 (1924). (18) Perkin, Ann. 129, 373-374 (1864). (19) Büchner, Ber. 26, 656-657 (1893). (20) McMaster, Magill, J. Am. Chem. Soc. 38, 1802-1803 (1916).

(21) Lyons, Reid, J. Am. Chem. Soc. 39, 1733 (1917). (22) Mommaerts, Bull. classe sci., Acad. roy. Belg. (5) 27, 579-597 (1941); Cent. 1943, I 615-616; C.A. 38, 3621 (1944).



188-189°

[See also the isomeric d,l or " β "-stilbene dichloride (3:2570).]

(20)

Colorless ndls. from alc., AcOH, C6H6, toluene, or lgr. — Spar. sol. hot alc., eas. sol. hot toluene. — Sublimes.

PREPARATION OF C

FROM BINUCLEAR INITIAL MATERIALS

From stilbene (trans-1,2-diphenylethylene). [For prepn. of \bar{C} from 1,2-diphenylethylene (stilbene) (1:7250) with Cl₂ in CHCl₃ (8) (16), with Cl₂ in ether in sunlight (17) (some " β "-stilbene dichloride (3:2570) is also formed), with Cl₂ in ethane soln. (note low temp.) in sunlight (gives 34.4% yield \bar{C} + 48.7% yield diastereomer (3:2570) (15)) see indic. refs.; with PCl₅ (2 moles) in CHCl₃ soln. (6) or with PCl₅ in POCl₃ in s.t. at 170° (2) see indic. refs.; with SO₂Cl₂ in presence of peroxides at room temp. (yield of crude mixt. is 100%; sepn. of isomers gives 45% \bar{C} + 33% diastereomer (3:2570) (7)), with nitryl chloride (CINO₂) in ether (57% yield (18)), see indic. refs.]

From isostilbene (cis-1,2-diphenylethylene). [For prepn. of \bar{C} from isostilbene with PCl₅ in C_6H_6 stood 2 days at room temp. see (6).]

From bibenzyl. [For formn. of C from bibenzyl (1:7149) with chromyl chloride (CrO₂Cl₂) in CS₂ (other prods. are also formed) see {19}.]

From α, α' -dibromobibenzyl (stilbene dibromide). [For formn. of \bar{C} from the higher-melting diastereomer (m.p. 236°) of stilbene dibromide [Beil. V-602, V₁-(282), V₂-(508)] with SnCl₄ in C₆H₆ on refluxing $\frac{1}{2}$ hr. (5) (note that at ord. temp. replacement is only

partial and yields (5) only stilbene chlorobromide, m.p. 225°) or with HgCl₂ in acetone/CHCl₃ refluxed 11 hrs. (poor yield (11)) see indic. refs.]

From
$$\alpha,\alpha'$$
-dihydroxybibenzyl (C_6H_5 — C — C — C_6H_5).

From meso-hydrobenzoin. [For prepn. of \bar{C} from meso-hydrobenzoin [Beil. VI-1003, VI₁-(490)] with PCl₅ (2 moles) (20) cf. (15) (yield 43% \bar{C} + 22% diastereomer (3:2570) (8) (16)), with PCl₃ (8) (16), or with SOCl₂ in C_6II_6 + pyridine (100% yield (10)) (13) see indic. refs.]

From d,l-hydrobenzoin (isohydrobenzoin). [For prepn. of \bar{C} from isohydrobenzoin [Beil. VI-1004, VI₁-(490)] with PCl₅ (27-32% \bar{C} + much resin (8)) (16) (20) or with PCl₅ (8) (16) see indic. refs.; note, also, that l-isohydrobenzoin with PCl₅ in CHCl₃ refluxed 2 hrs. gives (45% yield (1)) \bar{C} .]

From α -chloro- α' -hydroxybibenzyl. [For formn. of \bar{C} from α -chloro- α' -hydroxybibenzyl (m.p. 77°, corresp. p-nitrobenzoate, m.p. $103-104^{\circ}$ (3)) with SOCl₂ in CHCl₃ see (3); note that by this method \bar{C} is formed exclusively.]

From α -amino- α' -hydroxybibenzyl. [For prepn. of $\bar{\bf C}$ from d_il - α -amino- α' -hydroxybibenzyl with PCl₅ (42% yield (21)) or with NOCl (1) see indic. refs; note also that d- α -amino- α' -hydroxybibenzyl in HCl with NOCl gives (1) 13% $\bar{\bf C}$ + 24% of l-"stilbene dichloride (3:2570) while l- α -amino- α' -hydroxybibenzyl in HCl with NOCl gives (1) 14% $\bar{\bf C}$ + 17% d-" β "-stilbene dichloride (3:2570).]

From Mononuclear Initial Materials

From benzal (di)chloride. [For formn. of \bar{C} from benzal (di)chloride (3:6327) by bimolecular reduction with $II_2 + Pd$ in alc. soln. (22), or with $II_2 + Pd$ in alc. soln. (22), or with $II_2 + Pd$ in alc. soln. (22), or with $II_2 + Pd$ in alc. soln. (22), or with $II_2 + Pd$ in alc. soln. (22), or with $II_2 + Pd$ in alc. soln. (22), or with $II_2 + Pd$ in alc. soln. (22), or with $II_2 + Pd$ in alc. soln. (22), or with $II_2 + Pd$ in alc. soln. (23), or with excess $II_2 + Pd$ in alc. (24), or by action of $II_2 + Pd$ in alc. (25), soln. (25), soln. (26), all $II_2 + Pd$ in alc. soln. (26), or with $II_2 + Pd$ in alc. soln. (26), or with $II_2 + Pd$ in alc. soln. (27), or with $II_2 + Pd$ in alc. soln. (27), or with $II_2 + Pd$ in alc. soln. (28), or with $II_2 + Pd$ in alc. soln. (29), or with $II_2 + Pd$ in alc. soln. (29), or with $II_2 + Pd$ in alc. soln. (21), or with $II_2 + Pd$ in alc. soln. (21), or with $II_2 + Pd$ in alc. soln. (21), or with $II_2 + Pd$ in alc. soln. (21), or with $II_2 + Pd$ in alc. soln. (21), or with $II_2 + Pd$ in alc. soln. (21), or with $II_2 + Pd$ in alc. soln. (21), or with $II_2 + Pd$ in alc. soln. (22), or with $II_2 + Pd$ in alc. soln. (22), or with $II_2 + Pd$ in alc. soln. (22), or with $II_2 + Pd$ in alc. soln. (23), or with $II_2 + Pd$ in alc. soln. (24), or with $II_2 + Pd$ in alc. soln. (25), or with $II_2 + Pd$ in alc. soln. (25), or with $II_2 + Pd$ in alc. soln. (26), or with $II_2 + Pd$ in alc. soln. (26), or with $II_2 + Pd$ in alc. soln. (27), or with $II_2 + Pd$ in alc. soln. (28), or with $II_2 + Pd$ in alc. soln. (28), or with $II_2 + Pd$ in alc. soln. (28), or with $II_2 + Pd$ in alc. soln. (28), or with $II_2 + Pd$ in alc. soln. (28), or with $II_2 + Pd$ in alc. soln. (29), or with $II_2 + Pd$ in alc. soln. (29), or with $II_2 + Pd$ in alc. soln. (29), or with $II_2 + Pd$ in alc. soln. (29), or with $II_2 + Pd$ in alc. soln. (29), or with $II_2 + Pd$ in alc. soln. (29), or with $II_2 + Pd$ in alc. soln. (29), or with $II_2 + Pd$ in alc. soln. (29)

From benzotrichloride. [For formn. of \bar{C} from benzotrichloride (3:6540) by actn. of Ni on htg. in atm. of CO_2 see (23).]

From Miscellaneous Initial Materials

[For form. of \tilde{C} from diphenylace aldehyde [Beil. VII-438, VII₁-(234)] with PCl₅ in C_6H_6 under reflux 2 hrs. (41% yield) see (3)]

CHEMICAL BEHAVIOR OF C

Action of heat. C on repeated htg. above its m.p. is partially isomerized to its diastereo-isomer (3:2570) as a result of which the m.p. of the sample gradually falls to about 160° but not lower (8) (16).

Reduction. C with Zn dust + AcOH gives good yields (24) of trans-1;2-diphenylethylene (stilbene) (1:7250), m.p. 124°.

Hydrolysis. [No study of the direct hydrolysis of C appears to be recorded. — However, C with AgOAc in boilg. AcOH gives an ester which upon hydrolysis gives (60% yield (8) (16)) almost exclusively d_il-hydrobenzoin (isohydrobenzoin), accompanied by a little

hydrobenzoin; with AgOBz, however, much more of the latter results; however, see also below.]

Other reactions. \bar{C} with alc. KOH on warming under reflux (20) or in an autoclave at 180° (2) splits out 2 HCl yielding diphenylacetylene (tolane) [Beil. V-656, V₁-(319), V₂-(568)], m.p. 60°. — \bar{C} with pyridine in s.t. at 200° for 8 hrs. does not (17) split out HCl (dif. from the " β " stereoisomer (3:2570) q.v.)

[\bar{C} with LiI in alc. refluxed 2 hrs. is little affected but in s t at 200° for 3 hrs. gives (11) (presumably via halogen interchange and subsequent loss of l_2) a little trans-1,2-diphenylethylene (stilbene) (1:7250). — \bar{C} with NaI in alc. is unchanged even at 150° in s.t.; using AcOH as solvent, however, in s.t. at 210° stilbene (1:7250) is formed (11). — \bar{C} does not (11) react with alc. NaBr.]

[C with AgOAc (2 moles + 25% excess) in AcOH at 100° for 9 hrs. gives (25) mixts. of hydrobenzoin diacetate, m.p. 133-134°, and isohydrobenzoin diacetate, m.p. 114-116° (for m.p./compn. diagram of this pair see (25) (26)).]

3:4854 (1) Weissberger, Bach, Ber. 64, 1095-1108 (1931). (2) Kayser, Ann. chim. (11) 6, 220-222 (1936). (3) Newman, Joshel, Wise, J. Am. Chem. Soc. 62, 1862 (1940). (4) Reulos, Compt. rend. 216, 775-776 (1943). (5) Pferffer, Elstert, J. pratt. Chem. (2) 124, 174-175 (1930). (6) Bergmann, Bondt, Ber 64, 1457-1458, 1468 (1931). (7) Kharasch, Brown, J. Am. Chem. Soc. 61, 3434 (1939). (8) Zincke, Ann. 198, 129-141 (1879). (9) Higasi, Bull. Chem. Soc. Japan, 13, 159 (1938). (10) Kitassto, Sone, Ber 64, 1144 (1931).

(11) Pfeiffer, Praetorius, J. prakt. Chem. (2) 137, 30-31, 37-39 (1933). (12) Busch, Weber, J. prakt. Chem. (2) 146, 49-50 (1936). (13) Cairé, Mauclere, Compt. rend. 192, 1568-1569 (1931). (14) Fuson, Ross, J. Am. Chem. Soc. 55, 720-723 (1933). (15) Weissberger, Sangewald, Z. physik. Chem. B-9, 140 (1930). (16) Zincke, Ber. 10, 999-1004 (1877). (17) Pfeiffer, Ber. 45, 1816-1817 (1912). (18) Steinkopf, Kuhnel, Ber. 75, 1327 (1942). (19) Weiler, Ber. 32, 1054 (1899). (20) Fittig, Animann, Ann. 168, 73, 74, 77-78 (1873).

(21) Darapsky, Spannagel, J. prakt. Chem. (2) 92, 293 (1915). (22) Borsche, Heimburger, Btr. 48, 457 (1915). (23) Korczynski, Reinholz, Schmidt, Roczutki Chem. 9, 731-740 (1929); Cent. 1930, I 2075, C.A. 24, 1858 (1930). (24) Meisenheimer, Heim, Ann. 356, 274 (1907). (25) Winstein, Seymour, J. Am. Chem. Soc. 68, 119-122 (1946). (26) Boeseken, Elsen, Rectrav. chm. 47, 696 (1928).

3:4855 5-CHLOROBENZENETRICARBOXYLIC C₉H₅O₆Cl Beil. S.N. 1008 ACID-1,2,4 COOH

(5-Chlorotrimellitic acid)

COOH

M.P. 192-194° (1)

(For prepn. of \tilde{C} from 5-chloro-1,2,4-trimethylbenzene (5-chloropseudocumene) [Beil. V-402] by oxidn. in aq. pyridine with KMnO₄ see (1).]

 $[\bar{\mathbf{C}}$ on suitable treatment with alk. yields (1) 5-hydroxytrimellitic acid [Beil. X-580] for use as dye intermediate.]

3:4855 (1) I.G., Brit. 495,432, Dec. 8, 1938; Cent. 1939, I 1452; C.A. 33, 2913 (1939); French 839,454, April 4, 1939, C.A. 36, 5188 (1942).

3:4857 2,3-DICHLORONAPHTHOQUINONE-1,4 C₁₀H₄O₂Cl₂ Beil. VII - 729 VII₁-(386)

Golden yellow ndls. from AcOH (contg. a little CrO₃ (2)) or from alc. — Sublimes (use in purification (12)). — Insol. aq. (1 in 10,000,000 (13)), spar. sol. cold alc. AcOH, CCl₄, ethyleneglycol ethyl ether, gasoline, cottonseed oil, castor oil, "Nujol" (13); quite sol. (4% (13)) in xylene or o-dichlorobenzene (3:6055); fairly sol. in ether, C₆H₆, acetone, or dioxane (13).

[For use of C as agricultural and textile fungicide see impt. review article (13) cf. (37).] [For prepn. of C from naphthoquinone-1,4 (1:9040) in AcOH with Cl₂ in pres. of I₂ (yields: 90% (14), 80% (8)), from 2-chloronaphthoquinone-1,4 [Beil. VII-729] in AcOH with Cl₂ (15) (16), from naphthoquinone-1,4-N-chloromonimide [Beil. VII-726] in AcOH with 8-10 pts. conc. HCl on warming (70% yield (11)) see indic. refs.; from naphthol-1 (1:1500) with HCl + KClO₃ (6) or after preliminary sulfonation to naphthol-1-sulfoni acid-4 (Neville-Winther acid) followed by HCl + KClO₃ (yields: 83% crude (4), 47% (2), 40-47% (12)) (17) (18), from 4-nitrosonaphthol-1 (naphthoquinone-1,4-monoxime) [Beil. VII-727, VII₁-(386)] in ether with HCl gas (3), from 4-aminonaphthol-1 in AcOH with Cl₂ (17), from 2,3-dichloronaphthol-1 (3:2935) in AcOH with CrO₃ (19), or from 2,4-dinitrophenol (Martius Yellow) [Beil. VI-617, VI₁-(308)] with HCl + KClO₃ (24% yield (2)) (10) see indic. refs.]

[For formn. of \bar{C} from 1,4-dihydroxynaphthalene-3-pyridinium chloride (itself from naphthoquinone-1,4 (1:9040) + pyridine in MeOH + HCl) with SOCl₂ under reflux see (7); from naphthalene (1:7200) in AcOH with CrO₂Cl₂ see (20); from 1,2,3,4-tetrachloronaphthalene [Beil. V-546, V₂-(446)] in AcOH with CrO₃ or with conc. HNO₃ in s.t. at 110° see (9); from naphthalene tetrachloride-1,2,3,4 (3:4750) with conc. HNO₃ see (1): from 2,2,3,4,4-pentachloro-1-oxo-naphthalene tetrahydride [Beil. VII-370] with dil. alc. or dil. AcOH in s.t. at 120-130° see (15).]

[\tilde{C} on reduction by shaking ether soln. with aq. SnCl₂ (21), or with Sn + HCl (part of halogen is lost (10)), or by refluxing with HI + white P (10) gives 2,3-dichloro-1,4-di-hydroxynaphthalene [Beil. VI-979], colorless scales from alc., m.p. 135° (21), 135–140° (10); note that \tilde{C} is reduced by SO₂ + aq. only in s.t. at 130–140° (10). — Note that \tilde{C} with aq. K₂SO₃ or aq. KHSO₃ soln. replaces both chlorine atoms giving (10) K salt of 4-hydroxy-2,3-disulfonaphthyl-1 sulfuric acid [Beil. XI-304].]

 $\ddot{\mathbf{C}}$ on oxidn. with boilg. HNO₃ (D=1.35) slowly yields (10) phthalic acid (1:0820).— $\ddot{\mathbf{C}}$ with aqua regia htd. in s.t. yields (22) phthalic (or nitrophthalic) acid accompanied by some trichloronaphthoquinone-1,4 [Beil. VII-730], yel. ndls., m.p. 250°.

 \bar{C} with equal wt. MnO₂ + 4.8 wts. conc. HCl in s.t. at 230° for 10 hrs. (11) cf. (17) yields 2,2,3,3-tetrachloro-1,4-dioxonaphthalene tetrahydride-1,2,3,4 [Beil. VII-702], colorless pr. from ether, m.p 117° (11).

Č with PCi₅ (2 moles) dislvd. in POCl₃ htd. in s.t. at 180-200° (10), or at 200-250° for 4-5 hrs. (22) (with slow rise of temp. to avoid explosion), yields 1,2,3,4,5-pentachloronaphthalene [Beil. V-546], colorless ndls. from alc., m.p. 168.5° (10) (22).

[Č with large excess MeMgI in ether gives (45% yield (23)) (by replacement of 1 atom of chlorine and usual reactn. of the two carbonyl groups) 1,2,4-trimethyl-1,4-dihydroxy-3-chloro-1,4-dihydronaphthalene, cryst. from ether by pptn. with pet. ether, m.p. 115–117° (23); with certain other RMgX cpds., however, both chlorine atoms are replaced, e.g., Č with large excess C₆H₅MgBr in ether gives (34% yield (23)) 1,2,3,4-tetraphenyl-1,4-dihydroxy-1,4-dihydronaphthalene, cryst. from C₆H₆ + alc., m.p. 241.5° (23); with still other RMgX cpds. neither halogen is affected and only the carbonyl groups react; e.g., Č with large excess α-C₁₀H₇MgBr in ether gives (75% yield (23)) 1,4-di-α-naphthyl-1,4-dihydroxy-2,3-dichloro-1,4-dihydronaphthalene, m.p. 261° dec. (23).]

[C with 2 pts. Cu powder htd. in nitrobenzene or at 240° as directed (24) gives 3% yield triphthaloylbenzene (1,2,3,4-diphthaloylanthraquinone). — C with HBr in nitrobenzene htd. in pres. of CuCl₂ yields (25) 2-bromo-3-chloronaphthoquinone-1,4, m.p. 206-207° (25).]

[C with 2,3-dimethylbutadiene-1,3 (1:8050) in pres. of excess 5% alc. KOH and a little sodium hydrosulfite boiled 2 hrs. and then oxidized with air gives (26) 2,3-dimethylanthraquinone [Beil. VII-815, VII₁-(425)], yel. ndls. from alc., m.p. 205-206°.]

 \bar{C} with bolls alc. KOH hydrolyzes 1 chlorine yielding on acidification (10) 3-chloro-2-hydroxynaphthoquinone-1,4 [Beil. VIII-304], yel. ndls. from alc., m.p. 215°; note that \bar{C} with NaOAe htd. in alc. yields (27) the corresp. acetate, viz., 3-chloro-2-acetoxynaphthoquinone-1,4, yel. ndls. from hot alc, m.p. 98° (27). — [For reactn. of \bar{C} with Na₂S or with H₂S leading to bimolecular condensation with formn. of dibenzothianthrene diquinone or its derivs. see (28) (8).]

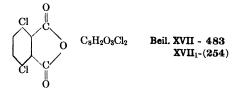
 \bar{C} with phenol (2 moles) + dry K_2CO_3 (i.e., K phenolate) htd for 1 hr. at 100° gives (96% yield (2)) 2,3-diphenoxynaphthoquinone-1,4, or.-yel. ndls. from xylene, m.p. 205° (2). — [For reactn. of \bar{C} with pyrocatechol (1:1520) in pres. of diethylaniline (2), with pyrogallol (1:1555) in pres. of pyridine (29), or with various anthrols and pyridine in prepn. of vat dyes (30) see indic. refs.]

 \tilde{C} in nitrobenzene treated with NH₃ gas or \tilde{C} in boilg. alc. treated dropwise with conc. NH₄OH (27) gives (probably by 1,4-addition and subsequent loss of 1 HCl (31)) (80% yield (2)) 3-chloro-2-aminonaphthoquinone-1,4, yel.-br. ndls. from AcOH, m.p. 193° (2) (corresp. acetyl deriv., m.p. 219° (27)). — Similarly, \tilde{C} with aniline (2 moles) in hot alc. gives (87% yield (12)) (32) 3-chloro-2-anilinonaphthoquinone-1,4 [Beil. XIV-168, XIV₁-(434)], copper-red ndls., m.p. 202° (32). — [For corresp. reactn. of \tilde{C} with many other aliphatic or arom. amines see (33), with β -naphthylamine see (34), with p-phenylenediamine (or its monoacetyl deriv.) see (12); with p-chloroaniline see (27); note that some amines, e.g., ρ -nitroaniline, 2-aminoanthraquinone, and 3-chloro-2-aminonaphthoquinone do not undergo this reactn. (27). — For reactn. of \tilde{C} with pyridine see (2).]

 \bar{C} on nitration, e.g., with 4 vol/pts. red fumg. HNO₃ (D=1.52) + $2\frac{1}{2}$ vol./pts. pure conc. H₂SO₄ at 100° for 6 hrs. (35) cf. (36), gives (40-45% yield (35)) 5-nitro-2,3-dichloronaphthoquinone-1,4, pale yel. cryst. from CHCl₃ (35), AcOH (36), or alc. (36), m.p. 175° (35) (36); this prod. with aniline (2 moles) in hot alc. yields (35) 3-chloro-2-anilino-5 (8)-nitronaphthoquinone-1,4, lfts. from nitrobenzene, m.p. 273° (35).

- 3:4857 (1) Helbig, Ber. 28, 505-506 (1895). (2) Ullmann, Ettisch, Ber. 54, 259-272 (1921).
 (3) Angeletti, Pirona, Atti accad. Torino, Classe sci. fis., mat. nat. 71, 602-606 (1926), Cent. 1937, I 1138; C.A. 31, 678 (1937). (4) Conant, Fieser, J. Am. Chem. Soc. 46, 1873, 1875 (1927).
 (5) Liebermann, Ber. 32, 264 (1899). (6) Darmstadter, Wichelhaus, Ann. 152, 301 (1869).
 (7) Koenigs, Greiner, Ber. 64, 1047 (1931). (8) Brass, Kohler, Ber. 55, 2554 (1922). (9) Claus, Mielcke, Ber. 19, 1184-1185 (1886). (10) Graebe, Ann. 149, 3-12 (1869).
 (11) Friedlander, Reinhardt, Ber. 27, 240 (1894). (12) Fries, Kerkow, Ann. 427, 286-287,
- (11) Friedlander, Reinhardt, Ber. 27, 240 (1894). (12) Fries, Kerkow, Ann. 427, 286-287, 295-296 (1922). (13) Ter Horst, Felix, Ind. Eng. Chem. 35, 1255-1259 (1943). (14) Bertheim, Ber. 34, 1554 (1901). (15) Zincke, Kegel, Ber. 21, 1039, 1045 (1888). (16) Zincke, Schmidt, Ber. 27, 2757 (1894). (17) Zincke, Cooksey, Ann. 255, 370, 372 (1889). (18) Kehrmann, Ber. 21, 1780 (1888). (19) Claus, Knyrim, Ber. 18, 2928-2929 (1885). (20) Carstanjen, Ber. 2, 633 (1869).
- (21) Claus, Ber. 19, 1142, 1144 (1886). (22) Claus, von den Lippe, Ber. 16, 1016-1017 (1883). (23) Clar, Engler, Ber. 64, 1597-1602 (1931) (24) Scholl, Wanka, Dehnert, Ber. 69, 2433 (1936). (25) I.G., Ger. 597,259, May 25, 1934, Cent. 1934, II 1688. (26) I.G., French 37,684, Jan. 14, 1931, Cent 1931, I 124. (27) Fries, Ochwat, Ber. 56, 1295-1300 (1923). (28) Brass, Kohler, Ber. 54, 594-597 (1921) (29) Ghosh, J. Chem. Soc. 107, 1595 (1915). (30) I.G., Brit. 300,407, Dec. 6, 1928, Cent. 1929, I 1622.
- (31) Lindemann, Pabst, Ann. **462**, 37 (1928). (32) Knapp, Schultz, Ann. **210**, 189–190 (1881). (33) Plagemann, Ber. **15**, 484–488 (1882). (34) Fries, Kohler, Ber. **57**, 509 (1924). (35) Fries, Pense, Peeters, Ber. **61**, 1401 (1928). (36) Stock (to I. G.), Ger 468,507, Nov. 15, 1928; Brit. 288,927, May 10, 1929; French 643,447, Sept. 17, 1928; Cent. **1929**, II 96 (37) Ter Horst (to U.S. Rubber Co.), U.S. 2,349,771–2, May 23, 1944, C.A. **39**, 1246 (1945)

3:4860 3,6-DICHLOROPHTHALIC ANHYDRIDE



B.P. 339° (3)

M.P.	193.5-194.5° cor. (1)		
	191° cor.	(2)	
	190-191°	(3)	
	187°	(4)	
	184-186°	(5)	
	185°	(6) (7)	

[See also 3.6-dichlorophthalic acid (3:4870).]

Long colorless ndls. — Sublimes.

[For prepn. of \bar{C} from 3,6-dichlorophthalic acid (3:4870) by htg. at 130-140° (2) (3) (4), at 160° (8), at 180-190° (5), by distn. under diminished press. (9), or by htg. in a current of dry air at 40° (?) (10) see indic. refs.: from ethyl hydrogen 3,6-dichlorophthalate by htg. at 200-220° see (2) (5): for formn. of \bar{C} (together with other isomers) from phthalic anhydride (1:0725) with Cl_2 in pres. of Fe or Fe salts at 160-260° (11) or with Cl_2 in fumg. H₂SO₄ (12) in pres. of I₂ (3), or from 3-chlorophthalic anhydride (3:3900) with Cl_2 in fumg. H₂SO₄ in pres. of I₂ (3), see indic. refs.]

[For sepn. of \bar{C} from isomeric dichlorophthalic anhydrides by means of salts of corresp. acids, etc., see (3) (13) (1); by means of differential hydrolysis with H_2SO_4 (prods. with no α -chlorine such as 4,5-dichlorophthalic anhydride require H_2SO_4 of 98–100% concn., those with 1 α -chlorine such as 3,4-dichlorophthalic anhydride hydrolyze with 56–95% H_2SO_4 , those with 2 α -chlorine atoms such as \bar{C} or 3,4,5,6-tetrachlorophthalic anhydride hydrolyze at H_2SO_4 concns. of less than 50%) see (14).]

C dislyd. in abs. EtOH yields the acid ester, viz., ethyl hydrogen 3,6-dichlorophthalate.

cryst. from CCl₄, m.p. 130–131° (3), 128–130° (2), 128–129° (5); note that this ester when dislvd. in EtOH and satd. with HCl gas, then warmed, does *not* convert to the neutral ester readily, and that even with 15 pts. EtOH and 7 hr. htg. only 16% diethyl 3,6-dichlorophthalate is formed (2).

[C with 1 mole PCl₅ htd in s.t. at 160° for 6–7 hrs. (8) or at 200° for 6 hrs. (15) yields pseudo-3,6-dichlorophthaloyl dichloride (3,3,4,7-tetrachlorophthalide), cryst. from C₆H₆, m.p. 122° (15); this prod. upon htg. above its m.p., or upon solution in inert solvents, or very rapidly upon treatment of such solns, with decolorizing carbon, or slowly even in solid condition, isomerizes to sym-3,6-dichlorophthaloyl dichloride, colorless pr., m.p. 31° (15), from low-boilg pet. ether (in which the pseudo-chloride is spar sol.). — With MeOH the pseudo chloride yields the pseudo dimethyl ester (4,7-dichloro-3,3-dimethoxyphthalide, m.p. 134° (15); the neutral dimethyl 3,6-dichlorophthalate (corresp. to the sym.-chloride) has m.p. 82° (15).] — [C with 2 moles PCl₅ htd. in s.t. several hrs. at 200° is claimed (8) to yield a prod. C₈H₂OCl₆, ndls. from ale, m.p. 117° (8).]

[C with 1 mole NH₂OH.HCl + Na₂CO₃ in aq. as directed (3) for 3,4-dichlorophthalic anhydride (3:4880) yields 3,6-dichlorophthalylhydroxylamine (N-hydroxy-3,6-dichlorophthalmide) [Beil. XXI-504], ndls from MeOH, m.p. 253-258° (3); the conv. of this prod. with boilg aq. Na₂CO₃ to 3,6-dichloroanthranilic acid (analogous to the corresp. process with its isomers) has not been reported (see, however, under the imide below).]

 $[\bar{C} \text{ with steam passed over cat. at } 380-420^{\circ} \text{ loses CO}_2 \text{ presumably yielding (16) 2,5-dichlorobenzoic acid (3 4340).}]$

 \bar{C} with AlCl₃ + C₆H₆ yields (8) (17) 3,6-dichloro-2-benzoylbenzoic acid [Beil. X-750, X₁-(357)], ndls. from C₆H₆ (17) or dil. alc. (8), m.p. 168.5° (18), cor. (17), 159° (8); this prod. on ring closure by htg. with cone H₂SO₄ (2) (17) (18) (19) yields 1,4-dichloroanthraquinone [Beil. VII₁-(411)], yel. ndls. from AcOH, m.p. 187.5-188° (20), 187.5° cor. (17), 187.5° (18), 186° (19). — [For corresp. reactns. of \bar{C} + AlCl₃ with chlorobenzene (22), with toluene (21), with o-chlorotoluene (3:8245) (23), with p-chlorotoluene (3:8287) (24), with fluorene (25), with acenaphthene (26), with pyrene (27), or with β -methylbenzanthrone (28) see indic. refs.]

[$\bar{\rm C}$ with hydroquinone (1:1590) + H₃BO₃ htd. at 190° and afterward treated with hot conc. H₂SO₄ (29), or htd. with AlCl₃ + NaCl at 200–220° for 20 min. (30), gives (yield: 30% (29), 84% (30)) 5,8-dichloro-1,4-dihydroxyanthraquinone (5,8-dichloroquinizarin) [Beil. VIII₁-(715)], cryst. from xylene (30) or AcOH (29), m.p. 275.5° (30), 266° (29) (diacetate, m.p. 180° (30), 170° (29))] — [For reactn. of $\bar{\rm C}$ with AlCl₃ + o-cresol (31), with o-cresol methyl ether (31) (19), or with p-cresol (7) see indic. refs.; for reactn. of $\bar{\rm C}$ with α -naphthol + H₃BO₃ see (9).]

|\tilde{\mathbb{C}} \text{ in fumg } \text{H}_2\text{SO}_4 \text{ treated with } \text{Br}_2 \text{ yields (33) (34) 3,6-dichloro-4,5-dibromophthalic anhydride, colorless ndls. from AcOH, m.p. 269-270° (34), 261° (33). -- \tilde{\mathbb{C}} \text{ in fumg. } \text{H}_2\text{SO}_4 (50\% SO_3) \text{ htd. with } \text{I}_2 \text{ as directed (32) gives (97\% yield) 3,6-dichloro-4,5-di-iodophthalic anhydride, yel. pr. from AcOH, m.p. 258°-258.5° \text{ cor (32).}

[For condens. of \bar{C} with substituted *m*-aminophenols in prepn. of phthalein dyestuffs see (35); for use of \bar{C} in piepn. of pigments of phthalocyanine type see (36) (37); for use of \bar{C} as plasticizer for cellulose esters see (38).]

Fused Č treated with dry NH₃ gas (39) or with urea (37) yields 3,6-dichlorophthalimide [Beil. XXI-504], ndls. from alc., m.p. 242° (39). [This prod. on ring opening and Hofmann degradation with aq. alk. NaOCl (3) or NaOBr (39) gives 3,6-dichloroanthranilic acid [Beil. XIV-367], ndls. from aq. or AcOH, m.p. 153° cf. (3). — [For behavior of Č with hydrazine hydrate yielding acc to conditions N-amino-3,6-dichlorophthalimide, N-(3,6-dichlorophthalimido)-3,6-dichlorophthalimide, or 3,6-dichlorocyclophthalhydrazide see (40).]

Č (1 pt.) dislvd. in 5 pts. boilg. AcOH and treated with 1 pt. aniline gives on cooling (82% yield (1)) 3,6-dichlorophthalanil [Beil. XXI₁-(391)], pale yel. lfts. or ndls. from AcOH, m.p. 201° (10), 197-198° cor. (1), 194° (41), 191° (39). [Note, however, that on protracted htg. with excess aniline first one and then the other nuclear halogen also reacts yielding, respectively, 3-anilino-6-chlorophthalanil, unstable form, m.p. 141° cor. (1), stable form, m.p. 160-160.5° cor. (1), and 3,6-dianilinophthalanil, m.p. 197° (41).]

C on saponification with standard alk. (Sap. Eq. = 108.5), followed by acidification, yields 3.6-dichlorophthalic acid (3:4870) q.v.

3:4860 (1) Pratt, Perkins, J. Am. Chem. Soc. 40, 214-218 (1918). (2) Graebe, Ber. 33, 2019-2022 (1900). (3) Villiger, Ber. 42, 3538-3541, 3549 (1909). (4) Faust, Ann. 160, 64 (1871). (5) Pfeiffer, Ber. 55, 425 (1922). (6) Widman, Bull. soc. chim. (2) 28, 512 (1877). (7) Krescheck, Ullmann, Ber. 55, 308 (1922). (8) Le Royer, Ann. 238, 350-361 (1887). (9) Harrop, Norris, Weizmann, J. Chem. Soc. 95, 282-283 (1909). (10) Tingle, Bates, J. Am. Chem. Soc. 32, 1323-1325 (1910).

(11) Dvernikoff (to Monsanto Chem. Co.), U.S. 2,028,383, Jan. 21, 1936; Cent. 1936, I 2830; C.A. 36, 1394 (1936). (12) Mueller (to General Anilme Works, Inc.), U.S. 1,997,226, April 6, 1935; Cent. 1935, II 1449. (13) Hodgson, J. Soc. Dyers Colourists 49, 215 (1933). (14) Imperial Chem. Ind., Ltd., French 749,954, Aug. 2, 1933; Cent. 1933, II 2748-2749. (15) Kirpal, Galuschka, Lassak, Ber. 68, 1332-1333 (1935). (16) Jacger (to Selden Co.), U.S. 1,964,516, June 26, 1934; Cent. 1934, II 3047. (17) Ullmann, Billig, Ann. 381, 14-16 (1911). (18) Dougherty, Gleascn, J. Am. Chem. Soc. 52, 1027 (1930). (19) Walsh, Weizmann, J. Chem. Soc. 97, 687, 691 (1910). (20) Egerer, Meyer, Monatsh. 34, 90 (1913).

(21) Eckert, Endler, J. prakt. Chem. (2) 162, 334 (1921). (22) Jaroschy, Monatsh. 34, 2 (1934). (23) Keimatsu, Hirano, J. Pharm. Soc. Japan 49, 20-26 (1929), 50, 61-63 (1930); Cent. 1929, I 2533, 1930, II 1551. (24) Keimatsu, Hirano, Yoshimi, J. Pharm. Soc. Japan 50, 95-98 (1930); Cent. 1936, II 2384. (25) Barnett, Goodway, Watson, Ber. 66, 1890 (1933). (26) I.G., French 642,662, Sept. 1, 1928; Cent. 1929, I 581. (27) Kramer (to I.G.), Ger. 589,145, Dec. 2, 1933; Cent. 1934, I 771. (28) Kranzlein, Greune, Sedlmayr (to I.G.), Ger. 430,558, Aug. 13, 1926, Cent. 1926, II 2230. (29) Frey, Ber. 45, 1359 (1912). (30) Waldmann, J. prakt. Chem. (2) 126, 251-253 (1930).

(31) Mariott, Robinson, J. Chem. Soc. 1934, 1633. (32) Pratt, Perkins, J. Am. Chem. Soc. 40, 234 (1918). (33) Juvalta, Ger. 50,117, Friedlander II-93. (34) Lesser, Weiss, Ber. 46, 3945 (1913). (35) Durand, Hueguenin, S.A. Brit. 251,644, July 7, 1926; Cent. 1927, I 1228. (36) Imperial Chem. Ind., Ltd., French 808,845, Feb. 16, 1937; Cent. 1937, 11 3820. (37) Imperial Chem. Ind., Ltd., Thorpe, Linstead, Brit. 390,119, April 27, 1933; French 737,392, Dec. 10, 1932; Cent. 1933, II 794. (38) Dreyfus, French 749,792, July 29, 1933; Cent. 1934, I 3154. (39) Graebe, Gourevitz, Ber. 33, 2024-2025 (1900). (40) Drew, Pearman, J. Chem. Soc. 1937, 31-32.

(41) Mariott, Robinson, J. Chem. Soc. 1939, 137-138.

3:4870 3,6-DICHLOROPHTHALIC ACID

M.P. See text.

[See also 3,6-dichlorophthalic anhydride (3:4860).]

Tbls. from aq.; eas. sol. hot aq. in which it readily gives supersatd. solns.; eas. sol. alc., ether.

 $\bar{\mathbf{C}}$ on htg. begins to lose aq. even at 100° with formn. of 3,6-dichlorophthalic anhydride (3:4860) cf. (1); this change proceeds with increasing speed as the temperature increases; for this reason no definite m.p. of $\bar{\mathbf{C}}$ is recorded and the m.p. observed is actually that of the anhydride.

[For prepn. of C from 3,6-dichlorophthalic anhydride by hydrolysis see the anhydride

(3:4860); from ethyl hydrogen 3,6-dichlorophthalate by htg. at 200° to convert to the anhydride and hydrolysis of the latter see (1); from 1,4-dichloronaphthalene (3:1655) by boilg, with HNO₃ (D=1.3) see (2); from 1,4,5-trichloronaphthalene (3:4005) by htg. with HNO₃ in s.t. see (3); from " α -tetrachloronaphthalene" [Beil. V-546] by oxidn, with HNO₃ see (4); from 1,4-dichloronaphthalene tetrachloride (1,2,3,4,5,8-hexachlorotetralin) [Beil. V-493] by boilg, with conc. HNO₃ (D=1.42) see (5) (6); from 5,8-dichloronaphthylamine-2 [Beil. XII-1310] on oxidn, with dil. HNO₃ in s.t. at 180-200° see (7).]

[For sepn. of \bar{C} from mixts. with the isomeric 3,4- (3:4880) and 4,5- (3:4890) dichlorophthalic acids see (8) (9).] [For use of \bar{C} as softener and/or plasticizer for cellulose derive. see (10).]

Salts. NH₄HĀ, NaHĀ, KHĀ, as well as $(NH_4)_2\bar{A}$, Na₂Ā, and K₂Ā, are all eas. sol. aq. (8); Ag₂Ā, insol. aq. (8) (12); CaĀ, 4H₂O (5) (12), spar. sol. aq. and pptd. by CaCl₂ from hot dil. aq. solns. of $(NH_4)_2\bar{A}$ (8) (12); BaĀ, H₂O, spar. sol. aq. (5) (12); ZnĀ, eas. sol. aq. (characteristic dif. from 3,4- and 4,5-dichlorophthalic acids and used in sepn. of \bar{C} (8)).

Esters. Dimethyl 3,6-dichlorophthalate, m.p. 82° (11) (from Ag₂Ā with MeI (11)); methyl hydrogen 3,6-dichlorophthalate, unreported; diethyl 3,6-dichlorophthalate, cryst. from 50% alc., m.p. 60° (12) (13) (from Ag₂Ā on htg. with EtI in s.t. at 100° (12) (13), or in very small yield from ethyl hydrogen 3,6-dichlorophthalate with EtOH (1) (14); ethyl hydrogen 3,6-dichlorophthalate, cryst. from CCl₄, m.p. 130-131° (8), 128-130° (1), 128-129° (15) (from 3,6-dichlorophthalic anhydride (3:4860) with EtOH).

[For studies of ionization consts. of first (16) and second (16) (17) acid groups see indic. refs.]

3:4870 (1) Graebe, Ber. 33, 2020-2023 (1900). (2) Atterberg, Bull. soc. chim. (2) 27, 409 (1877); Ber. 10, 547 (1877). (3) Atterberg, Bull. soc. chim. (2) 27, 407 (1877); Ber. 9, 1734-1735 (1876). (4) Widman, Bull. soc. chim. (2) 28, 511-512 (1877). (5) Faust, Ann. 160, 64-65 (1871). (6) Widman, Ber. 15, 2160 (1882). (7) Claus, Philipson. J. prakt. Chem. (2) 43, 61 (1891). (8) Villiger, Ber. 42, 3538-3539 (1909). (9) Hodgson, J. Soc. Dyers Colourists 49, 215 (1933). (10) Dreyfus, French 749,792, July 29, 1933; Cent 1934, I 3154

Kırpal, Galuschka, Lassak, Ber. 68, 1332-1334 (1935).
 Le Royer, Ann. 238, 351-354 (1887)
 Graebe, Gourevitz, Ber. 33, 2024 (1900).
 Graebe, Rostowzew, Ber. 34, 2108-2109 (1901).
 Pfeiffer, Ber. 55, 425 (1922).
 Wegscheider, Monatsh. 23, 325-326 (1902).
 Berger, Helv. Chim. Acta 23, 41-44, 50-52 (1940).

M.P. 194-195° (1) 194° (2) 193-194° (3)

[See also tetrachlorobenzoquinone-1,2 (3:3965).]

Colorless anhydrous cryst. from hot dil. alc. (1), lgr. (1) or C_6H_6 (2); \bar{C} from dil. AcOH seps. as monohydrate which over CaCl₂ loses half of its water and above 70–80° all of its aq. (3) (4); \bar{C} from AcOH seps. as a cpd., \bar{C} .AcOH, m.p. 123–124° (4), which can be recrystd. unchanged from lgr. but in air or more rapidly over alk. loses its cryst. AcOH; the above cpd. on soln. in alc. and pptn. with much aq. yields a trihydrate, \bar{C} .3H₂O, m.p. 94°, which can be recrystd. unchanged from aq., alc., or acetone but which from C_6H_6 or lgr. seps. \bar{C} in anhydrous form (4).

[For prepn. of C from pyrocatechol (1:1520) with Cl₂ in AcOH (5) (2) (13) or with ICl

(3) see indic. refs.; from hexachlorocyclohexene-3-dione-1,2 [Beil. VII-575] by reductn. with SnCl₂ in AcOH see (1).]

 $\bar{\mathbf{C}}$ with std. alk. (using phenolphthalein) titrates sharply as a monohydric phenol (4) (6), i.e., Neut. Eq. 248; similarly titration of the cpd. $\bar{\mathbf{C}}$.AcOH (above) gives Neut. Eq. 154 (4).

 $\bar{\mathbf{C}}$ on oxidn. with fumg. HNO₃ in AcOH gives (81% yield (13)) (1) (5) (7) (8) tetrachloro-o-benzoquinone-1,2 (3:3965). — For study of oxidn.-reductn. potential of system: $\bar{\mathbf{C}}$ + tetrachlorobenzoquinone-1,2 see (7) (8). — $\bar{\mathbf{C}}$ with equiv. tetrachlorobenzoquinone-1,2 (3:3965) in least possible hot CHCl₃ gives on cooling the corresp. quinhydrone (14). — [For other complex prods. obtd. from $\bar{\mathbf{C}}$ by action of conc. HNO₃ or N₂O₄ (9), HNO₃ + H₂SO₄ (10), or NaNO₂ in AcOH (2) see indic. refs.]

- **D** Tetrachloropyrocatechol diacetate: ndls. from AcOH, m.p. 190° (1). [From \bar{C} with Ac₂O (1).]
- Tetrachloropyrocatechol monomethyl ether (tetrachloroguaiacol) [Beil. VI-784]: ndls. from hot aq., m.p. 185-186° (11). [Reported only by indirect means (11).]
- Tetrachloropyrocatechol dimethyl ether (tetrachloroveratrole) [Beil. VI-784]: ndls. from alc., m.p. 88° (11) (12). [Reported only by indirect means (11) (12).]
- 3:4875 (1) Zincke, Küster, Ber. 21, 2729-2730 (1888). (2) Frejka, Sefranek, Zika, Collection Czechoslov. Chem. Commun. 9, 241-242 (1937), Cent. 1937, II 1816, C.A. 31, 7046-7047 (1937). (3) Jackson, Boswell, Am. Chem. J. 35, 528-531 (1906) (4) Willstatter, Muller, Bcr. 44, 2186 (1911). (5) Zincke, Ber. 20, 1779 (1887). (6) Weissberger, Ber. 65, 1820 (1932). (7) Conant, Fieser, J. Am. Chem. Soc. 46, 1873, 1875 (1924). (8) Kvalnes, J. Am. Chem. Soc. 56, 2487-2489 (1934). (9) Zincke, Ann. 435, 161-162 (1924). (10) Zincke, Weishaupt, Ann. 437, 93-94 (1924).
- (11) Bruggemann, J. prakt. Chem. (2) 53, 251 (1896). (12) Cousin, Ann. chim. (7) 29, 87 (1903). (13) Jackson, MacLaurin, Am. Chem. J. 37, 11 (1907). (14) Jackson, Carleton, Am. Chem. J. 39, 497 (1908).

3:4880 3,4-DICHLOROPHTHALIC ACID CLCOOH C8H4O4Cl2 Beil. IX-817 IX₁—

M.P. abt. 195° rap. htg. (1)

[See also 3,4-dichlorophthalic anhydride (3:3695).]

Rectangular tbls. from aq.; eas. sol. aq., ether. — \bar{C} can only with difficulty be separated from 4,5-dichlorophthalic acid (3:4890) by crystn. (1).

[For prepn. from 3,4-dichlorophthalic anhydride (3:3695) on boilg, with aq. see (1); from N-(hydroxy)-3,4-dichlorophthalimide (see under 3,4-dichlorophthalic anhydride) by hydrolysis with hot 10% HCl see (1)]

[For sepn. of \bar{C} from mixts, with the isomeric 3,6- (3:4870) and 4,5- (3:4890) dichlorophthalic acids see (1) (2).]

Salts. NaHĀ, Ag₂Ā, CuĀ, CaĀ, BaĀ, ZnĀ all spar. sol. aq. (1).

Esters. Methyl hydrogen 3,4-dichlorophthalate and dimethyl 3,4-dichlorophthalate are both unreported: both possible ethyl hydrogen 3,4-dichlorophthalates are known, viz., ethyl 2-carboxy-3,4-dichlorophthalate (from \bar{C} + abs. EtOH + few drops conc. H₂SO₄ refluxed 6 hrs. (3)), ndls. from dil. alc., m.p. 184° (3); and 3,4-dichloro-2-carbethoxybenzoic acid (from diethyl 3,4-dichlorophthalate by partial KOH saponification or from the anhydride with abs. EtOH (3)), pr. from dil. alc., m.p. 164° (3): diethyl 3,4-dichlorophthalate (from Ag₂Ā), m.p. 80° (3). [For the pseudo diethyl ester of \bar{C} see under 3,4-dichlorophthalic anhydride (3:3695).]

 $\bar{\rm C}$ on protracted htg. at 220° loses aq. yielding 3,4-dichlorophthalic anhydride (3:3695) q.v.

3:4880 (1) Villiger, Ber. 42, 3538-3539, 3541-3542 (1909). (2) Hodgson, J. Soc. Dyers Colourists 49, 215 (1933). (3) Kirpal, Galuschka, Lassak, Ber. 68, 1333-1334 (1935).

3:4885 1-CHLORONAPHTHOIC ACID-2

M.P. 196° (1) (2) 195° (3)

Ndls. from C₆H₆ (1) (2) or from 50% AcOH (3). — Volatile without decompn. (1).

[For prepn of C from 2-(1-chloronaphthyl)carbinol (2) by oxidn see (2); from 1-chloro-2-(trichloromethyl)naphthalene [Beil. V-568] by hydrolysis in boilg. AcOH contg. a little aq. see (1); from 1-chloro-2-naphthonitrile (see below) by hydrolysis with AcOH/H₂SO₄/aq. mixt. see (4); from methyl 1-chloro-2-naphthoate (see below) by hydrolysis with boilg. 15% alc. KOH (46% yield) see (3).]

 \bar{C} with 2% Na/Hg in eq. reduces (1) to β -naphthoic acid (1:0800), m.p. 184° (1).

[The direct conv. of \bar{C} to 1-chloro-2-naphthoyl chloride is not actually reported; however, this acid chloride, m p. 59-60 5° (6), b.p. 226° at 150 mm. (6), b.p. 199-200° at 11.2 mm. (5), has been obtained (5) (3) (6) from 1-hydroxy-2-naphthoic acid [Beil. X-331, X_1 -(145)] with PCl₅ (yield 60 7% (5)) (2).]

Salts. AgA, white flocks spar. sol. aq.; CaA2.2H2O, cryst from aq. (1).

- Methyl 1-chloro-2-naphthoate: ndls. from alc., m.p. 50° (2), cryst. from pet. eth. + acetone, m.p. 44-48° (5); b p. 189-193° at 17.5 mm. (3), 186.5-189° (but press. not given) (5). [From C in MeOH with HCl gas (2) or from the acid chloride (above) in boilg. MeOH (5) (3)] [This ester with Cu bronze + a trace of I₂ at 290° yields (5) dimethyl 1,1'-binaphthyl-2,2-dicarboxylate.]
- --- Ethyl 1-chloro-2-naphthoate: unreported.

3:4885 (1) Wolffenstein, Ber 21, 1190-1191 (1888). (2) Achmatowicz, Lindenfeld, Roczniki Chem. 18, 69-74 (1938), Cent 1939, II 389; not in C.A. (3) Bergmann, Hirshberg, J. Chem. Soc. 1936, 333. (4) Willstaedt, Scheiber, Ber. 67, 473-474 (1934). (5) Kuhn, Albrecht, Ann. 465, 283-285 (1928). (6) Strohbach, Ber. 34, 4161 (1901).

3:4890 4,5-DICHLOROPHTHALIC ACID

 $C_8H_4O_4Cl_2$ Beil. IX - 818 H IX₁-(366)

CI COOH

M.P. 199-200° (1) 200° rap. htg. (2)

[See also 4,5-dichlorophthalic anhydride (3:4830).]

Ndls, from ac

[For prepn. of C from 4,5-dichlorophthalic anhydride (3:4830) by hydrolysis see (2)

(3); from aq. soln. of alk. salts of phthalic acid (1:0820) with Cl_2 in pres. of Sb cpds. see (3) (4); from 4,5-dichloro-1,2-dimethylbenzene (1) by oxidn. with dil. HNO₃ (D=1.3) in s.t. at 180° for 7 hrs. see (1) cf. (5) (6).]

[For sepn. of C from mixts. with the isomeric 3,4- (3:4880) and 3,6- (3:4870) dichlorophthalic acids see (2) (8).] — [For use of C as softener for cellulose derivs. see (9).]

Salts. NH₄HĀ, NaHĀ, KHĀ (all from aq. solns. of the corresp. eas. sol. neutral salts by addn. of AcOH) are spar. sol. cold aq. (2): CuĀ, CaĀ, BaĀ, ZnĀ, and Ag2Ā are all spar. sol. (2).

Esters. Dimethyl 4,5-dichlorophthalate and diethyl 4,5-dichlorophthalate are unreported; methyl hydrogen 4,5-dichlorophthalate is unreported, but ethyl hydrogen 4,5-dichlorophthalate, ndls. from CHCl₃, m.p. 133–134°, is obtained from the anhydride (3:4830) with EtOH (2).

[Č on fusion with NaOH at 175–185° gives (small yield (3)) 4,5-dihydroxyphthalic acid [Beil. X-552, X₁-(276)], m.p. 175°.

C on htg. loses H₂O yielding (2) 4,5-dichlorophthalic anhydride (3:4830), m.p. 187°.

Di-(p-nitrobenzyl) 4,5-dichlorophthalate: cryst. from alc., m.p. 164.5° (10). [From Na₂Ā with p-nitrobenzyl bromide (2 moles) htd. in alc. (10).]

3:4890 (1) Hinkel, Ayling, Bevan, J. Chem. Soc. 1928, 1876. (2) Villiger, Ber. 42, 3538-3539, 3546-3547 (1909). (3) Rushchinskii, J. Applied Chem. (U.S.S.R.) 7, 1113-1115 (1934); Cent. 1936, II 2902. (4) Rushchinskii, Russ. 41,515, Feb. 28, 1935; Cent. 1935, II 3704; C.A. 30, II 2902. (5) Claus, Kautz, Ber. 18, 1369-1370 (1885). (6) Claus, Groneweg, J. prakt. Chem. (2) 43, 253-254 (1891). (7) Ref. 2, pp. 3532-3533. (8) Hodgson, J. Soc. Dyers Colourists 49, 215 (1933). (9) Dreyfus, French 749,792, July 29, 1933; Cent. 1934, I 3154. (10) Lyons, Reid, J. Am. Chem. Soc. 39, 1741, 1744 (1917).

3:4892 PENTACHLOROBENZALDEHYDE
$$C_7HOCl_5$$
 Beil. VII — VII₁-(134)

M.P. 202.5° (1) (2) 197-199° (3)

Colorless ndls. from C₆H₆/alc.; eas. sol. hot C₆H₆ or CS₂; spar. sol. alc., ether, lgr.

[For prepn. of \bar{C} from pentachlorobenzal (di)chloride (3:3590) by hydrolysis with conc. H_2SO_4 at 60–100° or fumg. H_2SO_4 at 40–50° (90% yield (2)) (3) see indic. refs.; from pentachlorobenzaldehyde diethylacetal (see below) by acid hydrolysis see (1).]

Č with aq. alk. KMnO₄ refluxed 7 hrs. oxidizes to (90% yield (1)) pentachlorobenzoic acid (3:4910).

Č in C₆H₆ shaken with satd. aq. NaHSO₃ soln. gives (1) the corresp. NaHSO₃ cpd.

Č with aq. 50% KOH at 100° for 5 hrs. suffers hydrolytic cleavage giving (88% yield (2)) pentachlorobenzene (3:2290) and potassium formate.

Č with EtOH + dry HCl gas gives (60% yield (1)) pentachlorobenzaldehyde diethylacetal, colorless cryst. from pet. ether, m.p. 45°.

[For use of C on prepn. of dyes of the triphenylmethane series see (4).]

Č reacts normally with RMgX reagents [e.g., Č with McMgBr gives (49% yield (1)) methyl-pentachlorophenyl-carbinol, colorless cryst. from alc., m.p. 126° (1); Č with C₆H₅-MgBr gives (1) phenyl-pentachlorophenyl-carbinol (pentachlorobenzohydrol), cryst. from C₆H₆, m.p. 117°.]

Č with anhydrous NaOAc + Ac₂O (Perkin synthesis) at 170-180° for 60 hrs. gives (30% yield (1)) 2,3,4,5,6-pentachlorocinnamic acid, cryst. from C₆H₆, m.p. 233° cor. (1).

Č with aniline at 100° condenses giving (1) pentachlorobenzaldehyde anil, greenish ndls. from C₆H₆/alc., m.p. 187.5° cor. (1).

- D Pentachlorobenzaldoxime: colorless ndls. from C₆H₆, m.p. 201° cor. (1). [From C with NH₂OH.HCl + Na₂CO₃ in dil. alc. on stdg. few days (1).]
- Pentachlorobenzaldehyde phenylhydrazone: citron-yel. ndls. from alc., m.p. 152.5° cor. (1). [From \(\tilde{C}\) in hot satd. C₆H₆ soln. with 1 mole phenylhydrazine (1).]
- —— Pentachlorobenzaldehyde p-nitrophenylhydrazone: unreported.
- ---- Pentachlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.
- ---- Pentachlorobenzaldehyde semicarbazone: unreported,

3:4892 (1) Lock, Ber. 72, 300-304 (1939). (2) Lock, Ber. 66, 1533 (1933). (3) Bayer and Co., Ger. 243,416, Feb. 10, 1912; Cent. 1912, I 618; [C.A. 6, 2292 (1912)]. U.S. 998,140, July 18, 1911; [C.A. 5, 2904-2905 (1911)]. (4) Bayer and Co., Ger. 234,519, May 12, 1911; Cent. 1911 I 1620; [C.A. 5, 2974 (1911)].

3:4893 OCTACHLORONAPHTHALENE

(Perchloronaphthalene)

M.P. B.P. 440-442° at 754 mm., dec. (2) 202° u.c. (7) 258-260° at 2.5 mm. (2) 200° (6) 246-250° at 0.5 mm. (2) 197.5-198° cor. (2) 197.3-198° cor. (3)

Ndls. from $CCl_4 + C_6H_6$ (2); fairly eas. sol. C_6H_6 , lgr., CHCl₃; spar. sol. alc. or AcOH. [For prepn. of \bar{C} from naphthalene (1:7200) with Cl_2 in pres. of 1% Fe powder + 0.1% I_2 first at 100° then at 150° for 10-12 hrs. (90% yield (2)) or with Cl_2 in pres. of SbCl₅ (1) (4) cf. (2) see indic. refs. (for extensive study of merits of many catalysts see (5)).]

[For prepn. of \bar{C} from mixt. of 2-hydroxynaphthalene-1,5-bis-(sulfonyl chloride) and 2-hydroxynaphthalene-1,6-bis-(sulfonyl chloride) (from β -naphthol with ClSO₃H) with PCl₅ in s.t. see (6); from 1-hydroxynaphthalene-tris-(sulfonyl chloride) with PCl₅ in s.t. at 250° see (7); from 1-amino-3,6,8-tris-(sulfonyl chloride) with 3-4 pts. PCl₅ in s.t. at 200-225° for 7 hrs. (40% yield) see (2).]

[For prepn. of \bar{C} from 2,5,6,7,8-pentachloronaphthoquinone-1,4 [Beil. VII-731] with PCl₅ in s.t. at 250° for 6 hrs. see (8); from hexachloronaphthoquinone-1,4 (see below) with PCl₅ see (3).]

[For study of action of \bar{C} (from insulation material on electric wiring) in production of acne see (9); for prepn. of aq. dispersions of \bar{C} see (10); for use of \bar{C} as insecticide see (11); for use of \bar{C} in prepn. of a red mordant dyestuff (by actn. of fumg. H_2SO_4) see (12).]

[\tilde{C} with H_2 passed through a red-hot tube (4) or \tilde{C} with Na + EtOH (2) gives naphthalene (1:7200) together with other prods.]

 \overline{C} on oxidn. with 10 pts. fumg. HNO₃ (D=1.52) in s.t. at 90° gives in good yield (2) (3) hexachloronaphthoquinone-1,4, m.p. 222.5° cor., b.p. 412-415° at 758 mm. dec., 265-267° at 14 mm., accompanied by some tetrachlorophthalic acid (3:4946).

[C̄ on htg. with SbCl₅ + ICl in s.t. at 350° (1) breaks down yielding (2) cf. (1) carbon tetrachloride (3:5100), hexachloroethane (3:4835), hexachlorobenzene (3:4939), and other prods.; under certain conditions (not specified in abstracts) C̄ can be broken down to decachloroindane (perchlorohydrindene) [Beil. V-487], m.p. 138° cor. (2).

 $[\bar{C}]$ with pyridine + CuO + hydrazine hydrate yields (13) a hexachloronaphthalene ndls. from chlorobenzene, m.p. 202-204° (13) (note that m.p. is close to that of \bar{C}).]

Č is stable toward 3% aq. KOH or NaOH for 12 hrs. in cold or even 2 hrs. boilg.; Č is stable to cold 3% alc. KOH or NaOH for 24 hrs., but on htg. for 2 hrs. splits off some 25-30% chlorine and in part resimfies (2).

© Color test with SbCl₅ in CCl₄; \bar{C} with SbCl₅ in CCl₄ gives stable cherry-red color (2). [This response is not given by carbon tetrachloride (3:5100), hexachlorocthane (3:4835), hexachlorobenzene (3.4939), or decachloroindane (2).]

3:4893 (1) Ruoff, Ber. 9, 1486-1488 (1876) (2) Shvemberg, Gordon, J. Gen. Chem. (U.S.S.R.) 2, 921-928 (1932); Cent. 1934, I 215, C.A. 27, 2439 (1933) (3) Shvemberg, Gordon, J. Gen. Chem. (U.S.S.R.) 4, 695-703 (1934); Cent. 1935, II 514, C.A. 29, 2162 (1935) (4) Berthelet, Jungfleisch, Bull. soc. chim. (2) 9, 446-455 (1868), Ann. chim. (4) 15, 330-313 (1868). (5) Shvemberg, Gordon, J. Gen. Chem. (U.S.S.R.) 4, 529-551 (1934), Cent. 1935, II 514, C.A. 29, 1804 (1935). (6) Pollak, Gebauer-Fulnegg, Blumenstock-Halward, Monatsh. 49, 199 (1928) (7) Claus, Mieleke, Ber. 19, 1186-1187 (1886). (8) Claus, Wenzlik, Ber. 19, 1169 (1886). (9) Haldin-Davis, Brit. J. Dermatol. Syphilis. 51, 380-383 (1939), C.A. 34, 1413 (1940). (10) Heckert. (50 du Pont Rayon Co.), U.S. 2,060,210, Nov. 10, 1936, Cent. 1937, 1 1604, C.A. 31, 555 (1937).

(11) Stern, Ger. 411,314, March 26, 1925, Cent. 1925, II 234 (12) B.A.S.F., Ger. 66,611, Friedländer 3, 271. (13) I.G., French 699,492, Feb. 16, 1931, Cent. 1931, 3519.

3:4895 PENTACHLORÓPROPIONIC ACID Cl
$$C_3HO_2Cl_5$$
 Beil. II — II_1 -(112) II_2 -(228)

M.P. 200-215° (see text (1)).

Colorless cryst. from CCl₄. — Eas sol cold aq.

[For prepn. of \tilde{C} from truchloroacrylic acid (3:1840) with Cl_2 in CCl_4 soln. in sunlight (yield not reported) see (1).]

 \bar{C} in aq. soln. behaves as a strong acid; on titration it gives a good Neut. Eq., calcd. 246.5; found 245.8 (1).

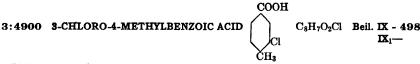
 $\bar{\mathbf{C}}$ is very unstable: e.g., $\bar{\mathbf{C}}$ in aq. soln. on warming dec. (1) (with loss of HCl and CO_2) into tetrachloroethylene (3:5460); presumably this same decomposition, occurs on process of taking its m.p., and the value given above refers to rapid htg on Hg bath.

Salts. The salts of \bar{C} can be obtd. by neutralization with metal hydroxide of a cold satd. aq. soln of \bar{C} followed by evaph. to dryness at low temp.; aq. solns. of the salts are also unstable and rapidly decompose yielding metal chloride $+ CO_2 +$ tetrachlorocthylene (3:5460) (1). [For studies of influence of light on decompn. of these salts see (2) (3) cf. (4).]

[For study of behavior of \bar{C} with H_2 + colloidal Pd see (5).]

Acid chloride. Pentachloropropionyl chloride (3:0470) has been obtd. indirectly, i.e., from trichlorogeryloyl chloride with Cl₂ in sunlight (6); colorless cryst., m.p. 42°.

3:4895 (1) Böeseken, Rec. trav. chim 46, 841-843 (1927). (2) Jaeger, J. Chem. Soc. 119, 2070-2076 (1921). (3) Jaeger, Berger, Rec. trav. chim 41, 72 (1921). (4) Jaeger, Cent. 1912, I 1817-1818; Cent. 1911, II 1851. (5) Boeseken, Rec. trav. chim. 35, 273-274 (1915). (6) Boeseken, Hasselbach, Rec. trav. chim. 37, 11-14 (1913).



Long colorless ndls. from dil. alc.; spar. sol. hot aq.; eas. sol. cold alc.

[For prepn. of $\bar{\rm C}$ from 2-chloro-4-isopropyl-methylbenzene (2-chloro-p-cymene) (3:8775) by oxidn. with dil. HNO₃ (7) of D=1.24 for 8–14 days (2) or htd. 6 hrs. with 5 pts. HNO₃ (D=1.39) + 5 pts. aq. (4) see indic. refs.; from 3-chloro-1,4-dimethylbenzene (2-chloro-p-xylene) (3:8600) by oxidn. with nitrosulfonic acid + fumg. HNO₃ see (1) (5); from 3-chloro-4-methylaecetophenone (8) by oxidn. with alk. KMnO₄ see (8); from 3-chloro-4-methylbenzaldehyde (5) with 50% KOII (Cannizzaro reactn.) see (5); from 3-chloro-4-methylbenzonitrile, m.p. 48–48.5° u.c. (3), 45–46° (6), by protracted boilg. with aq. KOH see (3); from 3-chloro-4-methylbenzamide (see below) on hydrolysis with 25% aq. NaOH see (6).]

Salts. $K\bar{A}.1\frac{1}{2}H_2O$, eas. sol. aq. (9); $Ca\bar{A}_2.3H_2O$, $Ba\bar{A}_2.4H_2O$ (7).

C on fusion with KOH yields (7) (2) 3-hydroxy-4-methylbenzoic acid [Beil. X-237].

[Č on mononitration (9) yields a mixt. of three mononitro derivs. containing 60–70% 3-chloro-4-methyl-6-mitrobenzoic acid [Beil. IX-503], ndls. from alc., m.p. 184–185° (9), 20–30% 3-chloro-4-methyl-5-nitrobenzoic acid [Beil. IX-503], ndls. from aq., m.p. 159° u.c. (9), and 5–10% 3-chloro-4-methyl-2-nitrobenzoic acid [Beil. IX-503], lfts. from aq., m.p. 211° (9).]

- Ethyl 3-chloro-4-methylbenzoate: oil, b.p. 129-130° at 9 mm., $D_4^{19.2} = 1.1658$, $n_{He}^{19.2} = 1.52531$ (10). [Note that for the b.p. 149-150° formerly reported (3) no pressure is given.]
- 3-Chloro-4-methylbenzamide: lfts. from aq., alc., or aq. alc., m.p. 173-175° (6) [From partial hydrolysis of 3-chloro-4-methylbenzonitrile (above) with aq. alk. (3) (6); further hydrolysis yields (6) \bar{C}]
- 3:4900 (1) Varma, Ramon, J. Indian Chem. Soc. 12, 541 (1935). (2) Vongerichten, Ber. 11, 365-368 (1878). (3) Claus, Davidsen, J. prakt Chem (2) 39, 497-498 (1889). (4) Hintikka, Ann. Acad Scs. Fennicae 19-A, No 10, 6 pp (1923); C.A. 19, 42 (1925). (5) Wahl, Compt. cred 198, 1613-1614 (1934). (6) Magidson, Trawn, Ber 69, 538 539 (1936). (7) Vongerichten, Ber. 10, 1249-1250 (1877). (8) Ganguly, LeFovre, J. Chem. Soc. 1934, 852. (9) Claus, Bocher, Ann. 265, 356-363 (1891). (10) von Auwers, Harres, Z. physik. Chem. A-143, 17-18 (1929).

200°

199.5°

199-200° u.c.

Colorless ndls. from aq.; spar. sol. aq., eas. sol. alc., C₆H₆, CHCl₃. — Volatile with steam; sublimes with slight decomposition.

[For prepn. of $\bar{\mathbb{C}}$ from *m*-chlorophenol (3:0255) by treatment of dry sodium salt with CO₂ at 140–150° under press. see (3); from 4-chloro-2-aminobenzoic acid (4-chloroanthranilic acid) [Beil. XIV-365, XIV₁-(548)] via diazotzation and boilg. with aq. see (3) (5); from 7-chloro-2,3-dimethylchromone [Beil. XVII₁-(177)] on boilg. with 4% aq. NaOH see (2); for formn. of $\bar{\mathbb{C}}$ from *p*-chlorobenzoic acid (3:4940) by electrolytic oxidn. in acid soln. see (4); from 4-chloro-2-methoxybenzoic acid (see below) by cleavage with HI see (1).

C in aq. soln. gives with FeCl₃ a purple color.

(3)

(4)

(5)

[The methyl ether of Č, viz., 4-chloro-2-methoxybenzoic acid, cryst. from aq., m.p. 148° (1), has been obtd. from 4-chloro-2-methoxybenzaldehyde (1) by oxidn. with aq. alk. KMnO₄ (1).]

3:4908 (1) Hodgson, Jenkinson, J. Chem. Soc. 1927, 1741-1742. (2) Simonis, Schuhmann, Ber. 50, 1146-1147 (1917). (3) Varnholt, J. prakt. Chem. (2) 36, 27-31 (1887). (4) Fichter, Adler, Helv. Chim. Acta 9, 283 (1926). (5) Cohn, Mitt. Technol. Gewerb.-Mus. Wien, 11, 178-182; Cent. 1901, I 925.

Ndls. or pr.; sublimes in vac. with slight decomposition (6). Very sol. toluene or alc. (5). — Best recrystd. from toluene + lt. pet. ether (5). — Can be recrystd. from C_0H_6 or dil. AcOH (6). — From alc. \tilde{C} (despite its high m.p.) first separates as an oil (5).

[For prepn. of \tilde{C} from pentachlorotoluene (3:4937) with conc. HNO₃ + Hg see (5); from pentachlorobenzaldehyde (3:4892) with KMnO₄ (90% yield) see (1); from asymtetrachlorophthalyl chloride + Cl₂ via conversion to and subsequent hydrolysis of pentachlorobenzoyl chloride (3:2295) see (3); from 2,3- (3:4650) or 3,4-dichlorobenzoic acid (3:4925) + MnO₂ + fumg. HCl at 180-200° see (4).]

Pentachlorobenzoyl chloride (3:2295), colorless lfts. from alc., m.p. 87° (3), has been prepd. indirectly (see above), but the reaction (if any) of either PCl_5 or $SOCl_2$ on \bar{C} has never been reported. Upon hydrolysis with alc. KOH the acid chloride yields \bar{C} (3).

- Methyl pentachlorobenzoate: pr. from MeOH, m.p. 97° (3). [Prepared from pentachlorobenzoyl chloride + MeOH by 30 hrs. reflux. (3).]
- Ethyl pentachlorobenzoate: unrecorded.
- Pentachlorobenzamide: unrecorded.
 Pentachlorobenzanilide: unrecorded.

3:4910 (1) Lock, Ber. 72, 303 (1939). (2) Steiner, Monatch. 36, 827 (1915). (3) Kirpal, Kunze, Ber. 62, 2105 (1929). (4) Claus, Bücher, Ber. 20, 1627 (1887). (5) Silberrad, J. Chem. Soc. 127, 2684 (1925). (6) Eckert, Steiner, Monatch. 36, 187 (1915).

3:4915 4-CHLORO-3-METHYLBENZOIC ACID C₈H₇O₂Cl Beil. IX - 478 IX₁— CH₈

Colorless ndls. from hot aq.; alm. insol. cold aq.; very spar. sol. even in hot aq.

[For prepn. of \bar{C} from 4-chloro-1,3-dimethylbenzene (3:8665) by oxidn. with $K_2Cr_2O_7$ + dil. H_2SO_4 see (8) (1); from 4-chloro-1-ethyl-3-methylbenzene (6) by oxidn. with dil. HNO₃ (1:10) at 100° for 10 hrs. see (6); from 4-chloro-3-methylacetophenone [Beil. VII-307] by oxidn. with alk. KMnO₄ see (4); from 4-chloro-3-methyl- ω , ω , ω -trichloroacetophenone (3) see (3); from β -chloroethyl 4-chloro-3-methylphenyl ketone (5) by oxidn. with mixt. of equal pts. conc. HNO₃ and aq. at 100° see (5); from 1,2-bis-(4-chloro-3-methyl-benzoyl)-1,2-dibromoethane (2) by fusion with NaOH see (2); from 4-amino-3-methyl-benzoic acid [Beil. XIV-480] via diazotization and use of Cu_2Cl_2 reactn. see (7).

 \tilde{C} on fusion with KOH yields (1) 4-hydroxy-3-methylbenzoic acid [Beil. X-225, X_1 -(97)], m.p. 173° (1), together with some 4-hydroxyisophthalic acid [Beil. X-502, X_1 -(256)].

Salts. $Ca\bar{A}_2.3H_2O$ (8); $Ba\bar{A}_2.3H_2O$ (8); both eas. sol. aq.

Č on further oxidn. with KMnO₄ yields (4) 4-chlorobenzenedicarboxylic acid-1,3 (4-chloroisophthalic acid) (3:4980).

— Ethyl 4-chloro-3-methylbenzoate: oil, b.p. $260-265^{\circ}$ (8). [From \bar{C} in alc. with HCl gas (8).]

3:4915 (1) Jacobsen, Ber. 18, 1761-1762 (1885). (2) Conant, Lutz, J. Am. Chem. Soc. 47, 891 (1925). (3) Houben, Fischer, Ber. 64, 2649 (1931). (4) Claus, J. prakt. Chem. (2) 43, 357-358 (1891). (5) Mayer, Müller, Ber. 60, 2281 (1927). (6) Mailhe, Bull. soc. chim. (4) 29, 291 (1921). (7) Beilstein, Kreusler, Ann. 144, 182 (1867). (8) Vollrath, Ann. 144, 266-267 (1867).

3:4916 9,10-DICHLOROANTHRACENE

(meso-Dichloroanthracene)

$$\begin{array}{c|c} Cl & & C_{14}H_8Cl_2 & \text{Beil. V - } \mathbf{664} \\ & & V_{1^-}(\mathbf{324}) \\ & & V_{2^-}(\mathbf{575}) \end{array}$$

M.P. 210° (1)
209-210° (2) (3)
209° (4) (5) (6) (7)
(8) (9) (10) (23)
208-209° (11) (12)

Yellow ndls. from CCl₄ or C_6H_6 or by sublimation; spar. sol. alc. or ether, eas. sol. C_6H_6 . [For prepn. of \bar{C} from anthracene (1:7285) with Cl₂ in o-dichlorobenzene (5) (30) polychlorobenzenes of b.p. 140–170° (4), nitrobenzene (4) (5), or in acetylene tetrachloride (5) (yields: 93–94% (4), 87–88% (5)) see indic. refs. (note that numerous attempts to use this reactn. are given in earlier literature (3) (13) (14) (15) (16) (17) (18) (19) (20) but none is well adapted for pure \bar{C} owing to simultaneous formin. of more highly chlorinated cpds.); from anthracene with SO_2Cl_2 in CCl₄ (7) (11) or in xylene (11) at ord. temp. (yields alm. quant. (7) (11)) see indic. refs. (note, however, that the results are sometimes influenced by the source of anthracene used (11)); for formin. of \bar{C} from anthracene (1:7285) with Cl₂-aq. (21), with S_2Cl_2 (10), or with NOCl in s.t. at 150° or at room temp. in sunlight (22) see indic. refs.; for formin. of \bar{C} from anthracene present in crude phenanthrene during treatment of latter in CS_2 with Cl_2 see (12).]

[For prepn. of \bar{C} from anthrone (9-hydroxyanthracene) [Beil VII-473, VII₁-(256)] with 2 wt. pts. PCl₅ in C₆H₆ or without solv. at 100° for 16 hrs. see (2); for formn. of \bar{C} from 9,9,10,10-tetrachloro-9,10-dihydroanthracene (9,10-dichloroanthracene dichloride-9,10) [Beil. V-641, V₁-(309)] by actn. of Zn dust, Cu powder, or phenylhydrazine (3) or on boilg, with anthrone (above) in xylene (6) see indic. refs.; for formn. of \bar{C} from 1,2,3,4-tetrachloro-9,10-dichloroanthracene by htg. with hydrazine hydrate + Cu powder in pyridine (23), or from 9-benzylanthracene with SOCl₂ in CHCl₃ (24), see indic. refs.; from α -[9,10-dichloroanthracene tetrabromide-1,2,3,4] (see below) by treatment with Zn dust in AcOH or with Cu powder in C₆H₆ see (3).]

[$\bar{\mathbf{C}}$ with Cl₂ in cold CHCl₃ or acetylene tetrachloride gives (17) 9,9,10,10-tetrachloro-9,10-dihydroanthracene (see above); $\bar{\mathbf{C}}$ with Cl₂ in C_6H_6 at 60° yields (17) 2,3,9,10-tetrachloro-2,3-dihydroanthracene; $\bar{\mathbf{C}}$ in warm CHCl₃ or cold C_6H_6 gives (17) a mixt. of these prods.: the end prod. of chlorination of $\bar{\mathbf{C}}$ in C_6H_6 at 20° appears (16) (3) to be 1,2,3,4,9,10-hexachloro-1,2,3,4-tetrahydroanthracene [Beil. V-611, V₁-(287)], m.p. 205-207° (3). — $\bar{\mathbf{C}}$ with SO₂Cl₂ in nitrobenzene at 100° yields (25) 2,9,10-trichloroanthracene.]

C adds 2 moles Br₂ giving according to conditions one or the other of two isomeric addn. compds.; i.e., \bar{C} moistened with CHCl₃ and treated with 2 Br₂ yields (3) (8) α -[9,10-dichloroanthracene-1,2,3,4-tetrabromide], colorless hexag. pr. from C₆H₆, m.p. 141-142° (3), while \bar{C} with Br₂ vapor gives (3) β -[9,10-dichloroanthracene-1,2,3,4-tetrabromide], ndls. from C₆H₃ (less sol. than α -isomer), m.p. 178-179° (3), 178° (16) (8), 166° (15); both α - and β -isomers with alc. KOH lose 2 HBr (the α - more rapidly than the β -) yielding (3) (8) 2,3-dibromo-9,10-dichloroanthracene, yel. ndls., m.p. 255-256° (3), 251-252° (15) (16) (8).

[\bar{C} in CHCl₃ treated with NO₂ gas gives (26) 9,10-dichloro-9,10-dinitro-9,10-dihydro-anthracene (very unstable white cryst. on strong cooling) which in boilg. CHCl₃ yields anthraquinone (1:9095). — \bar{C} with conc. HNO₃ (D=1.43) in AcOH at 15–18° yields (27) 9,10-dichloro-9-hydroxy-10-nitro-9,10-dihydroanthracene [Beil. VII₁-(258)].]

[\bar{C} with fumg. H₂SO₄ (20% SO₃) in nitrobenzene at 12-15° (4) (5) cf. (28) (30) or in benzenesulfonyl chloride below 50° (28), or \bar{C} with ClSO₃H in CHCl₃ or H₂SO₄ at 30° (29),

yields 9,10-dichloroanthracenesulfonic acid-2 [Beil. XI₁-(44)], cryst. with 2½ H₂O from alc., m.p. 158-159° (4), losing aq. in vac. at 140° to anhydrous acid, m.p. 212° cor. dec. (4) (corresp. sulfonyl chloride, m.p. 221-225° dec., corresp. sulfonamide, m.p. 279°, corresp. sulfonanilide, m.p. 247.8° cor. (4)).]—[For disulfonation of \bar{C} see (33).]

 \bar{C} is unaffected (13) by boilg, alc. KOH. — [For behavior of \bar{C} with pyridine see (31). — For reactn. of \bar{C} with NaSH in alc. yielding anthranol, anthrone, dianthrone, and other prods. see (32). — For use of \bar{C} in prepn. of sulfur dyes see (34).]

C on oxidation yields (18) anthraquinone (1:9095).

 $\bar{\mathbf{C}}$ like many other anthracene derivs. adds to suitable unsatd. linkages (35) (36) (37) in Diels-Alder fashion: e.g., $\bar{\mathbf{C}}$ with maleic anhydride (1:0625) in nitrobenzene, boiled for 15 mm., gives on cooling (50% yield (35)) adduct, colorless pr. from xylene, m.p. 258-259°, from chlorobenzene, m.p. 253° (36), in this adduct the halogen is stable toward boilg. ale. KOH (38) (39), but the adduct with AlCl₃ in C_6H_6 refluxed 10 min. yields (35) 9,10-diphenylanthracene [Beil. V-747, V₁-(377)], cryst. from toluene, m.p. 248° (35). — $\bar{\mathbf{C}}$ with β -chloropropionic acid (3:0460) (used as source of acrylic acid (1:1020) by loss of HCl) boiled for 8 hrs. in σ -dichlorobenzene yields an adduct, cryst. from anisole, m.p. 245° (38); the halogen of this adduct is stable toward hydrolysis and is not removed by boilg. with 10% ale. KOH for 40 min. (38). — $\bar{\mathbf{C}}$ does not (38) form an adduct with cinnamic acid.

3:4916 (1) Krollpfeiffer, Ann. 430, 225 (1923). (2) Barnett, Cook, Matthews, J. Chem. Soc. 123, 2007 (1923). (3) Meyer, Zahn, Ann. 396, 175-176, 178 (1913). (4) Fedorov, J. Gen. Chem. (U.S.S.R.), 6, 444 454 (1936); Cent. 1936, II 1538, C.A. 30, 6360 (1936). (5) Minaev, Fedorov, Zhur. Prikladnov Khim. 3, 881-893 (1930); Rev. gén. mat. color. 34, 330-332, 376-382 (1930); Cent. 1930, II 3558; C.A. 25, 1252 (1931). (6) Clar, Muller, Ber. 63, 873 (1930). (7) Barnett, Cook Grainger, J. Chem. Soc. 121, 2068 (1922). (8) Grandmougin, Compt. rend. 173, 1176-1178 (1921); Cent. 1922, I 1336. (9) Graebe, Liebermann, Ann. 160, 137 (1871). (10) Lippmann, Pollak, Ber. 34, 2768 (1901).

(11) Iljınsky, Afremoff, Ber **69**, 1824 (1936). (12) Sandquist, Ann. **417**, 20, 30-31 (1918). (13) Graebe, Liebermann, Ann Suppl. **7**, 282-284 (1870). (14) Perkin, Bull. soc. chrm. (2) **27**, 465 (1877). (15) Schwarzer, Ber **10**, 376-379 (1877). (16) Hammerschlag, Ber. **19**, 1106-1108 (1886). (17) M.L.B., Ger. 283,106, April 9, 1915, Cent. **1915**, I 863. (18) M.L.B., Ger. 282,818, March 22, 1915; Cent. **1915**, I 772. (19) M.L.B., Ger 284,790, June 5, 1915, Cent. **1915**, II 251. (20) M.L.B., Ger. 289,133, Dec. 9, 1915; Cent. **1916**, I 193.

(21) Fedorov, Semenova, J. Applied Chem. (U.S.S.R.) 13, 1076-1084 (1940); C.A. 35, 2139 (1941).
(22) Perrot, Compt. rend. 198, 1425 (1934).
(23) I G, French 699,492, Feb. 16, 1931; Cent. 1931, I 3518.
(24) Cook, J. Chem. Soc. 1926, 2168.
(25) M L.B., Ger. 292,356, June 2, 1916; Cent. 1916, II 81.
(26) Barnett, J. Chem. Soc. 127, 2042-2043 (1925).
(27) M.L.B., Ger. 296,019, Jan. 15, 1917; Cent. 1917, I 460.
(28) M.L.B., Ger. 292,590, June 16, 1916; Cent. 1916, II 208.
(29) B.A.S.F., Ger. 260,562, May 26, 1913; Cent. 1913, II 104.
(30) Minaev, Fedorov, Russ. 31,006, July 31, 1933, Cent. 1934, I 2491.

(31) Mieg, Heidenreich (to I.G.), Ger. 593,071, March 5, 1934; Cent. 1934, II 848. (32) Heilbron, Heaton, J. Chem. Soc. 123, 175-182 (1923) (33) B.A.S.F. 288,996, Nov. 30, 1915; Cent. 1916, I 84. (34) Kalischer, Salkowski, Frister (to I.G.), Ger. 480,377, Aug. 2, 1929; Cent. 1929, II 2381-2382. (35) Clar, Ber. 64, 2199-2200 (1931). (36) Kalischer, Scheyer (to I.G.), Ger. 539,832, Dec. 2, 1931, Cent. 1932, I 1952. (37) I.G., Brit. 303,389, July 7, 1927; French 639,359; Cent. 1928, II 2286. (38) Barnett, Goodway, Weekes, J. Chem. Soc. 1935, 1102-1103. (39) Barnett, Goodway, Higgins, Lawrence, J. Chem. Soc. 1934, 1224.

3:4920 3,4,5-TRICHLOROBENZOIC ACID

$$C_7H_3O_2Cl_3$$
 Beil. IX - 346
 Cl IX₁—
 $COOH$

M.P. 210-210.5° (1) 203° (2)

Ndls. from aq. alc. — Sublimes in long ndls. — Somewhat volatile with steam. — Eas.

sol. cold alc., ether, acetone; mod. sol. C₆H₆, CHCl₃; spar. sol. CS₂, pet. eth.; alm. insol. cold ac.

[For prepn. of \tilde{C} from 3,4,5-trichlorobenzaldehyde (3:2440) by oxidn. with alk. KMnO₄ see (1); from 3,5-dinitro-4-aminobenzoic acid (chrysanisic acid) [Beil. XIV-445] with fumg. HCl at 200° see (2); for formn. (together with other products) from benzotrichloride (3:6540) + Cl_2 see (3).]

[For study of AgA, CaA2.6H2O, BaA2.4H2O see (2).]

The direct nitration of \bar{C} has not been recorded. [However, 3,4,5-trichloro-2-nitrobenzoic acid, ndls. from alc., m.p. 181-181.5° (1), and 3,4,5-trichloro-2,6-dinitrobenzoic acid, m.p. 219-221.5° (1), have both been prepared from the corresponding aldehydes.]

C with PCl₅ yields (2) 3,4,5-trichlorobenzoyl chloride, m.p. 36° (2).

- Methyl 3,4,5-trichlorobenzoate: unrecorded.
- Ethyl 3,4,5-trichlorobenzoate: from \bar{C} + alc. + HCl (2), ndls., m.p. 86° (2).
- **3,4,5-Trichlorobenzamide:** from 3,4,5-trichlorobenzoyl chloride + conc. aq. NH₄OH at 100° (2); ndls. from C₆H₆, m.p. 176° (2).
- ---- 3,4,5-Trichlorobenzanilide: unrecorded.

3:4920 (1) van de Bunt, Rec. trav. chim. **48**, 132-133 (1929). (2) Salkowski, Ann. **163**, 28-33 (1872). (3) Claus, Bücher, Ber. **20**, 1626 (1887)

3:4922 2-CHLOROANTHRAQUINONE C₁₄H₇O₂Cl Beil. VII - 787 VII₁-(411) Ö M.P. 212.4° cor. (1) M.P. 208° (36)211.0° cor. (2) (Contd.) 207° (10) (11)210° cor. (3) 206-207° (12) (13)

205-207°

203-204°

204°

204.5-205.5°

(14)

(15)

(17)

(16) (18)

[See also 1-chloroanthraquinone (3:4480).]

208-209° (7) (8)

(4)

(9)

(5) (6)

210°

209°

209.5°

Pale yel. ndls. from C₆H₆, chlorobenzene, or toluene; eas. sol. boilg. C₆H₆, toluene, or AcOH; spar. sol. boilg. alc. — Sublimes in vac.

[For f.p./compn. data and diagram of system $\tilde{C}+1$ -chloroanthraquinone (3:4480) (eutectic, m.p. 143.9-144.2°, contg. about 75% \tilde{C}) see (5).]

[For use of \tilde{C} in coloring oils, fats, and waxes see (19); \tilde{C} is widely used as intermediate in prepn. of many dyestuffs, but no general summary can be given here although selected examples occur in the following text.]

[For prepn. of \bar{C} from anthraquinonesulfonic acid-2 [Beil. XI-337, XI₁-(83)] or its Na salt with 25% HCl + NaClO₃ at 100° (11) (20) (for use of this method in detn. of mixt. of anthraquinone- α - and β -sulfonic acids or their salts by f.p./compn. curve of resultant mixt. of 1-chloroanthraquinone (3:4480) + \bar{C} see (5)) see indic. refs.; from sodium anthraquinone-2-sulfonate in dil. HCl on exposure to light see (9), from anthraquinonesulfonic acid-2 on boilg. with dil. H₂SO₄ + NaCl + NaClO₃ see (21); from anthracenesulfonic

acid-2 [Beil. XI-194, XI₁-(44)] with HCl + NaClO₃ at 100° see (22); from anthraquinone-sulfonic acid-2 or its Na salt (23) or from anthraquinone-sulfonyl chloride-2 (24) with SOCl₂ in s.t. at 200-230° see indic. refs.]

[For prepn. of \tilde{C} from o-(4-chlorobenzoyl)benzoic acid [Beil. X-750, X_1 -(356)] by ring closure with conc. H_2SO_4 at 160- 170° (25) (16) (26) (27) (28) (4) (29) (34) (49) in pres. of AlCl₃ (30) see indic. refs. (for study of influence of conditions see espec. (27) (4) (31)); from o-(3-chlorobenzoyl)benzoic acid (32) or from 2-benzoyl-4-chlorobenzoic acid [Beil. X-750, X_1 -(356)] (33) by similar ring closure with H_2SO_4 see indic. refs.; from 4-chloro-2-benzoyl-benzoyl chloride on htg. see (33).]

[For prepn. of $\bar{\rm C}$ from 2-chlorobutadiene-1,3 (chloroprene) (3:7080) + naphthoquinone-1,4 (1:9040) in ${\rm C_6H_6}$ see (6); from α -chlorocrotonaldehyde (3:8117) + naphthoquinone-1,4 (1:9040) in ${\rm C_6H_6}$ with piperidine see (74); from 2-aminoanthraquinone (see below) via diazotization and rapid htg. of diazonium chloride at 150° see (8); from 2-chloroanthraquinonecarboxylic acid-4 by htg. at 286-290° (7) or from 2-chloroanthraquinonecarboxylic acid-5 by htg. in s.t. at 310-320° or by distn. of its Ba salt with BaO see (17) of (15); from 2,9,10-trichloro-9-hydroxy-10-nitro-9,10-dihydroanthracene [Beil. VII₁-(258)] in ${\rm C_6H_6}$, nitrobenzene, or AcOH by htg. at 90-95° see (35); from 2,9,10-trichloroanthracene [Beil. V₁-(325)] (36) or from 2-chloroanthrone-9 (or 10) (12) by oxidn. with CrO₃ see indic. refs.] [For prepn. of $\bar{\rm C}$ from 1-chloroanthraquinone (3:4480) by htg. with conc. H₂SO₄ at 200-205° for 9 hrs. see (37).]

[$\bar{\rm C}$ on reductn. with Zn dust + conc. aq. NH₄OH under reflux yields (18) (37) 2-chloroanthracene [Beil. V₁-(324)], m.p. 217° (37), 215° (18). — $\bar{\rm C}$ on reductn. with hydrazine hydrate in MeOH/KOH at 10 atm. and 135° for 1½ hrs. in pres. of Pd/CaCO₃ cat. yields (38) bis-(2,2'-anthraquinonyl) [Beil. VII₁-(495)], m.p. 387-388°. — $\bar{\rm C}$ on reductn. with Al powder + conc. H₂SO₄ (40) or with Sn + HCl (39) yields a mixt. of 3-chloroanthrone-9, m.p. 156° (38) (corresp. acetate, m.p. 146° (41) (42)), and 2-chloroanthrone-9, m.p. 155° (41) (corresp. acetate, m.p. 143° (41)); this mixt. of chloroanthrones can be septh by acetylation with Λ c₂O + pyridine and fractional crystn. of the resultant acetates (42). — For use of this reductn. method in prepn. of vat dyes see (43). — For study of oxidn./ reductn. potential of $\bar{\rm C}$ see (13).]

[\bar{C} with MeOH/KOH in s.t. at 130° yields (44) 2-methoxyanthraquinone [Beil. VIII-343, VIII₁-(658)], m.p. 196°. — \bar{C} with 2-hydroxyanthraquinone + NaOAc + Cu powder htd. at 250–260° for 12 hrs. gives (66% yield (45)) di-(2-anthraquinonyl) ether, pale yel. ndls. from pyridine, m.p. 324° (45). — \bar{C} with K xanthate + Cu powder boiled for 16 hrs. in AmOH gives (56% yield (45) (46) di-(2-anthraquinonyl) sulfide, cryst. from xylene, m.p. 290.5–291° (45). — \bar{C} with thiosalicylic acid (2-mercaptobenzoic acid) + solid KOH htd. in AmOH at 150° for 8 hrs. gives (77% yield (3)) S-(2-anthraquinonyl)thiosalicylic acid [Beil. X₁-(56)], m.p. 278° cor. (3); this prod. on htg. with H₂SO₄ or better with p-toluenesulfonyl chloride at 200° (3) (47) ring-closes by loss of H₂O to 1,2-phthalylthioxanthone [Beil. XVII₁-(291)], yel. ndls. from AcOH, m.p. 278° cor. (3).]

[Č with NaOH + glycerol htd. at 190° is claimed (48) to yield anthraquinone (1:9095).

— Č with NaOH + NaClO₃ htd. 28 hrs. at 195° (49) cf. (50) (51) (52) gives (95% yield (49)) 1,2-dihydroxyanthraquinone (alizarin) (1:9105). — Č with NaSH boiled in aq. alc. yields (53) 2-mercaptoanthraquinone [Beil. VIII-346, VIII₁-(659)], yel. ndls. from AcOH, m.p. 206° (54). — Č with Na₂Se boiled in dil. alc. yields (55) 2-selenomercaptoanthraquinone, but Č with Se + NaOAc htd. at 205–210° in a mixt. of trichlorobenzene + tetralin for 8 hrs. yields (56) di-(2-anthraquinonyl) selenide.]

[Č with conc. aq. NH₄OH in pres. of Cu salts under press. and at elevated temp. (180–200°) gives (yields: 97.5% (57), 98.6% (2)) (27) (58) (59) (60) 2-aminoanthraquinone [Beil. XIV-191, XIV₁-(449)], red ndls., m.p. 302° (for study of influence of conditions see

(57) (2) (27) (61) (62)). — \bar{C} with hydrazine hydrate + pyridine in s.t. at 170° for 8 hrs. gives (20% yield (63)) 2-hydrazinoanthraquinone [Beil. XV₁-(200)], or.-yel. ndls. from pyridine, m.p. 228-229° (63).]

[C with 4 moles C₆H₅MgBr in ether yields (64) (65) 2-chloro-9,10-diphenylanthracene, yel. cryst. powder, or. ndls. from AcOH, m.p. 194° (64), 193° (66), 185° (65).]

[For formn. of addn. cpds. of \bar{C} with SbCl₅ in CHCl₃ see (10); for formn. of 2-anthra-quinonylpyridinium chloride from \bar{C} + Λ lCl₃ in pyridine see (67).]

[The direct sulfonation of \bar{C} appears not to have been reported in the scientific literature although \bar{C} with fumg. H_2SO_4 at $125-130^\circ$ in pres. of Hg salts cf. (73) as directed is claimed in a patent (68) to yield 2-chloroanthraquinonesulfonic acid-5. — Two monosulfonic acids of \bar{C} are known, however, although prepared by indirect means; these are 2-chloroanthraquinonesulfonic acid-6 (corresp. sulfonyl chloride, deep yel. ndls. from chlorobenzene, m.p. 202° (69), from C_6H_6 , m.p. $202-203^\circ$ (71)), and 2-chloroanthraquinonesulfonic acid-7 (corresp. sulfonyl chloride, yel. cryst. from C_6H_6 , m.p. 205° (70), $200-201^\circ$ (71), 176° (69)); note that the alkali salts of both these acids are almost completely insoluble in aq. (71) and the above anomaly in m.p. of the sulfonyl chlorides may have been due to impure material. — \bar{C} on htg. with fumg. H_2SO_4 (40% SO₃) at 180° yields (72) a mixt. of sulfonated products which on alk. fusion give 1,2,6-trihydroxyanthraquinone (flavopurpurin) [Beil. VIII-513, VIII₁-(741)] and 1,2,7-trihydroxyanthraquinone (anthrapurpurin) [Beil. VIII-516, VIII₁-(742)].]

3:4922 (1) Phillips, Ind. Eng. Chem. 20, 874 (1928). (2) Groggins, Newton, Ind. Eng. Chem.
 21, 371-375 (1929). (3) Ullmann, Knecht, Ber. 44, 3128-3129 (1911). (4) Dougherty, Gleason,
 J. Am. Chem. Soc. 52, 1025 (1930). (5) Coppens, Rec tau chu. 44, 914-916 (1925). (6)
 Carothers, Wilhams, Collins, Kirby, J. Am. Chem. Soc. 53, 4206 (1931). (7) Keimatsu, Hırano,
 Tanabe, J. Pharm. Soc. Japan 49, 531 541 (1929). Cent. 1929, II 1536-1537, C.A. 23, 4696-4697 (1929). (8) Kaufler, Ber. 37, 62-63 (1904). (9) Eckert, Ber. 58, 318 (1925). (10) Brass,
 Eichler, Ber. 67, 783-784 (1934).

Schwenk, Waldmann, Angew. Chem. 45, 20 (1932).
 Steyermark, Gardner, J. Am. Chem. Soc. 52, 4887 (1930).
 Conant, Fieser, J. Am. Chem. Soc. 46, 1873, 1875 (1924).
 Moyer, Compt. rend 184, 609-611 (1927).
 Maki, Nagai, J. Soc. Chem. Ind. Japan, Suppl. 38-B, 487-493 (1935), Cent. 1936, I 4905, C.A. 29, 8337 (1935).
 Scholl, Seer, Ber. 55, 115 (1922).
 Schilling, Ber. 46, 1068-1069 (1913).
 du Pont, Brit. 432,867, Sept. 5, 1935; Cent. 1935, II 3996.
 Bayer and Co., Ger. 205,195, Dec. 28, 1908; Cent. 1909, I 414.

(21) Deinet (to Newport Co.), U.S. 1,761,620, June 3, 1930, Cent. 1931, I 1522, C.A. 24, 3520 (1930). (22) B.A.S.F., Ger. 228,876, Nov. 25, 1910, Cent. 1911, I 102. (23) Meyer, Monatsh. 36, 722 (1915). (24) M.L.B., Ger. 281,976, June 10, 1915, Cent. 1915, II 293. (25) M.L.B., Ger. 75,288, Freellander 3, 260. (26) Dodd, Sprent, & United Alkali Co., Brit. 204,528, Oct. 25, 1923; Cent. 1925, II 1228. (27) Phillips, Ind. Eng. Chem. 17, 721–725 (1925). (28) Scottish Dyes, Ltd. & Thomas, Brit. 248,411, April 14, 1926, Cent. 1929, I 144. (29) Imperial Chem. Ind., Ltd., & Loveluck, Thomson and Thomas, Brit. 356,728, Oct. 8, 1931; French 718,333, Jan. 23, 1932; Cent. 1933, I 3499. (30) Daniels (to National Aniline & Chem. Co.), U.S. 1,895,788, Jan. 31, 1933; Cent. 1933, II 1764.

(31) Oda, Tamura, Sci. Papers Inst. Phys Chem. 32, 263-273 (1937); Cent 1937, II 4027; C.A. 31, 8330 (1937). (32) Bailey (to Burrett Co), U.S. 1,515,325, Nov. 11, 1924, Cent. 1925, I 1014. (33) Egerer, Meyer, Monatsh. 34, 76, 84 (1913). (34) Muller, Kirchner (to I.G.), Ger. 499,587, June 10, 1930, Cent. 1931, I 1675. (35) M.L.B., Ger. 296,019, Jan. 15, 1917; Cent. 1917, I 460. (36) Liebermann, Beudet, Ber. 47, 1014-1015 (1914). (37) Atack, Clough, Brit. 169,732, Nov. 3, 1921; Cent. 1922, IV 377. (38) Busch, Weber, Zink, J. prakt. Chem. (2) 155, 166-167 (1940). (39) Barnett, Matthews, J. Chem. Soc. 123, 2550-2551, 2554-2555 (1923). (40) Eckert, Tomaschek, Monatsh. 39, 862 (1918).

(41) Barnett, Wiltshire, J. Chem. Soc. 1928, 1824. (42) Barnett, Goodway, J. Chem. Soc. 1930, 1350. (43) Bayer and Co., Ger. 203,436, Oct. 20, 1908; Cent. 1908, II 1756. (44) Bayer and Co., Ger. 229,316, Dec. 13, 1910, Cent. 1911, I 180. (45) Perkin, Sewell, J. Chem. Soc. 123, 3036-3038 (1923). (46) Ullmann-Goldberg, Ger. 255,591, Jan. 10, 1913; Cent. 1913, I 480. (47) Ullmann, Ger. 238,983, Oct. 7, 1911; Cent. 1911, II 1289. (48) Oda, Tamura, Maeda,

J. Soc. Chem. Ind. Japan 41 (Suppl. bindg.), 193-195 (1938); Cent. 1939, I 1360; C.A. 32, 7447 (1938).
(49) Karpukhin, Andinokrasochnaya Prom. 5, 317-321 (1935); Cent. 1936, I 2825; C.A. 30, 7112 (1936). (50) Davies and Scottish Dyes, Ltd., Brit. 174,101, Feb. 16, 1922; Cent. 1922, II 877.

(51) Rogers (to National Aniline and Chem Co), Brit. 181,673, Aug. 10, 1922; Cent. 1923, IV 882. (52) Scottish Dyes, Ltd, & Thomas & Hereward, Brit. 246,529, Feb. 25, 1926, French 591,489, July 4, 1925, Swiss 115,113, June 1, 1926, Cent. 1926, II 2949. (53) Bayer and Co., Ger. 206,536, Feb. 4, 1909; Cent. 1909, I 1059 (54) Gattermann, Ann. 393, 149-155 (1912). (55) Bayer and Co., Ger. 264,941, Sept. 25, 1913, Cent. 1913, II 1351. (56) Perkins (to du Pont Co.), U.S. 1,973,773, Sept. 18, 1934, Cent. 1935, I 3051. (57) Groggins, Stirton, Ind. Eng. Chem. 25, 42-49 (1933). (58) BASF, Ger. 295,624, Dec. 11, 1916, Cent. 1917, I 295. (59) Williams (to du Pont Co.), U.S. 1,775,360, Sept. 9, 1930, Cent. 1931, II 1195 (60) Groggins, U.S. 1,923,618, Aug. 22, 1933, Cent. 1933, II 2894, C.A. 27, 5339 (1933), U.S. 1,892,302, Dec. 27, 1932, Cent. 1933, II 1764; C.A. 27, 1893 (1933).

(61) Vorozhtsov, Nikitin, J. Gen. Chem. (U.S.S.R.) 7, 2080-2086 (1937), Cent. 1938, I 2355; C.A. 32, 539 (1938). (62) Vorozhtsov, Kobelev, J. Gen. Chem. (U.S.R.) 9, 1515-1516 (1939), C.A. 34, 2688 (1940). (63) Mohlau, Ber. 45, 2216 (1912). (64) Barnett, Cook, Wiltshire, J. Chem. Soc. 1927, 1728 (65) E. Bergmann, O. Blum-Bergmann, J. Am. Chem. Soc. 59, 1440 (1937). (66) Ingold, Marshall, J. Chem. Soc. 1926, 3087. (67) Miegs, Heidenreich (to I.G.), Ger. 593,671, March 5, 1934; Cent. 1934, II 848. (68) Whelen (to du Pont Co.), U.S. 2,074,306, March 16, 1937, Cent. 1937, I 1861, C.A. 31, 3508 (1937). (69) Fierz-David, Andereau, Helv. Chim. Acta 10, 225-227 (1927). (70) Jones, Mason, J. Chem. Soc. 1934, 1814. (71) Goldberg, J. Chem. Soc. 1932, 73-74, 77. (72) Bayer and Co., Ger. 217,552, Jan. 17.

(71) Goldberg, J. Chem. Soc. 1932, 73-74, 77 (72) Bayer and Co., Ger. 217,552, Jan. 17, 1910, Cent. 1910, I 700. (73) Ullmann, Ger. 223,642, June 27, 1910, Cent. 1910, II 427. (74) Nicodemus, Vollmann, Schloffer (to I G), Ger. 715,201, Dec. 16, 1941, Cent. 1942, I 1811, [C.A. 38, 2049 (1944)].

3:4925 3,4-DICHLOROBENZOIC ACID
$$C_7H_4O_2Cl_2$$
 Beil. IX - 343 IX₁-(141)

M.P. 211-212° (1) M.P. 204.1° (6)
208-209° (2) (20) (Conld.) 203° (7)
206° (3) 201-202° (8) (19)
205° (4) 201° (9)

Ndls. from aq., alc., 60% alc. (6), C_6H_6 (2) (6), or 30% AcOH (4) (18). — Volatile with steam. — Appreciably more sol. in hot aq. than in cold; very cas. sol. alc.

200° cor. (10)

[For prepn. of \overline{C} from 3,4-dichlorotoluene (3.6355) by oxidin. (2) with CrO_3 (8) (11), with dil. HNO₃ in s.t. at 130–140° (9) (3), or with KMnO₄ (6) see indic. refs.; for prepn. by oxidin. of 3,4-dichlorobenzyl chloride (8) (11), 3,4-dichlorobenzial chloride (3:6876) (8) (11), 3,4-dichlorobenzial chloride (3:0685) (10), or chlorinated isopropylbenzene (cumene) (5) see indic. refs.: for prepn. from benzoic acid (1:0715) by acti. of HCl + KClO₃ (11) (20) or $Ca(OCl)_2$ (11) see indicated refs.: for still other misc. methods see Bell. IX-343 + IX₁-(141) [

 \bar{C} is scarcely affected by htg. with fumg. HNO₃ (13) but on soln. in latter and treatment as directed (13) with conc. H₂SO₄ yields 3,4-dichloro-x-nitrobenzoic acid, m.p. 160° (13). [This prod. may or may not be identical with that of m.p. 165° obtd. indirectly (14).]

 \bar{C} with PCl₅ (15) or SOCl₂ (16) yields 3,4-dichlorobenzoyl chloride, b.p. 242° (8), 159-160° at 42 mm. (15), 88.0-88.3° (16). [For formn. of this prod. in chlorination of BzCl see (4).]

204-205° (5)

⁻⁻⁻ Methyl 3.4-dichlorobenzoate: unrecorded.

Ethyl 3,4-dichlorobenzoate: b.p. 262-263° (8). [For study of rate of hydrolysis see (17).]

- 3,4-Dichlorobenzamide: from 3,4-dichlorobenzoyl chloride + NH₃ (8); m.p. 133° (8); 166-168° (1), 169° (18).
- ---- 3,4-Dichlorobenzanilide: unrecorded.

3:4925 (1) Gough, King, J. Chem. Soc. 1930, 690-691. (2) Kraay, Rec. trav. chim. 49, 1086 (1930). (3) Wynne, J. Chem. Soc. 1936, 705. (4) Hope, Reilly, J. Chem. Soc. 123, 2476 (1923).
(5) Quist, Salo, Acta Acad. Aboensis Math. et Phys. 8, No. 4, 30 pp. (1934); Cent. 1934, II 594-595; 1936, I 538-540; C.A. 29, 6884 (1935). (6) Bornwater, Holleman, Rec. trav. chim. 31, 228-230 (1912). (7) Pieper, Ann. 142, 306 (1876). (8) Beilstein, Kuhlberg, Ann. 152, 224-234 (1869). (9) Lellmann, Klotz, Ann. 231, 313-314 (1885). (10) Scarborough, Waters, J. Chem. Soc. 1926, 560.

Beilstein, Ann. 179, 283 (1875).
 Gmelin, Banziger, Ber. 29, 875 (1896).
 Claus, Bucher, Ber. 20, 1624 (1887).
 Ruggli, Zaeslin, Helv. Chim. Acta 19, 434-437 (1936).
 Cohen, Briggs, J. Chem. Soc. 83, 1213 (1903).
 Onorris, Ware, J. Am. Chem. Soc. 61, 1418-1420 (1939).
 Blakey, McCombie, Scarborough, J. Chem. Soc. 1926, 2863-2868.
 Cohen, King, Strangeways, J. Chem. Soc. 1930, 3427.
 Hodgson, Beard, J. Chem. Soc. 1927, 25.
 Biswas, Das-Gupta, J. Induan Chem. Soc. 19, 497-498 (1942); C.A. 37, 5709 (1943).

M.P. 216.5° (1) 216° (2) 212-213° (3)

Cryst. from MeOH + aq. (2) or from C_6H_6 (3). — Eas. sol. org. solv.

[For prepn. of \bar{C} from 3-aminonaphthoic acid-2 [Beil. XIV-535, XIV₁-(623)] via diazotization and use of Cu₂Cl₂ reactn. (alm. quant. yield) see (3); from the corresp. acid chloride (below) by hydrolysis with aq. see (1).]

 \bar{C} with Cu bronze refluxed in nitrobenzene for 2 hrs. gives (48% yield (4)) β -naphthoic acid (1:0800), m.p. 185° (4).

[No record can be found of direct conv. of \bar{C} to the corresp. acid chloride (3-chloro-2-naphthoyl chloride); however, this compd., m.p. 56.5° (1), b.p. 248° at 160 mm. (1), has been obtd. indirectly from 3-hydroxy-2-naphthoic acid (1:0850), with PCl₅ in 49% yield (1); note that 3-hydroxy-2-naphthoic acid with SOCl₂ gives instead 3-hydroxy-2-naphthoyl chloride, m.p. 96° (5), 94.5° (6), in 82% yield (5).

[For condens. of C with pyrazolanthrone see (8).]

- Methyl 3-chloro-2-naphthoate: cryst. from MeOH, m.p. 58-59° (3), 58° (7). [From C in MeOH with conc. H₂SO₄ (88% yield (7)), from C with ethereal diazomethane (3), or from the acid chloride (above) with 5 pts. MeOH (3).] [For reactn. of this ester with 1-aminoanthraquinone see (7).]
- Ethyl 3-chloro-2-naphthoate: lfts. from lt. pet. or from alc., m.p. 57-59° (3), 50° (1); b.p. 218-222° at 160 mm. (1), 195-197° at 18 mm. (3), volatile with steam. [From C in EtOH with HCl gas (1) (3).]
- (1). [From the acid chloride (above) with conc. aq. NH₄OH (1).]
- 3:4928 (1) Strohbach, Ber. 34, 4158-4162 (1901). (2) Hosaeus, Ber. 26, 668-671 (1893). (3) Bergmann, Hirshberg, J. Chem. Soc. 1936, 333. (4) Clemo, Spence, J. Chem. Soc. 1928, 2818. (5) Bhat, Forster, Venkataraman, J. Soc. Dyers Colourists 56, 170 (1940). (6) Abrahart, J. Chem. Soc. 1938, 426. (7) Ullmann, Dootson, Ber. 51, 22-23 (1918). (8) I.G., Brit. 298,775, Nov. 8, 1928; French 644,589, Oct. 10, 1928.

3:4930
$$meso-\alpha,\alpha'$$
-DICHLOROSUCCINIC ACID $C_4H_4O_4Cl_2$ Beil. II - 619 $II_{1^-}(267)$ $II_{2^-}(558)$ $II_{1^-}(267)$ $II_{2^-}(558)$ $II_{1^-}(267)$ $II_{2^-}(558)$ $II_{1^-}(267)$ $II_{2^-}(558)$ $II_{1^-}(267)$ $II_{2^-}(558)$ $II_{1^-}(267)$ $II_{2^-}(558)$ $II_{1^-}(267)$ $II_{$

(9) [See also $d,l-\alpha,\alpha'$ -dichlorosuccinic acid (3:4711).]

209-213°

Hexag. pr. from aq. — \bar{C} is readily sol. aq. although less so than its d,l-isomer; e.g., 100 cc. satd. aq. soln. of \bar{C} at 0° conts. 12.0 g. \bar{C} (4); \bar{C} is eas. sol. alc., ether, acctone or CHCl3; spar. sol. C6H6 or lgr.

[For prepn. of C from disodium salt of maleic acid (1:0470) in satd. aq. NaCl soln. with Cl_2 at 0° in dark or diffuse daylight (yields: 74.5% (7), 66% (10), 65% (1)) cf. (16) see indic. refs. (note that as a side reactn. some addn. of HOCl also occurs leading to as much as 7% (1) chloromalic acid): from fumaric acid (1:0895) with excess Cl₂ in s.t. in sunlight for 3-4 days see (6); from $meso-\alpha,\alpha'$ -diaminosuccinic acid [Beil. IV-486, IV₂-(901)] in aq. HCl with NOCl or AgNO₂ (75% yield) see (3); from $meso-\alpha,\alpha'$ -dichlorosuccinyl (di)chloride (3:9087) by hydrolysis with ag. see (5).]

[For formn. of C from bis-acetyl peroxide (9) by decomposition in chloroacetic acid (3:1370) at 85-95° (CO₂ + CH₄ are also formed) see (9).]

 $\bar{\mathbf{C}}$ behaves as a normal dibasic acid: titration with standard dil. aq. alk. gives Neut. Eq. 93.5. — [For study of acid strength $(K_1 = 361 \times 10^{-4} \text{ at } 20.2^{\circ}, K_2 = 9.4 \times 10^{-4} \text{ at}$ 17.8° (4)) see (4) (8); (18) for study of conductivity see (11).]

[Salts (of metals). Ag₂A, amorphous ppt. (6) which on boilg, with aq. for 10 hrs. yields (12) both d,l-tartaric acid (1:0550) and meso-tartaric acid (1:0490); CaĀ.2H₂O, eas. sol. ag. and alc. (6); SrĀ.H₂O (6); BaĀ, very eas. sol. ag., insol. alc. (6); ZnĀ.3H₂O (6); $Cd\bar{A}.3H_2O$, very eas. sol. aq., insol. alc. (6).]

C with cold aq. KOH loses 1 HCl yielding (5) (7) (14) chlorofumaric acid (3:4853); C with NaOAc/AcOH on boilg. (13) (17) or aq. soln. of Na₂A on boilg. ½ hr. (12) loses 1 HCl yielding chloromaleic acid (3:3432); C on warming in dil. H₂SO₄ gives both (14) chlorofumaric and chloromaleic acids. [For study of rate of decompn. of C by aq., acids, or alkalies see (7) (8) (15).]

K₂Ā in aq. soln. maintained at neutrality at 100° dec. with formn. (14) of acetaldehyde (1:0100), CO_2 + meso-tartaric acid (1:0490).

C with Ac2O at 150° yields (12) chloromaleic anhydride (3:0280).

The acid chloride (3:9087) corresp. to C is known but is usually obtd. indirectly.

- Dimethyl meso- α, α' -dichlorosuccinate: m.p. 31.5-32° (see 3:0240).
- **Diethyl** meso- α, α' -dichlorosuccinate: m.p. 63° (see 3:1364).
- Acid salt of C with dl,-α-dhenylethylamine: tbls. from aq., m.p. 133-134° rap. htg. (13); satd, aq. soln, at 25° conts. 81.4 g./liter (13). [For the corresp. acid salts

of \overline{C} with the two opt. act. forms of this base see (13); both have m.p. 128-129°, and their satd. aq. solns. at 25° cont. 76.1 g./liter (13).

3:4930 (1) Kuhn, Wagner-Jauregg, Ber. 61, 501-502, 518-521 (1928). (2) Aminoff, Arkiv Kemi, Mineral. Geol. 7, No. 9, 11 (1918), Cent. 1919, III 319, C.A. 14, 2119 (1920). (3) Kuhn, Zumstein, Ber. 59, 485 (1926). (4) Kuhn, Wagner-Jauregg, Ber. 61, 484, 487-498 (1928). (5) Michael, Tissot, J. prakt Chem. (2) 46, 394-395 (1892). (6) Kirchhoff, Ann. 280, 210-215 (1894). (7) Robinson, Lewis, J. Chem. Soc. 1933, 1260-1262. (8) Holmberg, J. prakt. Chem. (2) 84, 148, 152, 164 (1911). (9) Kharasch, Gladstone, J. Am. Chem. Soc. 65, 17 (1943). (10) Terry, Eichelberger, J. Am. Chem. Soc. 47, 1088, 1076-1077 (1925).
 [11] Michael, Bunge, Ber. 41, 2912 (1908). (12) Michael, Tissot, J. prakt. Chem. (2) 52,

(11) Michael, Bunge, Ber. 41, 2912 (1908). (12) Michael, Tissot, J. prakt Chem. (2) 52, 331-335 (1805). (13) van der Riet, Ann. 280, 229 (1894). (14) Holmberg, Arkiv Kemi, Mineral. Geol. 8, No. 2, 6, 32 (1920), Cent 1921, I 830, CA 16, 2116 (1922). (15) Johansson, Z. physik. Chem. 79, 625-626 (1912). (16) Timmermans, van Laucker, Jaffe, Bull. soc. chim. Belg. 48, 42 (1939). (17) Ashton, Partington, Trans Faraday Soc. 30, 602 (1934). (18) Holmberg, Svensk. Kem. Tad. 24, 105-109 (1912); Cent. 1912, II 1618, C.A. 7, 80 (1913).

3:4933 4-CHLORO-3-HYDROXYBENZOIC ACID C7H5O3Cl Beil. S.N. 1068

M.P. 219.5-220.5° (1)

Colorless ndls from aq.

[For prepn. of \bar{C} from 4-amino-3-hydroxybenzoic acid (1) via diazotization and use of Cu_2Cl_2 reactn. see (1); note that the prod. formerly [Beil X-143] supposed to have been \bar{C} is now regarded (1) as probably the 6-chlorosomer (3:4720).]

3:4933 (1) Beyer, Rec. trav. chim. 40, 627 (1921).

3:4935 3,5-DICHLORO-2-HYDROXYBENZOIC $C_7H_4O_3Cl_2$ Beil. X - 104 X₁-(48) (3,5-Dichlorosalicylic acid) OH

M.P. 220-221° (1) 219-220° (2)

219.5° (3) (10)

219° (4) (5) (6) (7)

215° (8)

214° (9) (11) (12)

Colorless scales or ndls. from aq. alc.; very spar. sol. hot aq., eas. sol. alc., ether; sublimes with partial decomposition.

[For prepn. of \bar{C} from o-hydroxybenzoic acid (salicylic acid) (1 0780) in aq. KOH (3 moles) (11) (10), or in aq. KOH (1 mole) (14) (17), or in aq. KOH (2 moles) (15) (16), in EtOH (17), in AcOH (12) (10) (2), or in CS₂ susp. (17) with Cl₂ see indic. refs.; with 30% $H_2O_2 + HCl$ (80% yield) see (4); by htg. with SbCl₅ see (13). (Note that by most of these methods 5-chloro-2-hydroxybenzoic acid (5-chlorosalicylic acid) (3:4705) may also be formed; from this \bar{C} may also be sep. via its spar. sol. Ba \bar{A}_2 (17).)]

[For prepn. of C from sulfosalicylic acid with Cl₂ in aq. see (8); from K 2,4-dichlorophenolate with CO₂ at 140° see (11); from 3,5-dichlorosalicylaldehyde by oxidn. with alk.

KMnO₄ (yield 100%) see (9); from 3,5-dichloro-2-methoxybenzoic acid with 45% HI in s.t. at 120-130° see (3); from chloral-3,5-dichlorosalicylamide by hydrolysis see (1).]

 \bar{C} on htg. with CaO (17) (7) or at 200° in aniline (18) loses CO₂ yielding 2,4-dichlorophenol (3:0560).

Č with FeCl₃ gives (13) (2) a dark violet color.

[\ddot{C} in 60% fumg. H₂SO₄ treated with Cl₂ at 80–90° for 15 hrs. gives (70% yield (19)) 3,5,6-trichlorosalicylic acid, white pl. from aq. alc. or aq. AcOH, m.p. 207° cor. (19); (this with Ac₂O + trace H₂SO₄ gives corresp. acetate, ndls. from lgr., m.p. 129.5° cor. (19).]

C in AcOH treated with fumg. HNO₃ yields (20) 4,6-dichloro-2-nitrophenol, m.p. 122° (20).

 $\bar{\mathbf{C}}$ with PCl₅ (1 mole) yields (5) (10) 3,5-dichloro-2-hydroxybenzoylehloride (3,5-dichlorosalicyloyl chloride), ndls. from ether + pet. eth., m.p. 79°. [For details on various phosphorus compounds also formed in this reaction see (21).] [Note also existence of anhydride of $\bar{\mathbf{C}}$ (from the acid chloride + Ag $\bar{\mathbf{A}}$), cryst from CHCl₃, m.p. 186-187° (5) (28).]

[$\check{\mathbf{C}}$ in aq./alc./H₂SO₄ gives (22) on electrolytic reduction 3,5-dichloro-2-hydroxybenzyl alcohol, ndls. from C₆H₆, m.p. 82° (22); for study of prepn. and thermal rearr. of allyl (23), crotyl (23), benzyl (24), and other (25) ethers of $\check{\mathbf{C}}$ see indic. refs.]

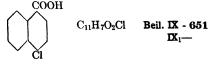
- Methyl 3,5-dichloro-2-hydroxybenzoate: ndls. from alc. or ether, m.p. 150° (15), 147° (5) (26), 143-144° (7) (3), 142° (12). [From AgĀ + MeI in s.t. at 135° (12), from 3,5-dichlorosalicyloyl chloride (above) with McOH (5), or from methyl salicylate (1.1750) in AcOH with Cl₂ (26).] [This ester with Ac₂O yields (7) corresp. acetate, ndls. from MeOH, m.p. 57° (7)]
- **D** Ethyl 3,5-dichloro-2-hydroxybenzoate: cryst. from ether, m.p. 57° (5), 47° (12). [From Ag $\overline{\Lambda}$ + C₂H₅I as above (12) (3), from 3,5-dichlorosalicyloyl chloride (above) with EtOH (5), or from ethyl salicylate (1 1755) with Cl₂ (27).]
- --- 3,5-Dichloro-2-hydroxybenzamide: m.p. 209° (11).

3:4935 (1) Hirwe, Rana, Ber. 72, 1353 (1939) (2) Hirwe, Rana, Gavankar, Proc. Indian Acad. Sci. A-8, 211 (1938). (3) Martin, Gazz chim ital. 29, II 62-63 (1899). (4) Leuler, Pinet, Bull. soc chim (4) 41, 1363-1364 (1927) (5) Anschutz, Mehring, Ann 346, 300-311 (1906). (6) Biltz, Stepf, Ber 37, 4030 (1904) (7) Zincke, Ann 261, 252-251 (1891). (8) Datta, Mitter, J. Am. Chem. Soc 41, 2037 (1919). (9) Dey, Row, J. Chem. Soc 125, 560 (1924). (10) Earle, Jackson, J. Am. Chem. Soc 28, 109 (1906).

(11) Tarugi, Gazz. chim. stal. 30, II 487 489 (1900). (12) Smith, Ber. 11, 1225-1227 (1878). (13) Lössner, J. prakt Chem. (2) 13, 429 431 (1876). (14) Cahours, Ann chim (3) 13, 108-111 (1845); Ann 52, 341-343 (1844). (15) Lassar-Cohn, Schultze, Ber 38, 3300 (1905). (16) Ullmann, Kopetschni, Ber. 44, 428 (1911). (17) Hecht, Am. Chem. J. 12, 503-506 (1890). (18) Cazeneuve, Bull soc. chim. (3) 15, 74 (1896). (19) Farinholt, Stuart, Twiss, J. Am. Chem. Soc. 62, 1239 (1940). (20) Smith, Knerr, Am. Chem. J. 8, 98 (1886).

(21) Anschutz, Ann. 454, 81-82, 105-106 (1927)
(22) Mettler, Ber. 39, 2939 (1906).
(23) Tarbell, Wilson, J. Am. Chem. Soc. 64, 607 612 (1942)
(24) Tarbell, Wystrach, J. Am. Chem. Soc. 65, 2149-2153 (1943).
(26) Claisen, Ann. 418, 85 (1919)
(27) Cahours, Ann. chim. (3) 27, 461-462 (1849), Ann. 74, 312 (1850).
(28) Anschutz, Ber. 30, 223 (1897).

3:4936 4-CHLORONAPHTHOIC ACID-1



M.P. 221-223°(2) 210° (1) Ndls. from alc.; eas. sol. alc. or AcOH; spar. sol. aq., CHCl3, ether, or hydrocarbons.

[For prepn. of Č from 4-aminonaphthoic acid-1 [Beil. XIV-533] by diazotization, conversion with CuCN to 4-chloronaphthonitrile (see below), and hydrolysis of the latter by boilg, with a mixt. of 50% AcOH (2 vols.) + conc. H₂SO₄ (1 vol.) see (1); from 1-chloro-4-(chloromethyl)naphthalene, m.p. 78-79° (2), by oxidn. with dil. HNO₃ see (2); or from 1-bromo-4-chloronaphthalene [Beil. V-548, V₂-(448)] by conv. to RMgBr and carbonation see (2).]

C does not react either with conc. NH₄OH at 200° or with (NH₄)₂CO₃ at 220° (1).

Salts. The alk. salts of \bar{C} are eas. sol. aq.; the calcium, barium, and silver salts are sparingly sol. aq.; the iron, lead, and copper salts are insol. aq. (1).

- ---- Methyl 4-chloro-1-naphthoate: unreported.
- ---- Ethyl 4-chloro-1-naphthoate: unreported.
- --- 4-Chloro-1-naphthonitrile: long white ndls. from AcOH, m.p. 110° (1).
- D p-Bromophenacyl 4-chloro-1-naphthoate: m.p. 130.5-131° (2).

3:4936 (1) Friedlander, Weisberg, Ber. 28, 1840, 1842–1843 (1895). (2) Horn, Warren, J. Chem. Soc. 1946, 144.

M.P. 224.5-225.5° (1) B.P. 301° (6) 224-224.5° (2) 224° (3) 218° (4) (5) (6) (7) 217.5° u.c. (8)

White ndls. from C_6H_6 or pet. eth. — Spar. sol. hot alc. or ether; spar. sol. cold CS_2 but eas. sol. hot CS_2 ; sol. at 17° in 22 vols. or at 87° in 3.4 vols. toluene (8). — Sublimes readily. — Closely resembles hexachlorobenzene (3:4939), and the m.p. of mixtures of the two are but very slightly depressed (7) (8); furthermore, soly. of \bar{C} in C_6H_6 at 4 different temps. is alm. identical with that of hexachlorobenzene (9).

[For studies on dielectric characteristics of C see (9) (10) (11) (12).]

[For prepn. of $\bar{\rm C}$ from toluene (1.7405) with SO₂Cl₂ + AlCl₃ + S₂Cl₂ at 100° for ½ hr. as directed (72% yield (8)), or by electrolysis in AcOH/conc. HCl in dark (7), or with Cl₂ in pres. of I₂ followed by further chlorination in pres. of SbCl₅ of the fraction boiling above 240° (6) see indic. refs.; for formn. of $\bar{\rm C}$ from isopropylbenzene (cumene) (1:7440) with Cl₂ in pres. of I₂ + Fe at 0°, or from *p*-cymene (1:7505) with Cl₂ in pres. of I₂ + Fe (1), or from 2-chlorotoluenesulfonyl chloride-4 with Cl₂ in pres. of SbCl₃ at 65-70° (4), or from 2,3,4-trichlorotoluene (3:0425) or 2,4,5-trichlorotoluene (3:2100) with SO₂Cl₂ + AlCl₃ + S₂Cl₂ (8), or from 2,3,4-trichlorobenzal (di)chloride on stdg. (5) see indic. refs.]

[C on further treatment with SO₂Cl₂ + AlCl₃ + S₂Cl₂ gives (8) a prod. m.p. 272-274°. — C on fusion and treatment with Cl₂ at 210-230° as directed (13) gives 70-80% yield pentachlorobenzal (di)chloride (3:3590) b.p. 199° cor. at 13 mm. (13).

 $[\ddot{\mathbf{C}}$ on partial hydrolysis with caustic alk. at 130–140° under press. yields (14) tetrachlorocresol.]

 \bar{C} is unaffected by boilg. fumg. HNO₃ (6), but \bar{C} on oxidn. with 14.2 wt. pts. conc. HNO₃ (D=1.42) in pres. of 0.1 pt. Hg by boilg. for 150 hrs. (8) yields pentachlorobenzoic acid (3:4910), m.p. 199.5° (8).

3:4937 (1) Qvist, Holmberg, Acta Acad. Aboensis Math. et Phys. 6, No. 14, 3-28 (1932); Cent. 1932, II 2816; C.A. 27, 5726-5727 (1933).
 Qvist Salo, Acta Acad. Aboensis Math. et Phys. 8, No. 4, 30 pp. (1934); Cent. 1936, I 540.
 White, Briggs, Morgan, J. Am. Chem. Soc. 62, 23 (1940).
 Davies, J. Chem. Soc. 119, 871 (1921).
 Riess, Berndt, Hitschmann, Monatsh. 50, 334 (1928).
 Beilstein, Kuhlberg, Ann. 150, 298-299 (1869).
 Fichter, Glantzstein, Ber. 49, 2485-2486 (1916).
 Sulbeirad, J. Chem. Soc. 127, 2682-2684 (1925).
 Smyth, Lewis, J. Am. Chem. Soc. 62, 949-952 (1940).
 Smyth, Lewis, J. Am. Chem. Soc. 62, 721-727 (1940).

K. S. Cole, R. H. Cole, J. Chem. Phys. 9, 348 (1941).
 Morgan, Yager, Ind. Eng. Chem. 32, 1526 (1940).
 Lock, Ber. 66, 1533 (1933).
 I.G., French 724,779, May 2,

1932.

3:4939 HEXACHLOROBENZENE

M.P.	228.6-229.8°	(1)	B.P.	326°			(13)
	229.5° cor.	(2)		322.2°	(cor.	(4)
	228°	(3)		309°	at '	742 mm.	(15)
	227.6° cor.	(4)		309-310°	at '	720–727 m	m. (16)
	227°	(5)	(6) (7)				
	226-227.5° cor.	(51)					
	226-227°	(8)					
	226°	(9)	(10) (11)			
		(12)	(13)				
	224°	(14)					

(Note that \tilde{C} is *not* the same as benzenehexachloride, q.v.)

Long thin colorless pr. from CCl₄ or from C₆H₆ + EtOH. — Insol. aq.; insol. cold but sl. sol. hot alc., sol. in hot C₆H₆ (cf. {10}) or CHCl₃; at 16.5° 100 ml. CS₂ dis. 2.0 g. \bar{C} ; spar. sol. cold CCl₄ or pet. ether; for soly. in *p*-cymene at various temps. see (17); insol. liq. SO₂ or liq. NH₃. — Sublimes without melting in long needles even at ord. temp.

[For studies of cryst. structure of \tilde{C} see (18) (19). — For study of toxicity see (20). — For employment in forms, solid solns, of I_2 for use in pharmacy see (21). — For use as seed disinfectant see (22). — Mol. f.p. lowering = 207.5. — \tilde{C} resists Carius anal., but for detn, of chlorine in \tilde{C} by combusion in hydrogen see (23).]

[For prepn. of C from phthalic anhydride (1:0725) with Cl₂ at 170–265° in pres. of FeCl₃ (79% yield) see (51).]

[For prepn. of \bar{C} from tetrachlorobenzoquinone-1,4 (chloranil) (3:4978) with equal wt. each of PCl₅ and PCl₃ by htg. in s.t. at 200° for 4 hrs. (95% yield) see (24); from p-dichlorobenzene (3:0980) with 20 pts. ClSO₃H + 100 pts. NaCl htd. 10 hrs. at 210-220° (50% yield (5)) or treated with SO₂Cl₂ + AlCl₃ + S₂Cl₂ (25) see indic. refs.; from the mother liquor from prepn. of p-dichlorobenzene on further treatment with Cl₂ (94-95% yield) see (14); from 1,2,4,5-tetrachlorobenzene (3:4115) with ClSO₃H (4 pts.) refluxed for 1 hr. (78% yield (26)) or with SO₂Cl₂ + AlCl₃ + S₂Cl₂ warmed for 8 hrs. (70% yield (12)) see indic. refs.]

[For form. of \bar{C} from a very large number of miscellaneous sources and reactions see Beil. refs. given in heading and also the following: from CCl₄ (3:5100) + H₂ through hot tube at 600-650° (9) or with F₂ as directed (27); from CHCl₃ (3:5050) during explosion with Na (28); from dodecachlorohexane on htg. (29); from trichloroethylene (3:5170) + AlCl₃ + HCl gas at 50° (30) or as by-product of htg. at 180-210° under press. in glass, porcelain, or enameled vessels (31); from C₆H₆ + Cl₂ under press. (32); from nitrobenzene

+ Cl₂ + anhyd. FeCl₃ at 125° (33), cf. (34); from various addn. prods. of chlorine with trichloro- (35), tetrachloro- (36), or pentachloro- (37) benzenes usually by means of MeOH/NaOH, from 2,3,5,6-tetrachloro-N-nitroaniline, 2,3,5,6-tetrachloro-N-nitroacetanilide, or 2,3,5,6-tetrachloro-4-nitro-N-nitroaniline in boilg. AcOH + conc. HCl (8), from tetra-chlorophthalyl sym-dichloride or from pentachlorobenzoyl chloride on distn. (38).]

 $\bar{\mathbf{C}}$ with \mathbf{H}_2 over Ni at 270° gives (39) $\mathbf{C}_6\mathbf{H}_6$, chlorobenzene, dichlorobenzene, trichlorobenzene, etc. — $\bar{\mathbf{C}}$ in boilg. alc. with large excess of Na is completely dehalogenated (40). $\bar{\mathbf{C}}$ is unattacked by ICl in s.t. at 300° (41) and does *not* react with MeMgI or with MeMgBr in ether even on long boilg. (42).

[\bar{C} with liq. Cl_2 in s.t. in sunlight yields (37) by addn. both decachlorocyclohexane, m.p. 92°, and dodecachlorocyclohexane, m.p. in sealed cap. tube 285°. — \bar{C} with F_2 in CCl_4 soln. at 0° yields (43) small amts. of both hexachlorotetrafluorocyclohexane, $C_6Cl_6F_4$, m.p. 113–114°, and hexachlorohexafluorocyclohexane, $C_6Cl_6F_6$, m.p. 94–96°. — \bar{C} in vapor phase with F_2 in pres. of Cu gives a mixt. of 12 individual prods. (44).]

Č with aq. NaOH at 135–138° and 11-12 atm. for 3–4 hrs. (14) or with excess 5–15% soln. of NaOH in MeOH at 135° under press. (45) or Č with NaOH in EtOH in s.t. at 150–160° (47) or in dry glycerol at 250–280° (47) gives (80% yield (14)) sodium salt of pentachlorophenol (3.4850). — Č with MeOH/NaOH in ethyl methyl ketone soln. at b.p. for ½ hr. gives (43% yield (46)) methyl pentachlorophenyl ether, ndls. from alc., m.p. 108–109°. [For studies of kinetics of reacti. of Č with MeOH/NaOH in s.t. at 151° (2), at 176° (48), at 180° (48), at 183° (49) see indic. refs.; of Č with EtOH/NaOH or with NaOEt soln. at 175° see (2).]

 \ddot{C} on boilg, with mixt, of fumg. HNO₄ + conc. H₂SO₄ gives (50) tetrachlorobenzoquinone-1,4 (chlorantl) (3:4978).

3:4939 (1) Dadieu, Pongratz, Kohlrausch, Monatsh. 61, 434 (1932). (2) Clark, Crozier, Trans. Roy. Canada (3) 19, 111, 153-154 (1925); Cent 1926, II 20, C.A. 20, 388 (1926). (3) Pollak, Gebauer-Fullnegg, Blumenstock, Monatsh. 46, 514 (1925). (4) Belistein, Kuhlberg, Ann 150, 309-310 (1869). (5) Gebauer-Fullnegg, Figdor, Monatsh. 48, 637 (1927). (6) Pollak, Gebauer-Füllnegg, Monatsh. 47, 552-553 (1926). (7) Fels, Z. Krist. 32, 367 (1900). (8) Peters, Rowe, Stead, J. Chem. Soc. 1943, 372-373. (9) Schwarz, Pflugmacher, J. prakt. Chem. (2) 158, 2-4 (1941). (10) Smyth, Lewis, J. Am. Chem. Soc. 62, 950 (1940).

(11) van der Linden, Rec. trav. chim. 57, 415 (1938). (12) Silberrad, J. Chem. Soc. 121, 1021 (1922). (13) Jungfleisch, Ann. chim (4) 15, 287-291 (1868). (14) Troitsku, Voronina, Org. Chem. Ind. (U.S.S. R.) 7, 240-241 (1940), C.A. 35, 3989 (1941). (15) Krafft, Ber 9, 1087 (1876). (16) Ruoff, Ber. 9, 1486 (1876). (17) Wheeler, J. Am. Chem. Soc. 42, 1844 (1920). (18) Lonsdale, Proc. Roy. Soc. London, A-133, 536-552 (1931). (19) Plummer, Phil. Mag. (6) 50, 1214-1220 (1925). (20) Cameron, Thomas, et al., J. Path. Bact. 44, 281-296 (1937).

(21) "Chemia" Ungarische Chem. Ind. & von Dalmady, Ger. 389,778, Feb. 7, 1924; Austrian 95,732, Jan. 25, 1924; Cent. 1924, I 2801. (22) I.G., French 701,032, March 10, 1931; Cent. 1931, II 618. (23) ter Meulen, Heslinga, Rec. trav. chim. 42, 1095 (1923). (24) Graebe, Ann. 263, 30 (1891). (25) Roberts Co. & Silberrad, Brit. 193,200, March 15, 1923, Cent. 1925, I 904. (26) Huntress, Carten, J. Am. Chem. Soc. 62, 513 (1940). (27) Simons, Boud, McArthur, J. Am. Chem. Soc. 62, 3478 (1940). (28) Davis, McLean, J. Am. Chem. Soc. 66, 720-722 (1938). (29) van der Linden, Rec. trav. chim. 57, 415-416 (1938). (30) Muller, Honn, J. prakt. Chem. (2) 133, 280-290 (1932).

(31) Consortium für Elektrochem. Ind., French 814,423, June 23, 1937; Cent. 1937, II 3953. (32) I.G., French 837,741, Feb 20, 1939; Cent. 1939, II 228. (33) Frezz-David, Stahelin, Hetv. Chim. Acta 20, 1458-1461 (1937). (34) van der Linden, Rec. trav. chim. 57, 342-344 (1938). (35) van der Linden, Rec. trav. chim. 55, 317-320 (1936). (36) van der Linden, Rec. trav. chim. 55, 421-430 (1936). (37) van der Linden, Rec. trav. chim. 55, 569-573 (1936). (38) Kirpal, Kunze, Ber. 62, 2104-2105 (1929). (39) Mailhe, Cent. 1921, III 467. (40) Stepanov, J. Russ. Phys.-Chem. Soc. 37, 15 (1905); Cent. 1905, I 1273.

(41) Krafft, Merz, Ber. 8, 1303 (1875).
(42) Durand, Hsun, Compt. rend. 191, 1460 (1930).
(43) Bigelow, Pearson, J. Am. Chem. Soc. 56, 2773-2774 (1934).
(44) Fukuhara, Bigelow, J. Am. Chem. Soc. 60, 427-429 (1938).
(45) Smith, Litvak (to Dow Chem. Co.), U.S. 2,107,650.

Feb. 8, 1938; Cent. 1938, I 3821; C.A. 32, 2548 (1938). (46) van der Linden, Rec. trav. chim. 57, 787-788 (1938). (47) Weber, Wolff, Ber. 18, 335-337 (1885). (48) Holleman, Rec. trav. chim. 39, 749 (1920). (49) de Crauw, Rec. trav. chim. 50, 787 (1931). (50) Istrati, Bull. soc. chim. (3) 3, 184-186 (1890).

(51) Dvornikoff, J. Am. Chem. Soc. 68, 142 (1946); Dvornikoff (to Monsanto Chem. Co.),

U.S. 2,028,383, Jan. 21, 1936; C.A. 30, 1394 (1936).

3:4940 p-CHLORO	BENZOIC ACID		C7H5O2Cl OH	Beil. IX - 340 IX ₁ -(140)
M.P. [245°	(160)]	M.P.	238-239°	(23) (70)
243°	(1) (2) (3) (4) (64)	(Contd.)	238°	(24)
243° in s.t.	(5)		237°	(66) (133)
242.5-243.5°	° (6) (7)		236-23 7°	(25) (126)
241.7°	(8)		236.5°	(67)
241.5°	(9) (10)		236°	(26) (27) (28) (29)
241°	(11) (12)			(51) (54) (61) (72)
240-241°	(13)			(77) (86) (156)
240°	(14) (15) (16) (17)		235.5-236°	(30)
	(18) (38) (40)		235-236°	(55)
239.7°	(19)		235.5°	(31) (53)
239° cor.	(20)		2 35°	(32) (33) (34) (36)
239°	(21) (22)		234-235°	(56) (71)
			234°	(50)
			233-234°	(69)

Cryst. from alc. — $\bar{\rm C}$ is almost insol. in cold aq.; e.g., 100 ml. satd. aq. soln. at 25° conts. 0.0068 g. $\bar{\rm C}$ (33); note that $\bar{\rm C}$ is thus much less sol in aq. than m-chlorobenzoic acid (3:4392) and far less sol. than o-chlorobenzoic acid (3:4150). — At 14–16° 100 ml. satd. soln. of $\bar{\rm C}$ in acctone conts. 2.6 g. $\bar{\rm C}$, in EtOAc 1.6 g. $\bar{\rm C}$, in 75% AcOH 0.3 g. $\bar{\rm C}$, in CCl₄ 0.04 g. $\bar{\rm C}$, in C₆H₆ 0.017 g. $\bar{\rm C}$, in CS₂ 0.16 g. $\bar{\rm C}$ (22). — [For study of soly. of $\bar{\rm C}$ in acctone (8), C₆H₆ (8) (9), heptane (9) see indic. refs.]

[For study of distribution at 25° of \bar{C} between aq. + toluene or aq. + CHCl₃ see (35); for adsorption of \bar{C} on charcoal from its solns. in acctone or C_6H_6 see (8); for soly. of \bar{C} in aq. solns. of various salts (including Na $\bar{\Lambda}$) see (33).]

 \bar{C} can be sublimed in vac. (19). — \bar{C} is but very slightly volatile with steam (for details see (10)). — [For crystallographic data see (36) (37).]

Binary systems contg. \bar{C} . [For f.p./compn. data on system \bar{C} + aq. see (38). — For f.p./compn. data and diagrams of system \bar{C} + BzOH (1:0715), eutectic, m.p. 115°, contg. about 10 wt. % \bar{C} , see (22) (16); for f.p./compn. data on systems \bar{C} + p-toluic acid (1:0795) (11), \bar{C} + p-hydroxybenzoic acid (1:0840) (11), or \bar{C} + p-methoxybenzoic acid (anisic acid) (1:0805) (15) see indic. refs.]

[For f.p./compn. data and diagrams on systems $\bar{\bf C}+o$ -chlorobenzoic acid (3:4150), eutectic, m.p. 132°, contg. abt. 14 mole % $\bar{\bf C}$, see (22) (39); on system $\bar{\bf C}+m$ -chlorobenzoic acid (3:4392), eutectic, m.p. 140.9°, contg. 20 mole % $\bar{\bf C}$ (22) (39) (40), see indic. refs.]

[For f.p./compn. data and diagrams on systems $\bar{\mathbf{C}}+m$ -bromobenzoic acid (16), $\bar{\mathbf{C}}+p$ -bromobenzoic acid (16), $\bar{\mathbf{C}}+p$ -nitrobenzoic acid (41), $\bar{\mathbf{C}}+p$ -iodobenzoic acid (42) see indic. refs.]

Ternary systems contg. \tilde{C} . [For influence of addn. of \tilde{C} to the eutectic mixt. of o-chlorobenzoic acid (3:4350) with m-chlorobenzoic acid (3:4392) see (43); for data on ternary system of all three chlorobenzoic acids, eutectic m.p. 104.9°, contg. 48.3 mole % ortho + 44.0 mole % meta + 7.7 mole % para isomers, see (39).]

Miscellaneous. [For study of fate of \bar{C} in animal organism see (44) (45) (46) (47); note that conjugation with glycine to yield the expected N-(p-chlorobenzoyl)glycine (p-chlorohippuric acid) [Beil. IX-341], m.p. 143° (45), does occur. — For study of toxicology of \bar{C} see (46) (48). — Note that sodium salt of \bar{C} (see also below) is widely used under name "Mikrobin" as preservative. — For use of \bar{C} as vulcanization regulator see (49).]

Preparation. [For prepn. of \bar{C} from p-chlorotoluene (3:8287) by oxidn. with boilg. 5% aq. KMnO₄ (60% yield (51)) (22) (50) (52) (53) (133), with MnO₂ + H₂SO₄ (100% yield (51)), with CrO₃ (54), with dil. HNO₃ in s.t. at 140-145° for ½ hr. (55) or at 115-120° for 5-6 hrs. (56) see indic. refs.; from p-chlorotoluene (3:8287) by oxidn. with air in the pres. of various catalysts (57), or at 235-240° and 50-60 atm. press. in pres. of FeO.OH (58), or in aq. alk. at 260° under press. (59) see indic. refs.; for formn. of \bar{C} from p-chlorotoluene (3:8287) by electrolytic oxidn. (2) (60), by action of NOCl (30), or by long exposure to \bar{I}_2 + aq. in light (28) see indic. refs.]

[For prepn. of \bar{C} from p-chloroacetophenone (3:6735) by oxidn. with alk. KMnO₄ (61), with CrO₃/AcOH/H₂SO₄ (95% yield (7)), with Cl₂ + NaOH(NaOCl) in aq. MeOH (93% yield (62)), by liquid phase cat. oxidn. with air in pres. of MnO₂ (91% yield (6)) see indic. refs.; for formn. of \bar{C} from p-chloroacetophenone (3:6735) with NOCl see (63).]

[For form. of \bar{C} from 4-chloro-isopropylbenzene (p-chlorocumene) (3:8705) by oxidn. with HNO₃ (64) (23), from 2,4'-dichloro-biphenyl (3:0670) (65) or from 4,4'-dichloro-biphenyl (3:4300) (66) by oxidn. with $CrO_3/AcOH$, from benzal-4-chloroacetophenone (24) by oxidn. with KMnO₄ in pyridine (90% yield (24)) see indic. refs.]

[For form. of \tilde{C} from p-chlorobenzaldehyde (3:0765) by oxidn. with KMnO₄ (67) (68) (69) (70) or CrO₃ (67) or even slowly by air see indic. refs.; from p-chlorobenzaldehyde copper during recrystn. (presumably as a result of oxidn. by air) see (31).]

[For prepn. of \bar{C} from p-chlorobenzonitrile [Beil. IX-341, IX₁-(140)] by hydrolysis with 75% H₂SO₄ (71), from p-chlorobenzoyl chloride (3:6550) by hydrolysis with aq., from p-chlorobenzotrichloride (3:6825) by hydrolysis, e.g., with aq. in s.t. at 200° (72) or with aq. alk., alk. carbonates, or alk.-earth carbonates (73) (note also formn. of \bar{C} as by-prod. of prepn. of o-chlorobenzaldehyde from o-chlorobenzenal (di)chloride (3:6700) with CrO₈ (74) or on boilg. with aq. for 20 hrs. followed by oxidn. with KMnO₄ (85% yield (17)); from a mixt. of p-chlorobenzotrichloride + p-chlorobenzal (di)chloride by hydrol. with 70% H₂SO₄ or 80% AcOH or 5% NaOH at 90-100° in stream of air to effect immediate oxidn. (75) see indic. refs.]

[For prepn. of \bar{C} from 2-(p-chlorobenzoyl)benzoic acid [Beil. X-750, X_1 -(356)] by hydrolytic cleavage with aq. + CaO under press. at 325° (93% yield (7)), or from p-chlorobromobenzene via conversion to p-chlorophenyl lithium bromide (76) or to p-chlorophenyl magnesium bromide (77) and subsequent carbonation (90% yield (76)) or from chlorobenzene (3:7903) with AlCl₃ + CO₂ at 100° and 60 atm. press. (82) see indic. refs.]

[For formn. of C from benzoic acid (1:0715) with alk. NaOCl (20) cf. (78) or Ca(OCl)₂ (79) cf. (25), or from 4-chlorophthalic acid (3:4390) by cat. monodecarboxylation (80), see indic. refs.]

[For formn. of C from di-(p-chlorobenzoyl) peroxide by htg. (2) (3), from p-aminobenzoic acid via diazotization and use of Cu₂Cl₂ reaction (82% yield (83)), from p,p'-diazoaminobenzoic acid (diazoaminobenzene-4,4'-dicarboxylic acid) [Beil. XVI-728] with conc. HCl (84), from p-chloroisonitrosoacetophenone with warm Ac₂O (21), from p-chlorophenacyl bromide by conv. to quaternary salt with quinoline and treatment with aq. NaOH (18), from p-borobenzoic acid with hot aq. CuCl₂ (26), from di-(p-chlorophenzoyl)butane on pyrolysis at 255–265° for 24 hrs. (85), from ethyl p-chlorophenyl-azo-carboxylate during oxidn. with H₂O₂ in AcOH (29), from p-hydroxybenzoic acid (1:0840) with PCl₅ followed by aq. (86) (87), or from treatment with aq. of the product from p-nitrotoluene with

SOCl₂ in s.t. at 200-220° (88), p-toluenesulfonyl chloride with SOCl₂ in s.t. at 230-250° (88), or sodium p-toluenesulfonate in chlorobenzene with SOCl₂ in s.t. at 250-260° (89) see indic. refs.]

Chemical behavior. No specific account of reduction of \tilde{C} to benzoic acid appears to be on record; note, however, detn. of chlorine in \tilde{C} by use of Na + alc. (90). — \tilde{C} on reduction with formic acid at 250–260° in pres. of TiO₂ gives p-chlorobenzaldehyde (3:0765) (89% yield on \tilde{C} consumed, or 41% on \tilde{C} used (91)). — \tilde{C} on electrolytic reduction in alc./ H_2 SO₄ gives (92) p-chlorobenzyl alcohol [Beil. VI-444, VI₁-(222)], m.p. 73°, b.p. 234° (92); note proximity of m.p. of this prod. to that (72°) of corresp. prod. obtd. by similar reduction of o-chlorobenzoic acid (3:4150). — For study of reduction of \tilde{C} with H_2 + Ni in aq. alk. at ord. temp. see (93).

[C on electrolytic oxidn. in AcOH/H₂SO₄ gives (2) 4-chloro-2-hydroxybenzoic acid (4-chlorosalicylic acid) (3:4908).]

 \bar{C} behaves normally as a monobasic acid; e.g., \bar{C} on titration with standard dil. aq. alk. gives Neut. Eq. 156.5; ionization constant at 25° is 0.93×10^{-4} (94), 0.78×10^{-4} (95), 1.04×10^{-4} (96) cf. (97) (12). — [For study of acid strength of \bar{C} in various alcohols see (98) (99) (100) (13) (101) (27).—For soly. of \bar{C} in aq. solns. of various salts (including Na \bar{A}) see (33). — For sepn. of \bar{C} from o-chlorobenzoic acid (3:4150) by use of difference in acid strength see (102).]

Salts of inorganic bases. NH₄ \overline{A} (103). — Hydroxylamine salt; m.p. 130° (104). — Na \overline{A} : widely used as food preservative under name "Mikrobin"; for prepn. from \overline{C} + Na phenolate see (105); for study of influence on enzymes see (106) (107); for study of use as preservative see (108); for studies of detection and/or detn. in foods see (109) (110) (111) (112) (113) (114); forms liquid cryst. on fusion (115).

AgĀ, sol. in hot aq. (50) (1 l. satd. aq. soln. at 20° conts. 1.08 g. (118)). (Note that this salt (1 mole) with I_2 (2 equivalents) in dry C_6H_6 refluxed 15-18 hrs. yields (116) phenyl p-chlorobenzoate, m.p. $100^\circ + CO_2 + AgI$, and that analogous behavior is shown to lesser degree by corresp. salt of m-chlorobenzoic acid (3:4392) but not by corresp. salt of o-chlorobenzoic acid (3:4150).)

Ca \bar{A}_2 .3H₂O (25), 1 l. satd. aq. soln. at 20° conts. 7.37 g. (118). — Ba \bar{A}_2 .3½H₂O (66); Ba \bar{A}_2 .4H₂O (34); Ba \bar{A}_2 .H₂O (118); 1 l. satd. aq. soln. of latter at 20° conts. 1.09 g. Ba \bar{A}_2 .H₂O (118) (for use of Ba salt in sepn. of the three isomeric chlorobenzoic acids see (43)). — Cd \bar{A}_2 .2H₂O (117); 1 l. satd. aq. soln. at 20° conts. 7.79 g. (118). — For similar data on salts of \bar{C} with other heavy metals see (118) (119). — For study of various metal ions as precipitants for \bar{C} see (120).

Salts of organic bases. \bar{C} with equiv. amt. benzylamine in boilg. EtOAc followed by evapn. of solvent yields (121) benzylammonium p-chlorobenzoate, m.p. 157.4–158.4° u.c., 160.3–161.3° cor., Neut. Eq. 263.6. — \bar{C} similarly treated with α -phenylethylamine yields (121) α -phenylethylammonium p-chlorobenzoate, m.p. 150.0–151.0° u.c., 152.2–153.2° cor., Neut. Eq. 277.6.

Č (1 mole) in alc. mixed with codeine (1 mole), m.p. 155°, htd. several minutes, solvent evapd. and resultant sirup recrystd. from aq., yields (122) codeine p-chlorobenzoate, C₁₈H₂₁O₃N.Č, m.p. 162° on "Maquenne block"; note that this value although close to that (166°) of codeine p-bromobenzoate is widely different from and higher than those for the corresp. salts of either o-chlorobenzoic acid (3:4392) which are 134° and 96° respectively. — Č (1 mole) in alc. (or CHCl₃) with strychnine (1 mole) in alc., boiled for a few minutes, then cooled, yields (123) strychnine p-chlorobenzoate, C₂₁H₂₂O₃N₂.Č, m.p. 251° on "Maquenne block"; note that the m.p. of this salt is far higher than the corresp. products from similar treatment of either the o- or m- isomers, which are 170° and 185°, respectively.

C with alcohols gives by conventional processes the corresp. esters: for details on methyl

p-chlorobenzoate (3:0535) or on ethyl p-chlorobenzoate (3:6750) see these compds. — [For study of rate of esterification of \bar{C} with MeOH (124) (125) (126), with EtOH (126) (1) (127), with cyclohexanol (128) see indic. refs.]

Č with oxalyl (di)chloride (3:5060) refluxed in C₆H₆ (129), or NaĀ htd. with p-chlorobenzoyl chloride (3:6550) (130) gives (50% yield (130)) p-chlorobenzoic acid anhydride, ndls. from dil. acetone or C₆H₆, m.p. 193−194° (129) (131), 194.8° (130), 191.5° (132); note that this prod. may also form in various other reactions involving C̄, especially in pres. of tertiary bases or Na₂CO₃ cf. (131) (132).

 $\ddot{\mathbf{C}}$ with PCl₅ (133) (50) (45) (132), with SOCl₂ (134) (135) (136), with SOCl₂ + AlCl₃ (137), or with *p*-chlorobenzotrichloride (3:6825) + ZnCl₂ (138) gives *p*-chlorobenzoyl chloride (3:6550).

[\bar{C} with chlorobenzene (3:7903) + AlCl₃ refluxed 5½ hrs. gives (98% yield (7)) a mixt. consisting mainly of 4,4'-dichlorobenzophenone (3:4270) accompanied by a small proportion of 2,4'-dichlorobenzophenone (3:1565).]

[\tilde{C} with KCN + CuCN in aq. alc. htd. in s.t. at elevated temp. (139) or \tilde{C} (as K \tilde{A}) with aq. KCN + CuCN refluxed 8-10 hrs. under H₂ in quartz flask exposed to ultra-violet light (140) gives (70% yield (140)) terephthalic acid (1:0910).]

Substitution of nucleus of \bar{C} . \bar{C} on mononitration, e.g., with HNO₃ (D=1.6) on warming until soln. occurs (141), or with 10 wt. pts. HNO₃ (D=1.5) at 55–60° for 10 minutes (142), or with 4 vols. HNO₃ (D=1.5) warmed until soln. occurs (143), followed by pouring into aq. gives (yields: 97% (141), 96% (142), 90% (143)) 4-chloro-3-nitrobenzoic acid [Beil. IX-402, IX₁-(165)], cryst. from hot aq., m.p. 184° (142), 182° cor. (141), 180° (143). — [Note that boilg. conc. HNO₃ (D=1.42) has no action (143) on \bar{C} , that the crude mononitration prod. sometimes (143) contains a small amt. of p-chloronitrobenzoic acid [Beil. IX-401, IX₁-(165)], m.p. 140°, is not formed in appreciable amt. by direct nitration of \bar{C} .]

 $\bar{\mathbf{C}}$ on dinitration, e.g., with 20 wt. pts. conc. $H_2SO_4+3.3$ wt. pts. KNO₃ at 140° for $1\frac{1}{2}$ hrs. (144), or with $12\frac{1}{2}$ wt. pts. conc. $H_2SO_4+2.4$ wt. pts. fumg. HNO₃ (D=1.5) at 135-140° for 2 hrs. (145), then poured into aq., gives (yields: 95% (144), 82% (145)) 4-chloro-3,5-dinitrobenzoic acid [Beil. IX-416], pr. from C_6H_6 , m.p. 159° (144) (145). For use in detection of $\bar{\mathbf{C}}$ see (161). — [Note that none of the three other isomeric 4-chloro-dinitrobenzoic acids has ever been reported.]

[Č on sulfonation with SO₃ in fumg. H₂SO₄ (52) (146) (147) gives 4-chloro-3-sulfobenzoic acid [Beil. XI-387].]

- Methyl p-chlorobenzoate: m.p. 43° (see 3:0535).
- Ethyl p-chlorobenzoate: oil, b.p. 238° (see 3:6750).
- **p-Nitrobenzyl** p-chlorobenzoate: m.p. 130° (148). [From \tilde{C} (as Na \tilde{A}) with p-nitrobenzyl bromide (m.p. 99°) in boilg. alc. (148).]
- ◆ Phenacyl p-chlorobenzoate: m.p. 89.5° (149), 87.6° (32). [From C as (NaA) with phenacyl bromide (m.p. 50°) in boilg. alc. (98% yield (32)). Note that the m.p. of this prod. is only slightly higher than that (85.5°) of the corresp. prod. similarly obtd. from o-chlorobenzoic acid (3:4150).]
- --- p-Chlorophenacyl p-chlorobenzoate: unreported.
- **p-Bromophenacyl** p-chlorobenzoate: m.p. 126° (32). [From C (as NaA) with p-bromophenacyl bromide (m.p. 109°) in boilg. alc. (80% yield (32)).]
- --- p-Iodophenacyl p-chlorobenzoate: unreported.
- p-Phenylphenacyl p-chlorobenzoate: m.p. 160° cor. (150). [From C (as NaA) with p-phenylphenacyl bromide (m.p. 126°) in boilg. alc. (150). Note that m.p. of this prod. is only slightly higher than that (154°) of corresp. prod. similarly obtd. from m-chlorobenzoic acid (3:4392).]

- --- S-Benzylthiuronium p-chlorobenzoate: unreported.
- © S-(p-Chlorobenzyl)thiuronium p-chlorobenzoate: cryst. from dioxane, m.p. 173° cor. (151). [From Č (as NaĀ or KĀ) in aq. with 1 equiv. of S-(p-chlorobenzyl)-thiuronium chloride, m.p. 197° (10% in alc.) (151).]
- ⑤ S-(p-Bromobenzyl)thiuronium p-chlorobenzoate: m.p. 163° cor. (152). [From Č (as NaĀ or KĀ) in aq. with 1 equiv. of S-(p-bromobenzyl)thiuronium bromide (m.p. 213°) in alc. (152). Note that m.p. of this prod. is only slightly lower than that (168° cor.) of the corresp. prod. similarly obtd. from o-chlorobenzoic acid (3:4150).]
- **D** p-Chlorobenzamide: ndls. from aq. or ether, m.p. 180° (153), 179° (154), 179° (67), 178.8° cor. (155), 175° (71). [From \tilde{C} by refluxing with AcOH + (NH₄)₂CO₃ (yield 80% (153), 51% (154)), from p-chlorobenzoyl chloride (3:6550) with conc. aq. NH₄OH (50) (155) (67), or from p-chlorobenzonitrile [Beil. IX-341, IX₁-(140)] by hydrolysis with hot conc. HCl (71).]
- p-Chlorobenzhydrazide: ndls. from hot aq., m.p. 163° (157), 162-163° (156)! [From ethyl p-chlorobenzoate (3:6750) with alc. hydrazine hydrate on htg. (yield 87% (156)); for use of this prod. as reagt. for identification of aldehydes and ketones see (156).]
 - N-(p-chlorobenzoyl)-N-phenylhydrazine: unreported.
- D p-Chlorobenzanilide: ndls. from alc., m.p. 194-195° (158), 194° (50), 193° (159). [From p-chlorobenzoyl chloride (3:6550) with aniline (2 moles) (50); also from α-(4-chlorobenzophenone oxime) by Beckmann rearr. (159). Note that the m.p. of this prod. is almost the same as that (192-193°) of the isomeric benz-p-chloroanilide [Beil. XII-612, XII₁-(306)].]
- p-Chlorobenz-p-toluidide: unreported.
- p-Chlorobenz-α-naphthalide: unreported.
- p-Chlorobenz-β-naphthalide: unreported
- 3:4940 (1) Kailan, Antropp, Monatsh 52, 297, 310-313 (1929). (2) Fichter, Adler, Helv. Chim. Acta 9, 281-286 (1926). (3) Gelissen, Hermans, Bcr 58, 292 (1925). (4) Fels, Z. Krist. 32, 389-391 (1900). (5) Davies, Wood, J. Chem. Soc. 1928, 1126. (6) Stubbs, Senseman, Ind. Eng. Chem. 28, 559-560 (1936). (7) Newton, Groggins, Ind. Eng. Chem. 27, 1397-1399 (1935). (8) Berger, Rec. trav. chim. 50, 379, 390, 395 (1931). (9) Sadgwick, Ewbank, J. Chem. Soc. 119, 981, 984, 988 (1921). (10) Sidgwick, J. Chem. Soc. 117, 403-404 (1920).
- Lettré, Barnbeck, Lege, Ber 69, 1151-1154 (1936) (12) Dippy, Williams, Lewis, J. Chem. Soc. 1935, 343-346. (13) Wooten, Hammett, J. Am. Chem. Soc. 57, 2289-2295 (1935).
 Brooks, Hobbs, J. Am. Chem. Soc. 62, 2851 (1940) (15) Lettré, Ber. 73, 1152 (1940).
 Lettré, Barnbeck, Fuhst, Hardt, Ber. 70, 1415 (1937). (17) Asinger, Lock, Monatsh. 62, 336 (1933). (18) Krohnke, Ber 66, 609 (1933). (19) Andrews, Lynn, Johnston, J. Am. Chem. Soc. 48, 1282 (1926) (20) Smith, J. Chem. Soc. 1934, 213-218.
- (21) Borsche, Ber 62, 1365-1366 (1929) (22) Bornwater, Holleman, Rec. trav. chim. 31, 225, 242-248 (1912). (23) Qvist, Salo, Acta Acad. Aboensis Math. et Phys. 8, No. 4, 30 pp. (1934), Cent 1936, I 540, 1934, II 595, C A 29, 6884 (1935). (24) Dilthey, J. prakt. Chem. (2) 101, 200 (1921). (25) Beilstein, Schlun, Ann 133, 243-244, 250 (1865). (26) Ainley, Challenger, J. Chem. Soc. 1930, 2176. (27) Kuhn, Wassermann, Helv. Chim. Acta 11, 34, 41 (1928). (28) Silberrad, J. Chem. Soc. 125, 2196-2197 (1924) (29) Pieroni, Giannini, Gazz. chim. ital. 54, 174-175, (1924). (30) Schwarschmidt Smolla, Ber. 57, 39 (1924)
- 174-175 (1924). (30) Schaarschmidt, Smolla, Ber. 57, 39 (1924).
 (31) Bernouilli, Schaaf, Helv. Chim Acta 5, 729 (1922). (32) Kelly, Howard, J. Am. Chem. Soc. 54, 4383-4385 (1932). (33) Osol, Kilpatrick, J. Am. Chem. Soc. 55, 4430-4440 (1933). (34) Müller, Zeit. für Chemie 1869, 137. (35) Smith, White, J. Phys. Chem. 33, 1958, 1970 (1929). (36) Steinmetz, Z. Krist. 53, 473-474 (1913) (37) Groth, Chem. Krist. 4, 466-468 (1917). (38) Flaschner, Rankin, Monatsh. 31, 44 (1910). (39) Johnston, Jones, J. Phys. Chem. 32, 599-601 (1928). (40) Holleman, Vermeulen, de Mooy, Rec. trav. chim. 33, 30 (1914).
- (41) Lettré, Ber. 73, 386-390 (1940); C.A. 34, 5831 (1940). (42) Lettré, Lehmann, Ber. 71, 416 (1938). (43) Hope, Riley, J. Chem. Soc. 121, 2518-2527 (1922). (44) Quick, Cooper, J. Biol. Chem. 96, 83-101 (1932). (45) Novello, Miriam, Sherwin, J. Biol. Chem. 67, 558-559 (1926). (46) Schubel, Manger, Arch. exptl. Path. Pharmakol. 146, 223-231 (1929). Cent. 1938, I 1650; C.A. 24, 4834 (1930). (47) Wührer, Arch. exptl. Path. Pharmakol. 161, 719-729 (1931);

Cent. 1931, II 3115; C.A. 26, 1341 (1932). (48) Schübel, Münch. med. Wochschr. 77, 13-14 (1930); Cent. 1930, I 858. (49) Goodyear Tire and Rubber Co., French 761,220, March 14, 1934; Cent. 1934, II 854. (50) Emmerling, Ber. 8, 880-883 (1875).

(51) Montagne, Rec. trav. chim. 24, 112-114 (1905). (52) Ulmann, Am. Chem. J. 16, 533-539 (1894). (53) Steinkopf, Buchheim, Ber. 54, 2968 (1921). (54) Beilstein, Geitner, Ann. 139, 336 (1866). (55) Cohen, Miller, J. Chem. Soc. 85, 174-177, 1629-1630 (1904). (56) Cohen, Dawson, Blockey, Woodmansey, J. Chem. Soc. 97, 1626 (1910). (57) Charlot, Ann. chim. (11) 2, 470 (1934). (58) I.G., Brit. 331,100, July 17, 1930, Cent. 1930, II 2186; French 676,826, Feb. 27, 1930; Cent. 1930, I 3831. (59) Schrader, Ges. Abhandl. Kenntus Kohle, 4, 310-341 (1920); Cent. 1921, I 537; C.A. 15, 2850-2851 (1921). (60) Dunbrook, Lowy, Cent. 1924, II 2838.

(61) Gautier, Ann. chim. (6) 14, 375-376 (1888). (62) Van Arendonk, Cupery, J. Am. Chem. Soc. 53, 3184-3186 (1931). (63) Rheinboldt, Schmitz-Dumont, Ann. 444, 129 (1925). (64) Meyer, Bernhauer, Monatsh. 53/54, 741 (1929). (65) de Crauw, Rec. trav. chim. 50, 776-777 (1931). (66) Schmidt, Schultz, Ann. 207, 339 (1881). (67) Montagne, Rec. trav. chim. 19, 53, 61 (1900). (68) Jackson, White, Am. Chem. J. 3, 32 (1881/82). (69) Jackson, White, Ber. 14, 1043 (1878). (70) Mayer, English, Ann. 417, 79 (1918).

(71) Van Scherpenzeel, Rec. trav. chim.: 16, 114 (1897). (72) Bellstein, Kuhlberg, Ann. 159, 295-296 (1869). (73) Britton (to Dow Chem. Co.), U.S. 1,878,463, Sept. 20, 1932; Cent. 1933, 131; C.A. 27, 308 (1933). (74) Beilstein, Kuhlberg, Ann. 146, 328 (1868). (75) Heller (to Chem. Fabrik von Heyden), Ger. 639,578, Dec. 8, 1936; Cent. 1937, I 2025; C.A. 31, 3943 (1937). (76) Gilman, Langham, Moore, J. Am. Chem. Soc. 62, 2330 (1940). (77) Bodroux, Compt. rend. 137, 711 (1903); Bull. soc. chim. (3) 31, 29 (1904). (78) Lossen, Ger. 146,174, Nov. 6, 1903; Cent. 1903, II 1224. (79) Stenhouse, Ann. 55, 9-12 (1845). (80) Jaeger (to Selden Co.), U.S. 1,953,231, 1,953,232, April 3, 1934; Cent. 1934, II 669, 1688.

(81) McEwen, Org. Syntheses, Coll. Vol. 2 (1st ed.), 133-135 (1943); 12, 12-14 (1932). (82) Meyer, Hopff (to I.G.), Ger 524,186, May 11, 1931; Cent. 1931, II 497; Brt. 307,223, March 28, 1929; Cent. 1929, I 3144. (83) Bryd, Roczniki Chem. 7, 436-445 (1927), C.A. 22, 2372 (1928). (84) Wilbrand, Beilstein, Ann. 128, 270-272 (1863). (85) Skraup, Guggenheimer, Ber. 58, 2497-2498 (1925). (86) Ladenburg, Fitz, Ann. 141, 258-259 (1867). (87) Anschütz, Moore, Ann. 239, 343-349 (1887). (88) Meyer, Monalsh. 36, 730 (1915). (89) M.L.B., Ger. 282,133, Feb. 15, 1915; Cent. 1915, I 464. (90) Iremescu, Chirnoaga, Z. anal. Chem. 125, 32-37 (1942); C.A. 37, 6212 (1943).

(91) Davies, Hodgson, J. Chem. Soc. 1943, 84-86; C.A. 37, 4360 (1943).
(92) Mettler, Ber. 38, 1750 (1905).
(93) Keller, Ber. 54, 2257-2259 (1921).
(94) Ostwald, Z. physik. Chem. 3, 256 (1889).
(95) Smith, Jones, Am. Chem. J. 50, 28 (1913).
(96) Saxton, Menet, J. Am. Chem. Soc. 56, 1918-1921 (1934).
(97) Bodforss, Z. physik. Chem. 102, 43 (1922).
(98) Ellhott, Krk-patrick, J. Phys. Chem. 45, 454-465, 466-471, 472-485, 485-492 (1941).
(99) Dippy, J. Chem. Soc. 1941, 550-552.
(100) Kilpatrick, Mears, J. Am. Chem. Soc. 62, 3047-3051, 3051-3054 (1940).

(101) Bright, Briscoe, J. Phys. Chem. 37, 787-796 (1933). (102) Mills (to Dow Chem. Co.), U.S. 1,942,826, Jan. 9, 1934; Cent. 1934, I 2196; C.A. 28, 1719 (1934). (103) McMaster, Godlove, J. Am. Chem. Soc. 37, 2184 (1915). (104) Oesper, Ballard, J. Am. Chem. Soc. 47, 2424-2427 (1925). (105) Dobmaier (to I.G.), Ger. 508,097, Sept. 24, 1930, Cent. 1931, I 159. (106) Bleyer, Diemair, Leonard, Arch. Pharm. 271, 539-552 (1933). (107) Landsteiner, van der Scheer, Proc. Soc. Expl. Biol. Med. 24, 692-693 (1927); Cent. 1929, I 2543. (108) Sabalitschka, Dietrich, Desinfektion 11, 67-71, 94-104 (1926); Cent. 1927, I 2670; C.A. 20, 3712 (1926). (109) Toth, Kardos, Z. Untersuch. Lebenem. 79, 565-567 (1940). (110) Olejnicck, Hanzelka, Z. Untersuch. Lebeneum. 84, 419-429 (1942); C.A. 37, 6401 (1943).

(111) von Fellenberg, Krauze, Mitt. Lebensm. Hyg. 23, 111-137 (1932); Cent. 1932, II 1092; C.A. 26, 5348 (1932). (112) Hostettler, Mitt. Lebensm. Hyg. 23, 65-70 (1932); Cent. 1932, II 463; C.A. 26, 4888 (1932). (113) Hostettler, Mitt. Lebensm. Hyg. 24, 247-258 (1933); Cent. 1933, II 3931; C.A. 27, 5833 (1933). (114) Weiss, Z. Untersuch. Lebensm. 67, 84-86 (1934). (115) Vorländer, Huth, Ber. 43, 3129 (1910). (116) Birckenbach, Meisenheimer, Ber. 69, 723-729 (1936). (117) Pfeiffer, Nakatsuka, J. prakt. Chem. (2) 136, 247 (1933). (118) Ephraim, Pfister, Helv. Chim. Acta 8, 370, 379-380 (1925). (119) Ephraim, Ber. 55, 3482 (1922). (120) Rosenthaler, Mikrochemie 14, 364-365 (1933) 3/4).

(121) Buehler, Carson, Edds, J. Am. Chem. Soc. 57, 2181-2182 (1935). (122) Poe, Strong, J. Am. Chem. Soc. 57, 380-381 (1935). (123) Poe, Suchy, J. Am. Chem. Soc. 56, 1640-1641 (1934). (124) Hartman, Borders, J. Am. Chem. Soc. 59, 2107-2112 (1937). (125) Michael, Oechslin, Ber. 42, 319 (1909). (126) Kellas, Z. physik. Chem. 24, 222-225, 230, 240-241 (1897), (127) Wightman, Wiesel, Jones, J. Am. Chem. Soc. 36, 2254 (1914). (128) Hartman, Storms,

Gassmann, J. Am. Chem. Soc. 61, 2167-2169 (1939). (129) Adams, Wirth, French, J. Am. Chem. Soc. 40, 426-427 (1918). (130) Rule, Paterson, J. Chem. Soc. 125, 2161 (1924).

(131) Lockemann, Ber. 43, 2229 (1910). (132) Frankland, Carter, Adams, J. Chem. Soc. 161, 2476, 2479 (1912). (133) Van Raalte, Rec. trav. chim. 18, 394-395 (1899). (134) Mayer, Monatsh. 22, 778 (1901). (135) Bergmann, Bondi, Ber. 64, 1471-1472 (1931). (136) Thompson, Norris, J. Am. Chem. Soc. 58, 1956 (1936). (137) Kissling (to I.G.), Ger. 701,953, Jan. 2, 1940; C.A. 36, 99 (1942). (138) Scottish Dyes Ltd. & Bangham & Thomas, Brit. 308,231, April 18, 1929; Cent. 1929, II 1348. (139) Rosenmund, Struck, Ber. 52, 1755 (1919). (140) Rosenmund, Luxat, Tiedemann, Ber. 56, 1950-1955 (1923).

(141) Bogert, Conklin, Collection Czechoslov. Chem. Commun. 5, 445-446 (1933). (142) Thompson, Turner, J. Chem. Soc. 1938, 35. (143) King, March, J. Chem. Soc. 127, 2646-2647 (1925). (144) Ullmann, Ann. 366, 92-93 (1909). (145) Mauthner, Ber. 39, 1341 (1906). (146) Cöllen, Ann. 193, 29-32 (1878), Ber. 9, 758-760 (1876). (147) Collen, Bottinger, Ber. 9, 1247-1251 (1876). (148) Lyons, Reid, J. Am. Chem. Soc. 39, 1734 (1917). (149) Chen. Trans. Science Soc. China 7, 73-80 (1931). (150) Kelly, Morisant, J. Am. Chem. Soc. 58, 1502-1503 (1936).

Soc. China 7, 73-80 (1931). (150) Kelly, Morisani, J. Am. Chem. Soc. 58, 1502-1503 (1936). (151) Dewey, Sperry, J. Am. Chem. Soc. 61, 3251-3252 (1939). (152) Dewey, Shasky, J. Am. Chem. Soc. 63, 3526-3527 (1941). (153) Kao, Ma, J. Chem. Soc. 1931, 443. (154) Kao, Ma, Sci. Repts. Natl. Tsing Hua Univ. A-1, 21-22 (1931). (155) Remsen, Reed, Am. Chem. J. 21, 290 (1899). (156) Shih, Sah, Sci. Repts. Natl. Tsing Hua Univ. A-2, 353-357 (1934). (157) Kahl, Cent. 1904, II 1493. (158) Bellavita, Gazz. chim. ital. 65, 894 (1935). (159) Wegerhoff, Ann. 252, 7-9 (1889). (160) Herz, Wittek, Monatsh. 74, 277 (1941).

(161) Deshusses, Mitt. Lebensm. Hyg. 35, 1-2 (1944); C.A. 39, 3595 (1945).

[See also tetrachlorobenzoguinone-1,4 (chloranil) (3:4978).]

Colorless scales or ndls. from C_6H_6 ; solvated pr. from AcOH losing solvate in air (2) (8). — For crystallographic data see (9). — \bar{C} sublimes with partial decompn. (10); for study of sublimation pressure see (11).

 \tilde{C} is insol. aq.; almost insol. C_0H_0 , CCl_4 , CS_2 ; eas. sol. alc., ether; spar. sol. AcOH. [For study of ht. of formn. of \tilde{C} see (12); for studies of heat of combustion see (13) (14).] [For patent on use of \tilde{C} as vulcanization accelerator see (15).]

PREPARATION OF C

From tetrachlorobenzoquinone-1,4. For prepn. of \bar{C} from chloranil (3:4978) by reduction with various reagents see the following. [For use of aq. SO_2 see (10) (16) (note, however, that this reduction is so slow that it has been used (18) as a method of sepn. of 2,3,5-trichlorobenzoquinone-1,4 (3:4672) from tetrachlorobenzoquinone-1,4 (3:4978), and also that during the process substantial amounts of trichlorohydroquinonesulfonic acid and of dichlorohydroquinone disulfonic acid are formed (19)); for use of boilg. conc. HCl (9), conc. HBr (9) (40) in AcOH (3), with conc. HI + red (18) or yellow (20) phosphorus, or

with KI or NaI in cold acetone (38) see indic. refs.; for use of H_2S (5), $SnCl_2 + HCl$ (9) (8) (6), aq. slightly alkaline hydroxylamine (13), alc. hydrazine hydrate (21), with EtOH on exposure to direct sunlight (7) (study of quantum efficiency of the photochemical reduction (22)), or with hydroquinone (1:1590) in ether (39) see indic. refs.]

[For formn. of \bar{C} as by-product of use of tetrachlorobenzoquinone-1,4 (chloranil) (3:4978) in low-temp. dehydrogenations see (23) (24); for formn. of derivatives (ethers) of \bar{C} as by-products of reaction of chloranil (3:4978) with free radicals see (25) (26) cf. (27); for formn. of \bar{C} as by-product of reaction of chloranil (3:4978) with C_6H_8MgBr see (31).]

From 2,3,5-trichlorobenzoquinone-1,4. [For prepn. of \bar{C} from 2,3,5-trichlorobenzoquinone-1,4 (3:4672) with conc. HCl on protracted boilg. (9) (28), with fumg. HCl in s.t. at 120° for 12 hrs. (29), or in AcOH soln. with dry HCl gas (30) see indic. refs.]

From other sources. [For formn. of \bar{C} from hydroquinone (1:1590) in AcOH with Cl₂ (32), or from *p*-nitroaniline (or certain derivatives) with conc. HCl in s.t. at 180° (2), see indic. refs.]

CHEMICAL BEHAVIOR OF C

Oxidation of \bar{C} . \bar{C} on oxidation, e.g., with aq. alc. AgNO₃ (10), NH₄OH/AgNO₃ (2), boilg. conc. HNO₃ (2) (20), etc., gives tetrachlorobenzoquinone-1,4 (chloranil) (3.4978). [For studies of oxidin-reduction potential of system \bar{C} + chloranil see (33) (34) (35) (1) (27) (6).]

[Note also that the quinhydrone to be expected from \bar{C} with 1 mole of the corresp. tetrachlorobenzoquinone-1,4 (chloranil) (3:4978) is not reported.]

[Note also that, although \bar{C} dissolves in aq. KOH without discoloration, the soln. upon exposure to air turns brown and on stdg. ppts. (16) di-potassium salt of chloranille acid (2,5-dichloro-3,6-dihydroxybenzoquinone-1,4) (3:4970).]

Other reactions of $\tilde{\mathbf{C}}$. $[\tilde{\mathbf{C}}$ with PCl₅ (2 moles) gives (16) hexachlorobenzene (3:4939). — $\tilde{\mathbf{C}}$ with 2,3,5-trichlorohydroquinone (3:4052) + a little aq. htd. at 100° for $\frac{1}{2}$ hr. undergoes a redistribution reaction (28) cf. (36).]

- Tetrachlorohydroquinone dimethyl ether: m.p. 164° (37), 160° (5). [From C by action of diazomethane in ether soln. (5).]
- **D** Tetrachlorohydroquinone diethyl ether: m.p. 112° (16). [From C with EtI (2 moles) + KOH (2 moles) in alc. in s.t. at 130-140° (16).]
- (3:7065) (16) or from chloranil (3:4978) with AcCl in s.t. at 160-180° (16).
- Tetrachlorohydroquinone dibenzoate: m.p. 233° (9). [From Č with BzCl (3:6240) (9).]

3:4941 (1) Hall, Conant, J. Am. Chem. Soc. 49, 3050-3052 (1927). (2) König, J. prakt. Chem. (2) 70, 32-35 (1904). (3) Koenigs, Greiner, Ber. 64, 1047 (1931). (4) Sutkowski, Ber. 19, 2316 (1886). (5) Binz, Räth, Ber. 58, 312 (1925). (6) Conant, Fieser, J. Am. Chem. Soc. 45, 2207 2219 (1923). (7) Klinger, Ann. 382, 221 (1911). (8) Bouveault, Ann. chim. (8) 13, 144 (1908). (9) Levy, Schultz, Ann. 210, 154-156 (1891). (10) Städeler, Ann. 69, 327-329 (1849).

(9) Levy, Schultz, Ann. 210, 154-156 (1891). (10) Städeler, Ann. 69, 327-329 (1849). (11) A. S. Coolidge, M. S. Coolidge, J. Am. Chem. Soc. 49, 100-104 (1927). (12) Sjöstrom, Svensk Kem. Tid. 48, 121-124 (1936), Cent. 1937, I 58; C.A. 30, 6634 (1936). (13) Valeur, Ann. Chim. (7) 21, 501-507 (1900). (14) Swietoslawski, Starczewska, J. chim. phys. 22, 399-401 (1925). (15) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; Cent. 1933, I 3134; C.A. 27, 2845 (1933). (16) Graebe, Ann. 146, 9-12, 18-21 (1868). (17) Bouveault, Compt. rend. 129, 55 (1899). (18) Graebe, Ann. 263, 28-30 (1891). (19) Dodgson, J. Chem. Soc. 1936, 2501-2502. (20) Stenhouse, Ann. Suppl. 6, 213-216 (1868).

(21) Purgotti, Gazz. chim. ital. 24, I 581-584 (1894). (22) Leighton, Dresia, J. Am. Chem. Soc. 52, 3556-3562 (1930). (23) Arnold, Collins, Zenk, J. Am. Chem. Soc. 62, 983-984 (1940). (24) Arnold, Collins, J. Am. Chem. Soc. 61, 1407-1408 (1939). (25) Ziegler, Orth, Ber. 65, 628-631 (1932). (26) Clar, John, Ber. 63, 2974-2977 (1930). (27) Conant, Small, Taylor,

J. Am. Chem. Soc. 47, 1959-1974 (1925). (28) Graebe, Ann. 263, 21-22 (1891). (29) Andresen, J. prakt. Chem. (2) 28, 425- (1883). (30) Niemeyer, Ann. 228, 324 (1885).

(31) Clar, Engler, Ber. 64, 1600 (1931) (32) Eckert, Endler, J. prakt. Chem. (2) 104, 82 (1922). (33) Wallenfels, Mohle, Ber. 76, 927, 936 (1943). (34) Kvalnes, J. Am. Chem. Soc. 56, 667-670 (1934). (35) Hunter, Kvalnes, J. Am. Chem. Soc. 54, 2869-2881 (1932). (36) Kehrmann, Ber. 31, 979 (1898); 33, 3066-3067 (1900). (37) Ciamician, Silber, Gazz. chim. ital. 22, II 60 (1892). (38) Torrey, Hunter, J. Am. Chem. Soc. 34, 714-715 (1912). (39) Siegmund, J. prakt Chem. (2) 92, 362 (1915). (40) Sarauw, Ann. 209, 125 (1881).

3:4942 7-CHLORONAPHTHOIC ACID-1

C₁₁H₇O₂Cl Beil. S.N. 951

238-240° (3)

235° (3)

Cryst. from 60% alc. or by sublimation. — Very sol. alc. or AcOH; sol. ether, C_6H_6 . [For prepn. of \bar{C} from 7-aminonaphthoic acid-1 (1) (2) via diazotization and use of Cu₂Cl₂ reactn. see (1); from 7-chloro-1-(chloromethyl)naphthalene, m.p. 75° (3), by oxidn. with dil. HNO₃ see (3); from 7-chloro-1-bromonaphthalene [Beil. V-548] via conv. to RMgBr and carbonation see (3).]

Č with PCl₅ or SOCl₂ yields (1) 7-chloro-1-naphthoyl chloride, yel. cryst. from pet. eth., m.p. 106° cor. (1).

- Methyl 7-chloro-1-naphthoate: cryst. from 60% McOH, m.p. 54° cor. (1). [From C in MeOH with conc. H₂SO₄ (90% yield (1)).]
- Ethyl 7-chloro-1-naphthoate: unreported.
- D p-Bromophenacyl 7-chloro-1-naphthoate: m.p. 145-146° (3).
- ① 7-Chloro-1-naphthoamide: colorless ndls. from 50% alc., m.p. 237° cor. (1). [From the acid chloride (above) with 4 pts. conc. aq. NH₄OH at ord. temp. for 2 hrs. (75% yield (1)).]
- **T-Chloro-1-naphthoanilide:** brownish ndls. from dil. alc., m.p. 185° cor. (1). [From the acid chloride (above) with 5 pts. aniline at 100° (80% yield (1)).]

3:4942 (1) Goldstein, Fischer, Helv Chim. Acta 21, 1519-1521 (1938). (2) Harrison, Royle, J. Chem. Soc. 1926, 87. (3) Horn, Warren, J. Chem. Soc. 1946, 144.

3:4944 5-CHLORONAPHTHOIC ACID-1

Ndls. which sublime even below m.p. — Eas. sol. alc., spar. sol. C6H6 or AcOH.

[For prepn. of \bar{C} from α -naphthoic acid (1:0785) with Cl_2 in AcOH contg. I_2 (some of the isomeric 8-chloronaphthoic acid-1 (3:4680) also being formed) see (1); from 5-chloronaphthonitrile (see below) on hydrolysis with fumg. HCl in s.t. see (1); from 5-aminonaphthoic acid-1 [Beil. XIV-533] via diazotization and use of Cu_2Cl_2 reactn. see (1); for

formn. (together with other prods.) from α -naphthoic acid (1:0785) via reactn. with $Hg(OAc)_2$ followed by treat. with Cl_2 in AcOH see (3).]

488

Salts. CaĀ2.2H2O; sol. in 116 pts. aq. at ord. temp. (1).

 \bar{C} on soln. in red. fumg. HNO₃ gives (2) on cooling 5-chloro-8-nitronaphthoic acid-1 [Beil. IX-654], ndls. from alc., m.p. 224-225° dec. (2) (ethyl ester, m.p. 121° (2)); if the soln. of \bar{C} in red fumg. HNO₃ be heated there is also formed (2) some 4-chloro-1,8-dinitronaphthalene [Beil. V-561], pale yel. ndls. from AcOH, m.p. 180° (3), 175° (2).

- ---- Methyl 5-chloro-1-naphthoate: unreported.
- Bthyl 5-chloro-1-naphthoate: tbls. from alc., m.p. 42° (1). [From AgA with EtI in s.t. at 100° (1).]
- ---- 5-Chloro-1-naphthonitrile: ndls. from alc., m.p. 145° (1). [From α-naphthonitrile [Beil. IX-649, IX₁-(275)] with Cl₂ in CS₂ contg. I₂ (1).]
- ---- 5-Chloro-1-naphthoamide: lfts. or ndls. from warm alc., m.p. 239° (1). [From 5-chloro-1-naphthonitrile (above) on boilg. with alc. KOH for several hrs. (1).]

3:4944 (1) Ekstrand, J, prakt. Chem. (2) 38, 147-150 (1888). (2) Ref 1, pp 170-171. (3) Atterburg, Ber. 9, 928 (1876). (3) Whitmore, Fox, J. Am. Chem. Soc. 51, 3366-3367 (1929).

3:4946 TETRACHLOROPHTHALIC ACID Cl C₈H₂O₄Cl₄ Beil. IX - 819 Cl COOH COOH

M.P. See text.

[See also tetrachlorophthalic anhydride (3:4947).]

Colorless lfts., tbls., or ndls. from aq. invariably contg. $\frac{1}{2}$ H₂O, and therefore giving in this form Neut. Eq. = 156.5. — This hemihydrate can be recrystd. from anhyd. ether without change. — From anhyd. acetone the acid separates in cryst. contg. combined solv. lost in stream of dry air at room temp., yielding anhyd. \bar{C} , Neut. Eq. 152, which absorbs aq. from air giving hemihydrate. — \bar{C} on htg. at 98° or above, or on attempts to recryst. from dry C₈H₈, CHCl₃, or higher-boilg. solvents, or on long drying over P₂O₅ in vac., is converted to tetrachlorophthalic anhydride (3:4947), for this reason the m.p. observed for \bar{C} is always actually that of the corresponding anhydride. — For purification of comml. \bar{C} see (1) (13).

 $\ddot{\mathbf{C}}$ is spar. sol. aq., e.g., 100 g. aq. at 14° dis. 0.57 g., at 99° 3.03 g. of hemihydrate (2); $\ddot{\mathbf{C}}$ is eas. sol. alc. or ether (2); extremely sol. in acetone (1); spar. sol. C_6H_6 or $CHCl_3$ (2). — $\ddot{\mathbf{C}}$ is sol. in hot aq. Na_2CO_3 soln. (dif. from tetrachlorophthalic anhydride (3:4947)).

[For prepn. of Ĉ via hydrolysis of tetrachlorophthalic anhydride (3:4947) see that epd.; other methods include the following: from phthalic anhydride (1:0725) (3), from phthalyl dichloride (3:6900) (4), or phthalic acid (1:0820) (5) with Cl₂ in pres. of Fe or FeCl₃ see indic. refs.; from 2-(trichloroacetyl)-3,4,5,6-tetrachlorobenzoic acid [Beil. X-693], with dil. aq. NaOH see (6); from 2-(pentachlorobenzoyl)-3,4,5,6-tetrachlorobenzoic acid [Beil. X₁-358], with conc. H₂SO₄ at 200-250° (pentachlorobenzene (3:2290) is also formed) see (7); from naphthoquinone-1,2 (1:9062), anthraquinone (1:9095), 1,2,3,4,5,6,7-heptachloroanthraquinone [Beil. VII₁-(414)], or 2-(pentachlorobenzoyl)-3,4,5,6-tetrachlorobenzoic acid (see above) on boilg. with excess SbCl₅ + a little I₂ see (7) (8); from 1,2,3,4,5-pentachloronaphthalene [Beil. V-546] (9) (10), 1,2,3,4,5,6,8-heptachloronaphthalene [Beil. V-547] (11), or octachloronaphthalene (3:4893) (12) by oxidn. with HNO₃ in s.t. as directed

see indic. refs.; from 2,5,6,7,8-pentachloronaphthoquinone-1,4 [Beil. VII-731] by oxidn. with CrO₃ or HNO₃ see (11).]

[Č with Na/Hg in dil. aq. alc. (10) (2) yields phthalic acid (1:0825), but Č in 96% alc. with Na/Hg is practically unaffected (1) (2). — Č with H₂ in pres. of finely divided Ni at 190° and 20 atm. press. yields (14) 4,5,6,7-tetrachlorophthalide [Beil. XVII-312], m.p. 208.5° cor. — Č with HI + P in s.t. at 230° for 6 hrs. yields (2) 4,5,6,7-tetrachlorophthalane [Beil. XVII-51], ndls. from toluene, m.p. 218° (2) (insol. in boilg. aq. NaOH), accompanied by a little 4,5,6,7-tetrachlorophthalide (above) (sol. in boilg. aq. NaOH).]

 \bar{C} with CrO₃ oxidizes much more slowly (2) than phthalic acid (1:0825) and is very resistant toward HNO₃ (2); for detn. of chlorine in \bar{C} see (1) (16).

[\bar{C} with aq. KOH + KCN + CuCN htd. under press. at 180° for 8–10 hrs. gives (60% yield (15)) benzenehexacarboxylic acid (mellitic acid) [Beil. IX-1008, IX₁-(443)]. — \bar{C} with HBr + H₃PO₄ in nitrobenzene in pres. of CuCl₂ yields (17) mixts. of bromotrichlorophthalic acids and dibromodichlorophthalic acids. — For actn. of PCl₅ see under tetrachlorophthalic anhydride (3:4947). — \bar{C} with hydrazine hydrate at 150° gives only (18) N-aminotetrachlorophthalimide, colorless ndls. from AcOH, m.p. 288° dec. (18); earlier opinions (19) (20) that this prod. was tetrachlorophthalcyclohydrazide have been shown (18) to be erroneous. — \bar{C} with steam passed over cat. at 380–420° loses CO₂ presumably yielding (21) 2,3,4,5-tetrachlorobenzoic acid [Beil. IX-346], m.p. 186°.]

[For use of \bar{C} as softener for animal fibers see (22) (23). — For use of \bar{C} in prepn. of α -borneol (1:5990) from turpentine oil (crude pinene) by htg. at 108° for 12 hrs., removal of unchanged terpenes by distn. and alc. NaOH saponification of the remaining di-bornyl tetrachlorophthalate, white cryst. from ether, m.p. 128-129° (24), see (24) (25).]

Salts. K₂Ā, very sol. aq., spar. sol. alc. (2), BaĀ.2½H₂O see (2); CaĀ, on htg. gives octachloroanthraquinone [Beil. VII-789] (17); CuĀ.2H₂O, spar. sol. aq. (2) (earlier report (27) that on dry distn. it gives dodecachlorofi orane later seriously questioned (28)); ZnĀ, very sol. aq. (more sol. cold aq. than hot aq.) (2); Ag₂Ā, spar. sol. aq.

- Dimethyl tetrachlorophthalate: cryst. from MeOH, m.p. 92° (2). [From Ag₂Ā with MeI (2), from sym.-tetrachlorophthalyl (di)chloride with NaOMe (2) or from C in 10% aq. NaOH (3 moles) on warming with Me₂SO₄ (29); note that C in MeOH satd. with HCl gas gives (30) only the half ester, methyl hydrogen tetrachlorophthalate, cryst. from C₆H₆ on addn. of lgr., m.p. 142° (30) with elimination of MeOH and conversion to tetrachlorophthalic anhydride (3·4947) q.v.]
- ① Diethyl tetrachlorophthalate: cryst., m.p. 60-60.5° (2) (31). [From Ag₂Ā + EtI (2) or from sym.-tetrachlorophthalyl (di)chloride + NaOEt (2); note that unsym.-tetrachlorophthalyl (di)chloride with abs. alc. at room temp. gives (31) pseudo-diethyl tetrachlorophthalate, tbls. from alc., m.p. 126° (19), and that this cpd. on stdg. in the reactn. mixt. is partially conv. to the normal ester of m.p. 60.5° (31).]
- **Di-(p-nitrobenzyl)** tetrachlorophthalate: ndls. from C_6H_6 , or from aq. alc., m.p. $180-181^\circ$ (32), $179-180^\circ$ (33). [From Na₂ $\bar{\Lambda}$ + p-nitrobenzyl bromide on refluxing in alc. (32), or from Ag₂ $\bar{\Lambda}$ + p-nitrobenzyl iodide (33).]
- Di-(p-phenylphenacyl) tetrachlorophthalate: cryst. from acetone, m.p. 193° (34). [From Na₂Ā with p-phenylphenacyl bromide (2 moles) on htg. in alc. (34).]

3:4946 (1) Delbridge, Am. Chem. J. 41, 393-415 (1909). (2) Graebe, Ann. 238, 318-332 (1887). (3) Zal'kind, Belikova, Simonova, Russ. 39,761, Nov. 30, 1934; Cent. 1935, II 3441; C.A. 36, 3443 (1936); Russ. 46,568, April 30, 1936; Cent. 1936, II 2798. (4) Zal'kind, Belikova, Russ. 35,188, March 31, 1934; Cent. 1935, II 1090; C.A. 30, 3443 (1936) Russ. 46,607, April 30, 1936; Cent. 1936, II 2798. (5) Zal'kind, Belikova, J. Applied Chem. (U.S.S.R.) 8, 1210-1213 (1935); Cent. 1936, II 3414; C.A. 30, 5203 (1936). (6) Zincke, Günther, Ann. 272, 266 (1892). (7) Eckert, Steiner, Monatsh. 36, 179-185 (1915); Ber. 47, 2628-2630 (1914). (8) Steiner, Monatsh.

36, 827 (1915). (9) Graebe, Ann. **149**, 18-20 (1869). (10) Claus, Spruck, Ber. **15**, 1402-1403 (1882).

(11) Claus, Wenzlik. Ber. 19, 1166-1167 (1886). (12) Shvemberger, Gordon, J. Gen. Chem. (U.S.S.R.) 2, 921-928 (1932), Cent. 1934, I 215; C.A. 27, 2439 (1933); J. Gen. Chem. (U.S.S.R.) 4, 695-703 (1934); Cent. 1935, II 514; C.A. 29, 2162 (1935). (13) Pratt. Perkins, J. Am. Chem. Soc. 40, 203-204 (1918). (14) M.L.B., Ger. 368,414, Feb 5, 1923, Cent. 1923, II 911. (15) Feist, Ber. 68, 1941-1943 (1935). (16) Heslinga, Rec. trav. chim. 43, 182 (1924). (17) Bruck (to I.G.), Ger. 597,259, May 25, 1934; Cent. 1934, 1688. (18) Drew, Pearman, J. Chem. Soc. 1937, 27, 32-33. (19) Phelps, Am. Chem. J. 33, 586 (1905). (20) Radulescu, Alexa, Bul. Soc. Chim. România 12, 163 (1930); C.A. 25, 4001 (1931).

(21) Jaeger (to Sciden Co.), U.S. 1,964,516, June 26, 1934; Cent. 1934, II 3047. (22) Schwen, Krzikalla (to I.G.), U.S. 1,887,958, Nov. 15, 1932; French 704,423, May 20, 1931; Cent. 1931, II 3286. (23) Dreyfus, French 749,792, July 29, 1933; Cent 1934, I 3154. (24) Haller, Compt. rend. 178, 1933-1937 (1924), Cent 1924, II 642. (25) Haller, U.S. 1,415,340, May 9, 1922; Cent. 1923, IV 946, C.A. 16, 2335 (1922); Brit. 158,533, March 3, 1921; Cent. 1921, IV 422. (26) Kircher, Ber. 17, 1170 (1884). (27) Ekely, Mattison, J. Am. Chem. Soc. 52, 3003-3004 (1930). (28) Ekely, J. Am. Chem. Soc. 54, 406 (1932). (29) Graebe, Ann. 240, 247 (1905). (30) Meyer, Sudborough, Ber. 27, 3148 3149 (1894).

(31) Kirpal, Junze, Ber. 62, 2105 (1929). (32) Lyons, Reid, J. Am. Chem. Soc. 39, 1741, 1744 (1917). (33) Meyer, Jugilewitsch, Ber. 30, 785-786 (1897). (34) Drake, Sweeney, J. Am. Chem. Soc. 54, 2059-2061 (1932).

3:4947 TETRACHLOROPHTHALIC ANHYDRIDE $C_8O_3Cl_4$ Beil. XVII - 484 O XVIII - (254)

[See also tetrachlorophthalic acid (3:4946).]

Colorless pr. or ndls. by sublimation. — Insol. cold aq., but sol. in boilg. aq. because of hydrolysis to tetrachlorophthalic acid (3:4946); spar. sol. ether. — Č is insol. in Na₂CO₃ soln. (dif. from tetrachlorophthalic acid (3:4946)).

[For prepn. of \bar{C} from tetrachlorophthalic acid (3:4946) by htg. above m.p. (6), by htg. 8 hrs. at 110° (7), by htg. 120 hrs. at 100° (8) (9), by sublimation, htg. at 98°, by crystn. from hot C_6H_6 , CHCl₃, AcOH (2), or by protracted drying over P_2O_5 in vac. (1) cf. (5) (10) see indic. refs.; from phthalic anhydride (1:0725) with Cl_2 in pres. of Fe salts at 160–260° (11), or with Cl_2 in pres. of SbCl₅ at 200° (10) (12), or with Cl_2 in pres. of fumg. H_2SO_4 (50–60% SO_3) and I_2 (2) (13) see indic. refs.; from naphthalene (1:7200) with $ClSO_3H$ in s.t. at 180° see (3).]

[\tilde{C} on reduction with Zn dust + hot AcOH (10) or with H_2 + Ni at 190° and 20 atm. yields (14) 4,5,6,7-tetrachlorophthalide [Beil. XVII-312], m.p. 208.5° cor.]

Č reacts with monohydric alcs. to yield corresp. half esters: e.g., Č dislvd. in excess warm MeOH, htd. 5–10 min., evapd. yields (15) methyl hydrogen tetrachlorophthalate [Beil. IX-820], cryst. from hot C₆H₆ on addn. of lgr., m.p. 139–140° (15), 142° (16), Neut. Eq. 318; Č with abs. EtOH treated as for preceding case gives (15) ethyl hydrogen tetrachlorophthalate, m.p. 93–94° (15), 94–95° (10), Neut. Eq. 332. — [Č with ter-butyloxymagnesium

bromide in ether + dioxane at 50-55° for 1 hr. gives (54% yield (17)) ter-butyl hydrogen tetrachlorophthalate, decomposing at 142°, Neut. Eq. 360; for analogous formn. of teramyl, triethylcarbinyl, tri-n-propylcarbinyl, tri-n-butylcarbinyl and tri-n-amylcarbinyl hydrogen tetrachlorophthalates see (17).] -- [For reactn. of \bar{C} with glycerol and use in prepn. of resuns of glyptal type see (3) (18).]

[\bar{C} with 1 mole PCl₅ in s.t. 4 hrs. at 220° (19) cf. (10) or \bar{C} with 1 mole PCl₅ + POCl₃ refluxed 72 hrs. (20) gives (90% yield (20)) unsym.-tetrachlorophthalyl (di)chloride (3,3,4,5,6,7-hexachlorophthalide) [Beil. XVII₁-(484)], cryst. from C₆H₆ with 1 mole solvent, m.p. 118° (10) (20), 118–120° (19), but losing C₆H₆ in air to give solvent free epd., ndls. from pet. ether, m.p. 137° (19) (20); this prod. on distn. (19) undergoes partial rearr. to sym.-tetrachlorophthalyl (di)chloride, pr. from pet. ether, m.p. 48° (19). — Note that the latter sym.-phthalyl (di)chloride (which is very soluble in most org. solvents) gradually changes even in solid form and very rapidly in solution (particularly in pres. of animal charcoal) to the unsym.-tetrachlorophthalyl (di)chloride (which is spar. sol. in most org. solvents) (19). — \bar{C} with SOCl₂ + ZnCl₂ at 200–240° yields (21) cf. (22) tetrachlorophthalyl (di)chloride but whether the unsym. or sym. forms or their mixture is not stated. — Note also that with abs. EtOH the unsym. acid chloride yields (19) pseudo diethyl tetrachlorophthalate, tbls. from alc., m.p. 126° (19), while the sym. acid chloride gives (19) sym. diethyl tetrachlorophthalate, m.p. 60.5° (19).]

[C with 2 moles PCl₅ in s.t. at 200° for 5-6 hrs. yields (10) a prod. (regarded as either 1,1,3,3,4,5,6,7-octachlorophthalide or 2-(trichloromethyl)-3,4,5,6-tetrachlorobenzoyl chloride), cryst. from ether, m.p. 140° (10), and practically unaffected by warm alc. KOH.]

[\bar{C} with arom. hydrocarbons + AlCl₃ yields corresp. o-aroyl-tetrachlorobenzoic acids: e.g., \bar{C} with C_6H_6 + AlCl₃ (23) (24) (25) or \bar{C} with C_6H_5MgBr (26) gives 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid [Bell. X-750], ndls. from 80% AcOH or C_6H_6 , m.p. 201° (24), 200° (23), 188–189° (26), which on ring closure with 20 pts. conc. H_2SO_4 at 200° for 5 min. (23) gives 1,2,3,4-tetrachloroanthraquinone [Bell. VII-789], gold-yel. lfts., m.p. 191° (23). — \bar{C} with toluene + AlCl₃ gives (yields: 100% (27), 95% (28), 94% (29)) 2-(p-toluyl)-3,4,5,6-tetrachlorobenzoic acid, cryst. from C_6H_6 , m.p. 174.5° cor. (29), 172° (28) (30) (the value of 142° (27) may be a misprint for 172°), which on ring closure with 12 pts. $H_2SO_4.H_2O$ at 190–200° for 2 min. (27) or with 9 pts. fumg. H_2SO_4 (2% SO_3) at 120–130° for 30 min. (28) gives (21% yield (28)) 2-methyl-5,6,7,8-tetrachloroanthraquinone, yel. ndls. from toluene, m.p. 195–196° (27), or from EtOAc, m.p. 192° (28). — For corresp. reactns. of \bar{C} with o-xylene (1:7430), m-xylene (1:7420), p-xylene (1:7415), and ethylbenzene (1:7410) and use in identif. of these cpds. see (7). — For reactn. of \bar{C} with α -naphthyl MgBr, γ -methoxyphenyl MgBr, or γ -bromphenyl MgBr yielding corresp. o-aroyl-tetrachlorobenzoic acids see (26).]

[\bar{C} with chlorobenzene (3:7903) + AlCl₃ at 140° for 3 hrs. gives (92% yield (31)) 2-(p-chlorobenzoyl)-3,4,5,6-tetrachlorobenzoic acid, cryst. from AcOH, m.p. 162-165° (31), which with conc. H₂SO₄ at 140° for 30 min. gives 2,5,6,7,8-pentachloroanthraquinone, yel. cryst. from AcOH, m.p. 192° (31). — For corresp. reactns. of \bar{C} with p-dichlorobenzene (3:0980), with 1,2,4-trichlorobenzene (3:6420), or with nitrobenzene see (31).]

[C with phenols and appropriate condensing agents gives two different types of reactns. according to circumstances, viz., formation of corresp. o-hydroxyaroyltetrachlorobenzoic acids (cf. above) or of corresp. tetrachlorophthaleins. — E.g., C with 1 mole phenol + AlCl₃ in acetylene tetrachloride at 125° for 3 hrs. gives (yields: 79% (32), 82% (33)) 2-(o-hydroxybenzoyl)-3,4,5,6-tetrachlorobenzoic acid [Beil. X₁-(470)], lfts. from xylene/AcOH, m.p. 216-218° cor. (32), 210° (33), which with boilg. NaOH loses HCl and ring-closes to 2,3,4-trichloroxanthonecarboxylic acid-1 [Beil. XVIII₁-(499)], colorless ndls. from alc., m.p. 261-264° cor. (32), 262-265° dec. (33). — For corresp. reactns. of C with

o-cresol (1:1400) (32) (34), m-crosol (1:1730) (32), p-cresol (1:1410) (32), α-naphthol (1:1500) (38), β-naphthol (1:1540) (32), anisole (1:7445) (34) see indic. refs., with hydroquinone (1:1590) + AlCl₃ + NaCl at 150-155° for $1\frac{1}{2}$ hrs. giving 82% yield 2-(2',5'-dihydroxybenzoyl)-3,4,5,6-tetrachlorobenzoic acid, m.p. 231°, or on further htg. in the above melt at 210-215° for 1 hr. ring closing to 1,4-dihydroxy-5,6,7,8-tetrachloroanthraquinone, red cryst. from xylene, m.p. 247°, see (35). — However, \bar{C} with 2 moles phenol in pres. of fumg. H₂SO₄ (20% SO₃) as directed (8) (36) gives 65% yield phenoltetrachlorophthalein [Beil. XVIII-148, XVIII₁-(375)], m., 316-317° dec. (36), accompanied by about 10% (37) of 3',4',5',6'-tetrachlorofluoran [Beil. XIX-148, XIX₁-(676)], colorless pr. from C_6H_6 , m.p. 298° dec. (33), 290-291° (37) (for sepn. of this by-prod. from the phenoltetrachlorophthalein see (37)). — For condens. of \bar{C} with σ -cresol (1:1400) to σ -cresoltetrachlorophthalein see (45); with resorcinol (1:1530) to 3',4',5',6'-tetrachlorofluorescein [Beil. XIX-227, XIX₁-(722)] see (10) (9).]

[For condens. of \bar{C} with *m*-diethylaminophenols see (39); with *N*-aryl-*m*-aminophenols in prepn. of phthalein dyes see (40); for condens. of \bar{C} with hydroxyisodibenzanthrone in prepn. of vat dyes see (41); for use of \bar{C} as textile softener see (42).]

[C with steam passed over cat. at 380-420° loses CO₂ presumably yielding (43) 2,3,4,5-tetrachlorobenzoic acid [Beil. IX-346], m.p. 186°.]

 \bar{C} on fusion and treatment with NH₃ gas (10) (4), or on warming with formamide (2), or on fusion with (NH₄)₂CO₃ (47) gives (yields: 91% (2), 90% (47)) tetrachlorophthalimide [Beil. XXI-505, XXI₁-(391)], lfts. from AcOH, dimethylaniline or nitrobenzene, m.p. 338-339° cor. (2), 336-337° (47); for reactn. of this prod. with KOMe forming K tetrachlorophthalimide and use of latter in identification of alkyl halides, etc., see (47). — [For reactn. of \bar{C} with hydrazine hydrate in dil. alc. yielding N-aminotetrachlorophthalimide, ndls. from AcOH, m.p. 288° dec., see (48); for reactn. of \bar{C} with hydroxylamine in aq. and in MeOH see (49). — \bar{C} in boilg. AcOH treated with aniline yields (2) cf. (50) N-phenyltetrachlorophthalimide (tetrachlorophthalanil) [Beil. XXI-505, XXI₁-(391)], m.p. 274–275° cor. (2). — For reactn. of \bar{C} with o-phenylenediamine see (6).]

 \bar{C} on warming with aq., or with aq. alk. followed by acidification, yields tetrachlorophthalic acid (3:4946) q.v. [For use of differential hydrolysis of \bar{C} in sepn. from 3,4-dichlorophthalic anhydride (3:3695), 3,6-dichlorophthalic anhydride (3:4860), or 4,5-dichlorophthalic anhydride (3:4830) see under these cpds.]

3:4947 (1) Delbridge, Am. Chem. J. 41, 400, 402, 406, 408-409, 415-416 (1909). (2) Pratt, Perkins, J. Am. Chem. Soc. 40, 204-214 (1918). (3) Walter, Monatsh. 64, 287-288 (1934). (4) Pfeiffer, Ber. 55, 421-425 (1922). (5) Graebe, Ann. 149, 18-20 (1869). (6) Bistryzycki, Lecco, Helv. Chim. Acta 4, 430-431 (1921). (7) Underwood, Walsh, J. Am. Chem. Soc. 57, 941 (1935). (8) Orndorff, Black, Am. Chem. J. 41, 359-393 (1909). (9) Orndorff, Adamson, J. Am. Chem. Soc. 40, 1239-1257 (1918). (10) Graebe, Ann. 238, 318-338 (1887).

(11) Dvornikoff (to Monsanto Chem. Co.), U.S. 2,028,383, Jan. 21, 1936; Cent. 1936, I 2830; C.A. 30, 1394 (1936). (12) Gnehm (to Soc. Chem. Ind. Basel), Ger. 32,564, Feb. 1, 1885; Fried-lander, 1, 318. (13) Juvalta, Ger. 50,177, Friedlander 2, 93. (14) M.L.B., Ger. 368,414, Feb. 5, 1923; Cent. 1923, II 911. (15) Ashdown, Monier, Ph.D. Thesis, M.I.T. (16) Meyer, Sudborough, Ber. 27, 3149 (1894). (17) Fessler, Shriner, J. Am. Chem. Soc. 58, 1384-1386 (1936). (18) Kogan, Ponomarenko, Org. Chem. Ind. (U.S.S.R.) 7, 382-385 (1940); C.A. 35, 4118 (1941). (19) Kirpal, Kunze, Ber. 62, 2102-2106 (1929). (20) Kaufmann, Voss, Ber. 56, 2511-2512 (1923).

(21) Kyrides (to Monsanto Chem. Co.), U.S. 1,951,364, March 20, 1934; Cent. 1934, II 333.
(22) Kyrides, J. Am. Chem. Soc. 59, 206-208 (1937). (23) Kircher, Ann. 238, 338-346 (1887).
(24) Meyer, Monatsh. 25, 1189-1191 (1904). (25) Müller (to I.G.), Ger. 495,447, April 7, 1930; Cent. 1931, I 1675. (26) C. Weizmann, E. Bergmann, F. Bergmann, J. Chem. Soc. 1935, 1367-1369. (27) Eckert, Endler, J. prakt. Chem. (2) 102, 335-336 (1921). (28) Ruggli, Brunner, Helv. Chim. Acta 8, 160-161 (1925). (29) Lawrance, J. Am. Chem. Soc. 43, 2580 (1921). (30) M.L.B., French 520,542, June 27, 1921; Cent. 1921, IV 804: Brit. 160,433, April 14, 1921; Cent.

1921, IV 127: Swiss 89,059, Aug. 1, 1921; Cent. 1922, II 145: Ger. 360,422, Oct. 2, 1922; Cent. 1923, II 190.

Hofmann, Monatsh. 36, 812-818 (1915). (32) Ullmann, Schmidt, Ber. 52, 2113-2118 (1919). (33) Orndorff, Parsons, J. Am. Chem. Soc. 48, 283-285 (1926). (34) Orndorff, Murray, J. Am. Chem. Soc. 39, 686-689 (1917). (35) Waldmann, J. prakt. Chem. (2) 147, 333 (1936/1937). (36) Orndorff, Kennedy, J. Am. Chem. Soc. 38, 2487 (1916). (37) Orndorff, Kennedy, J. Am. Chem. Soc. 38, 2487 (1916). (37) Orndorff, Kennedy, J. Am. Chem. Soc. 38, 286 (1909). (39) Orndorff, Rose, J. Am. Chem. Soc. 38, 2101-2119 (1916). (40) Durand, Huguenin, Brit. 251,644, July 7, 1926; Cent. 1927, I 1228.

(41) Imperial Chem. Ind., Ltd. & Shaw & Thomson, Brit. 383,624, Dec. 15, 1932; Cent. 1933, 1 1358. (42) Dreyfus, French 749,792, July 29, 1933; Cent. 1934, I 3154. (43) Jaeger (to Selden Col.), U.S. 1,964,516, June 26, 1934, Cent. 1934, II 3047. (44) Orndorff, Schade, J. Am. Chem. Soc. 48, 769-773 (1926). (45) Orndorff, Patel, J. Am. Chem. Soc. 47, 863-867 (1925). (46) Orndorff, Hitch, J. Am. Chem. Soc. 36, 680-725 (1914). (47) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934). (48) Drew, Pearman, J. Chem. Soc. 1937, 32-33. (49) Orndorff, Nichols, Am. Chem. J. 48, 491-499 (1912). (50) Tingle, Bates, J. Am. Chem. Soc. 32, 1325-1327 (1910).

3:4948 8-CHLORONAPHTHOIC ACID-2

C₁₁H₇O₂Cl

Beil. IX - 662 IX₁—

M.P. 260° (1)

Fine ndls. best purified by sublimation (1).

[For prepn. of \bar{C} from 8-aminonaphthoic acid-2 [Beil. XIV-536] via diazotization and use of Cu_2Cl_2 reactn. see (1).]

Salts. (1). CaĀ₂.7H₂O; BaĀ₂.6H₂O; both spar. sol. cold aq. but eas. sol. hot aq.

Č with Cl₂ in AcOH contg. I₂ yields (1) 5,8-dichloronaphthoic acid-2 [Beil. IX-662], ndls. from alc., m.p. 287° (1) (ethyl ester, m.p. 64-65° (1)).

- Methyl 8-chloro-2-naphthoate: unreported.
- Ethyl 8-chloro-2-naphthoate: lfts. from alc., m.p. about 29° (1). [From C in EtOH with dry HCl gas (1).]

3:4948 (1) Ekstrand, J. prakt. Chem. (2) 43, 417-418, 421 (1891).

3:4950 3,5-DICHLORO-4-HYDROXYBENZOIC C₇H₄O₃Cl₂ Beil. X - 176 X₁-(78)

White ndls. from dil. alc. or dil. AcOH; spar. sol. cold but more sol. hot aq.; eas. sol. alc., ether; sublimes at 250-260° (7) without appreciable decompn. (6).

[For prepn. of \bar{C} from p-hydroxybenzoic acid (1:0840) in 10% AcOH (4) or in aq. KOH (3 moles) (7) with Cl₂, or on htg. with SbCl₅ (4 moles) (6) or with 30% H₂O₂ + HCl as directed (80% yield (8)) see indic. refs.; from 3-sulfo-4-hydroxybenzoic acid in aq. with

Cl₂ see (9); from potassium 2,6-dichlorophenolate with CO₂ at 140° see (7); from ethyl 3,5-dichloro-4-hydroxybenzoate (see below) by hydrolysis with 35% aq. KOH (5) or with Claisen's alk. (95% yield (1)) see indic. refs.; from 3,5-dichloro-4-methoxybenzoic acid with 45% HI for 15 hrs. in s.t. at 130-140° see (3) (2).]

C on htg. with CaO (4) (7), or with dimethylaniline at 190° (78% yield (1)), or with quinoline at 190-200° (80-85% yield (10)) loses CO₂ giving 2,6-dichlorophenol (3:1595).

C in conc. aq. soln. gives with FeCl₃ a brown ppt. (4).

[\bar{C} on electrolytic reduction in aq./alc./ H_2SO_4 gives (11) 3,5-dichloro-4-hydroxybenzyl ethyl ether [Beil. VI-898], m.p. 86° (11); for prepn. and study of thermal rearr. of the crotyl ether of \bar{C} see (1).]

- Methyl 3,5-dichloro-4-hydroxybenzoate: ndls. from dil. alc. or lgr., m.p. 124° (3), 122° (12), 121-122° (4) (5). [From C in MeOH by satn. with HCl gas (3) (4); also from methyl p-hydroxybenzoate (1:1549) with SO₂Cl₂ (2 moles) (5).] [This prod. with acetyl chloride yields (5) corresp. acetate, lfts. from MeOH, m.p. 70-71° (5), 68-69° (4).]
- ⊕ Ethyl 3,5-dichloro-4-hydroxybenzoate: ndls. of monohydrate, m.p. 108-116° cor.

 ⟨1), 116° ⟨5⟩ from 80% alc.; after long drying in vac. over P₂O₅ lose aq. yielding anhydrous ester, m.p. 111-112° cor. ⟨1⟩; note that this ester is extracted from ether soln. by aq. NaHCO₃ and is also titratable with stand. alk. (Neut. Eq. of monohydrate 253). [From ethyl p-hydroxybenzoate (1:1534) with excess SO₂Cl₂ ⟨5⟩ in 85% yield ⟨1⟩.]

3:4950 (1) Tarbell, Wilson, J. Am. Chem. Soc. 64, 1066-1070 (1942). (2) Durrans, J. Chem. Soc. 123, 1426 (1923). (3) Bertozzi, Gazz. chim. ital. 29, II 39 (1899). (4) Zincke, Ann. 261, 250-252 (1891) (5) Mazzara, Gazz. chim. ital. 29, I 387-388 (1899) (6) Lossner, J. prakt. Chem. (2) 13, 434 (1876). (7) Tarugi, Gazz. chim. ital. 30, II 490-491 (1900). (8) Leulier, Pinet. Bull. soc. chim (4) 41, 1365-1366 (1927). (9) Datta, Mitter, J. Am. Chem. Soc. 41, 2038 (1919) (10) Blicke, Smith, Powers, J. Am. Chem. Soc. 54, 1468 (1932).

(11) Mettler, Ber. 39, 2940 (1906). (12) von Auwers, Reis, Ber. 29, 2359 (1896).

M.P. 270° cor. (1) 263° (2)

Ndls. from alc. or AcOH. — Sol. in hot alc., in C_6H_6 or AcOH. — Sublimes in ndls. even below m.p.

[For prepn. of C from 5-amino-2-naphthoic acid [Beil. XIV-536] via diazotization and use of Cu₂Cl₂ reactn. see (2), from 5-chloro-2-naphthonitrile (below) by hydrolysis in AcOH/H₂SO₄/aq. medium (alm. 100% yield (1)) or with alc. KOH (2) see indic. refs.]

 \bar{C} with PCl₅ yields (1) 5-chloro-2-naphthoyl chloride, m.p. 89° cor., sol. in pet. eth. or C_6H_6 , but only very slowly hydrolyzed by aq. even on htg. (1).

 $\bar{\mathbf{C}}$ on mononitration by soln. in excess conc. HNO₃ (D=1.42) yields (2) on cooling 5-chloro-x-nitronaphthoic acid-2, ndls. from AcOH, m.p. 271° (ethyl ester, m.p. 118°); $\bar{\mathbf{C}}$ on dinitration with red fumg. HNO₃ + a little conc. H₂SO₄ yields (1) 5-chloro-x,y-dinitronaphthoic acid-2, ndls. from AcOH, m.p. about 243° (ethyl ester, m.p. 132°); $\bar{\mathbf{C}}$ on trinitration by conversion to mononitro- $\bar{\mathbf{C}}$ (above) and treatment with excess fumg. HNO₃ + conc. H₂SO₄ yields (1) 5-chloro-x,y,z-trinitronaphthoic acid-2, yel. cryst. from AcOH, m.p. 260-261° dec. (ethyl ester, m.p. 188°).

Salts (2). Na \overline{A} .2H₂O sol. aq.; Ca \overline{A} 2.3½H₂O, sol. in 4430 pts. cold aq.; Ba \overline{A} 2.4½H₂O, very spar. sol. cold aq.

- **D** Methyl 5-chloro-2-naphthoate: m.p. 81° cor. (1). [From $\bar{\mathbf{C}}$ in MeOH with conc. H_2SO_4 (90% yield (1)).]
- D Ethyl 5-chloro-2-naphthoate: ndls. from alc., m.p. 45° (2).

- © 5-Chloro-2-naphthoanilide: m.p 202.5° cor (1). [From the acid chloride (above) with 3 pts. aniline at 100° (90% yield (1)).]

3:4952 (1) Goldstein, Matthey, Helv. Chim. Acta 21, 65-66 (1938). (2) Ekstrand, J. prakt. Chem. (2) 43, 411-417 (1891).

3:4960 5-CHLOROISOPHTHALIC ACID COOH $C_8H_5O_4Cl$ Beil. IX - 838 (5-Chlorobenzenedicarboxylic acid-1,3)

M.P. 278° (1)

 \bar{C} cyrst. from aq. in ndls. which even after drying over conc. H_2SO_4 cont. $\frac{1}{2}$ mole H_2O ; this water is lost, however, on htg. at 120° (1). — \bar{C} is sol. at 15° in 3450 pts. aq. (1).

[For prepn. of \bar{C} from 5-aminobenzenedicarboxylic acid-1,3 (5-aminoisophthalic acid) [Beil. XIV-556, XIV₁-(636)] via diazotization and htg. sepg. diazonium salt with strong HCl see (1), from 5-chloro-3-methylbenzoic acid (3:4715) by oxidn. with KMnO₄ in dil. aq. KOH see (2)]

Salts. Na₂ $\bar{\Lambda}$, $\bar{K}_2\bar{\Lambda}$, eas. sol. aq. or alc.; Ag₂ $\bar{\Lambda}$, ndls. from aq.; Mg $\bar{\Lambda}$, 7H₂O; Ca $\bar{\Lambda}$, 2H₂O, sol. at 15° in 28 pts. aq.; Sr $\bar{\Lambda}$, H₂O, sol at 15° in 108 pts. aq.; Ba $\bar{\Lambda}$, 2H₂O sol. at 15° in 71 pts. aq.; Cd $\bar{\Lambda}$, sol. at 15° in 330 pts. aq. (for details see (1)).

- Dimethyl 5-chloroisophthalate: unrecorded.
- Diethyl 5-chloroisophthalate: pr. from alc., m.p. 45° (1). [From C in EtOH with HCl gas (1).]

3:4960 (1) Beyer, J. prakt. Chem. (2) 25, 506-515 (1882). (2) Klages, Knoevenagel, Ber. 28, 2045-2046 (1895).

M.P. 279-281° (1) 280° u.c. (2)

Colorless ndls. from hot aq. or dil. alc.; eas. sol. alc., ether, CHCl₃; insol. cold aq. [For prepn. of $\bar{\rm C}$ from 4,6-dichloro-1,3-dimethylbenzene [Beil. V-373, V₂-(291)] by

oxidn. with 20 pts. HNO₃ (D=1.18) in s.t. at 220° for several hrs. (2) or with CrO₃/AcOH (2) see indic. refs.; from 1,3-dimethylbenzene-4,6-bis-(sulfonyl chloride) (1) with SOCl₂ in s.t. at 240° for 36 hrs. see (1).]

Ag2A, white ppt. (2), BaA, H2O spar. sol. cold aq. but eas. sol. hot aq. (2).

- ① Dimethyl 4,6-dichloroisophthalate: cryst. from dil. MeOH, m.p. 97-98° (1). [From Č in MeOH on htg. (1).]
- **4,6-Dichloroisophthaldianilide:** m.p. 205° (1). [From \bar{C} on htg. with aniline (1).]

3:4965 (1) Pollak, Rudich, Monatsh. 43, 221 (1922). (2) Claus, Burstert, J. prakt. Chem. (2) 41, 558-560 (1890).

3:4970 2,5-DICHLORO-3,6-DIHYDROXYBENZOQUINONE-1,4
(Chloranilic acid)

OH
O
OH
OH
OH
OH
OH
OH
OH
OH

M.P. 283-284° s.t. (1) 282-284° s.t. (2)

Lustrous red lfts. with $2H_2O$ (3) (4) (lost at 100° or slowly on stdg. over conc. H_2SO_4 (3) (4)). — \tilde{C} on slow heating (even in s.t.) sublimes without melting; in s.t. inserted in bath or block preheated to about 278° , however, melts as stated above (1).

[For prepn. of \bar{C} from chloranil (tetrachlorobenzoquinone-1,4) (3:4978) by actn. of dil. NaOH at 70-80° see (3) (2); for other methods see Beil. VIII-379.]

 \bar{C} is sol. in aq. yielding violet-red solns.; at 13.5 g. 100 pts. aq. dis. 0.19 pt., at 99° 1.4 pt. anhyd. \bar{C} (3); addn. of HCl or H₂SO₄ ppts. \bar{C} decolorizing soln. (5).

Č behaves as strong dibasic ac. forming stable Na, K, Ba, Ag salts. — Na₂Ā.4H₂O, dark red (7) triclinic (8) pr. sepg. on rapid cooling of warm soln. to 18° (6); loses 2H₂O over H₂SO₄ and becomes anhyd. at 110° (7). — Na₂Ā.3H₂O, black cryst. sepg. from soln. above 35° (6). — Na₂Ā; 100 pts. aq. at 21° dis. 1.06 g., at 99° 6.19 g. (3). — Ag₂Ā, red ppt. spar. sol. aq. (8a).

 \tilde{C} htd. in s.t. with conc. H_2SO_3 soln. for some hrs. (9) or treated with Sn + HCl (9) or Na/Hg (9) yields 3,6-dichloro-1,2,4,5-tetrahydroxybenzene (hydrochloranilic acid) [Beil. VI-1156], colorless cryst., no m.p. recorded but with AcCl in s.t. at 100° yielding tetraacetyl deriv., colorless ndls. from alc. or by subl., m.p. 235° (9). [Use of insufficient SO_2 for reduction of \tilde{C} leads to pptn. of corresp. quinhydrone, fine black ndls. (9).] [For studies of oxidn.-reductn. potential of \tilde{C} see (2) (10) (11).]

 $\ddot{\mathbf{C}}$ with alk. + $\mathbf{I_2}$ - KI soln. yields (12) iodoform, m.p. 119°.

- Φ 2,5-Dichloro-3,6-dimethoxybenzoquinone-1,4 (dimethyl chloranilate) [Beil. VIII-380]: from Ag₂Ā + CH₃I (13) or from anhydrous K₂Ā + Me₂SO₄ (14); red pr. from C₆H₆ or CHCl₂, m.p. 141-142° (13) (14).
- **② 2,5-Dichloro-3,6-diacetoxybenzoquinone-1,4** (chloranilic acid diacetate) [Beil. VIII-381]: from finely pdrd. Ag₂Ā + AcCl in dry ether (15); yel. ndls., m.p. 182.5° (15).

3:4976 (1) Michael, Ber. 28, 1631 (1895). (2) Conant, Fieser, J. Am. Chem. Soc. 46, 1866-1867 (1924). (3) Graebe, Ann. 263, 24-27 (1891). (4) Jackson, MacLaurin, Am. Chem. J. 37, 98-100 (1907). (5) Erdmann, J. prakt. Chem. (1) 22, 285 (1841). (6) Valeur, Ann. chim. (7) 21, 510-512 (1900). (7) Hesse, Ann. 114, 304 (1860). (8) Pope, J. Chem. Soc. 61, 583-584 (1892). (8a) Erdmann, Ann. 48, 317 (1843). (9) Graebe, Ann. 146, 32-36 (1868). (10) Conant, Luts, J. Am. Chem. Soc. 46, 1257 (1924).

(11) Schwarzenbach, Suter, Helv. Chim. Acta 24, 626-628 (1941).
(12) Jackson, Torrey, Am. Chem. J. 20, 429-430 (1898).
(13) Kehrmann, J. prakt. Chem. (2) 40, 370 (1888); 43, 260 (1891).
(14) Graebe, Ann. 340, 248-249 (1905).
(15) Nef, Am. Chem. J. 12, 471-472 (1890); J. prakt. Chem. (2) 42, 169-171 (1890).

3:4975 2-CHLOROBENZENETRICAR- COOH $C_9H_5O_6Cl$ Beil. IX - 980 BOXYLIC ACID-1,3,5 Cl IX1— (Chlorotrimesic acid)

M.P. 285° (1) (anhydrous) 278° (2) (hydrate)

Ndls. or tbls. with 1 H₂O from aq. (2); very readily sol. cold aq. (1) (contrast (2)), extremely eas. sol. hot aq. (1) (2); eas. sol. alc., ether (2); insol. CHCl₃ (2). — Sublimes largely undecomposed (2).

[For prepn. of \bar{C} from chloromesitylene (3:8725) by oxidn. with aq. KMnO₄ either with or without MgSO₄ (63.5% yield) see (1); from 2-hydroxybenzenetricarboxylic acid-1,3,5 (hydroxytrimesic acid) [Beil. X-580] with PCl₅ (4 moles) followed by hydrolysis (with warm aq. or aq. alk.) of the intermediate *tris* acid chloride see (2).]

Ba₃ \bar{A}_2 .7H₂O (from \bar{C} + BaCO₃ (2)), fairly eas. sol. cold aq. but spar. sol. in hot aq. (2). [\bar{C} on boilg. with aq. alkali does *not* give chloride ion (2) but \bar{C} with Zn + HCl (or H₂SO₄) or \bar{C} in 10 pts. aq. with 10 pts. 4.5% Na/Hg yields trimesic acid (1:0559) (2).]

3:4975 (1) Davies, Wood, J. Chem. Soc. 1928, 1126-1127. (2) Ost, J. prakt. Chem. (2) 15, 308-314 (1877).

3:4978 2,3,5,6-TETRACHLOROBENZO-QUINONE-1,4

(Tetrachloro-p-benzoquinone; chloranil)

Cl Cl Cl Beil. VII - **636** VII₁-(**347**)

[See also tetrachlorohydroquinone (3:4941).]

Golden-yellow cryst. from AcOH, acetone, C₆H₆, toluene, or by sublimation. — For crystallographic data see (13) (14) (15).

C on careful htg. sublimes without melting (16); for purification of C by sublimation (4) under reduced press. (17) (18) see indic. refs.; for study of sublimation press. of C see (19).

Č is insol. aq.; alm. insol. in cold alc.; sparingly sol. hot alc. but somewhat more readily in ether; Č is sparingly sol. CHCl₂, CCl₄, CS₂; insol. lgr.

[For study of heat of formn. of C see (20); for studies of heat of combustion see (21) (22).]

[For studies of bactericidal properties of C (23) or toxicity of C (or its associated by-products or contaminants) (24) (25) (26) see indic. refs.

 \bar{C} comprises the essential constituent (99% (27)) of the commercial fungicide "Spergon" [for studies on use of \bar{C} as (seed) fungicide see (27) (28) (29) (30) (31) (32); for studies on toxicity of \bar{C} in such use see (33)].

PREPARATION OF C

 \bar{C} because of its great resistance to further oxidation is formed as the end product of the oxidation with HCl + KClO₃ of a very large number of aromatic organic compounds [e.g., for a list of 16 such which do and 31 which do not give \bar{C} , see (34); for extension to 130 cases which do, see (35) cf. (36).]

 \bar{C} can also be prepared by a very large number of methods (see below): of these the best appear to be those from benzoquinone-1,4 (1:9025) using conc. HCl + 30% H₂O₂ at 60° (97% yield (37)) cf. (38), and from p-aminophenol by conversion with SO₂Cl₂ (10 moles) at 70° (6) or at 40-45° for 4 days (73% yield (1)) to N,N-dichloro-2,3,5,6-tetrachloro-4-aminophenol, m.p. 71.5° (6), and reaction of the latter with boilg. EtOH (1) (6) in pres. of an inert solvent (39) to give (80-85% overall yield from p-aminophenol (1)) of \bar{C} of exceptional purity and free from 2,3,5-trichlorobenzoquinone-1,4 (3:4672).

FROM VARIOUS PHENOLS

From phenol. [For prepn. of \bar{C} from phenol (1:1420) with conc. $HNO_3 + fumg$. HCl (i.e., with aqua regia) on htg. in open flask in direct sunlight (25% yield (17)) (40), or in fumg. HCl with Cl_2 followed by htg. with conc. HNO_3 at 100° for 20 hrs. (34% yield (17)) cf. (40), by electrolysis in HCl/AcOH (41), or by action of conc. $HCl + KClO_3$ (42) (43) (note, however, that this method gives (17) (44) (45) (46) (47) a product seriously contaminated with 2,3,5-trichlorobenzoquinone-1,4 (3:4672) q.v.) see indic. refs. — For prepn. of \bar{C} from phenol-contg. industrial waste waters with Cl_2 in alk. soln. followed by oxidn. with HNO_3 see (48) (49) (50) (51) (52).]

From various halophenols. From 2,4,6-trichlorophenol. [For prepn. of \bar{C} from 2,4,6-trichlorophenol (3:1673) with ClSO₃H (53), with Cl₂ + fumg. H₂SO₄ followed by ClSO₃H (90% yield (54)), with aqua regia (17) (40), with HCl + KClO₃ (42) (55), with CrO₃/AcOH (15), or with K₂Cr₂O₇/H₂SO₄ (15) see indic. refs. — Note also that many of the processes starting from phenol (above) doubtless pass through 2,4,6-trichlorophenol.]

From pentachlorophenol. [For prepn. of \tilde{C} from pentachlorophenol (3:4850) with ClSO₃H (53) (54), with cold fumg. HNO₃ (56) (57) (58), or with Cl₂ + conc. HCl at 100° (58) see indic. refs.]

From "hexachlorophenol." [For form. of \bar{C} from "hexachlorophenol" (hexachlorocyclohexadien-1,4-one-3) (3:3180) with conc. (68) or fumg. (69) HNO₃, with conc. H₂SO₄ at 100° (68) (69), with aq. or HCl in s.t. at 160° (69), or with AlCl₃ ($\frac{1}{8}$ mole) in s.t. at 160° (70) see indic. refs.]

From 2,4,6-triiodophenol. [For prepn. of \bar{C} from 2,4,6-triiodophenol with Cl_2 in boilg. AcOH soln. (100% yield) see (10).]

From various nitroso- and nitro-phenols. [For prepn. of \bar{C} from p-nitrosophenol in conc. HCl at 90° with Cl₂ see (59).]

[For form. of \tilde{C} from o-nitrophenol (17) (40) (60), p-nitrophenol (17) (40) (60), 2,4,6-trinitrophenol (picric acid) (17) (40) (61) with aqua regia, or from picric acid with Cl_2 (61) or $Cl_2 + I_2$ (62) in hot aq. soln., or from picric acid with $HCl + KClO_3$ (42) (47) see indic. refs.; for formn. of \tilde{C} from p-nitrophenol or 2,4-dinitrophenol with aq. NaOCl soln. see (63).]

From polyhydric phenols. From resorcinol. [For formn. of C from resorcinol (1:1530) with ClSO₃H (40 wt. pts.) at 150-160° for 25 hrs. (note that much 2,3,5-trichlorobenzo-quinone-1,4 (3:4672) is also formed) see (64) cf. (54).]

From hydroquinone. [For formn. of \bar{C} from hydroquinone (1:1590) with Cl_2 in AcOH (5), with Cl_2 + conc. HCl at 100° (65) (53), with aqua regia (4), with $ClSO_3H$ at 150-160° (8) see indic. refs.; for formn. of \bar{C} from hydroquinone-pyridinium chloride with SOCl₂ (2) or from hydroquinone-2,6-bis-(sulfonyl chloride) with PCl_5 in s.t. at 140-150° for 6 hrs. (67) see indic. refs.]

From pyrogallol. [For formn. of C from pyrogallol (1:1555) with ClSO₃H at elevated temp. see (66).]

From various quinones. From p-benzoquinone. [For form. of \bar{C} from benzoquinone-1,4 (1:9025) with Cl_2 in conc. HCl (53) (65) with Cl_2 in AcOH (71) cf. (72), or with $HCl + KClO_3$ (42) see indic. refs.]

From the dichloro-p-benzoquinones. [For form. of C from 2,3-dichlorobenzoquinone-1,4 (3:2855), from 2,5-dichlorobenzoquinone-1,4 (3:4470), or from 2,6-dichlorobenzoquinone-1,4 (3.3750) with Cl₂ in CHCl₃ see (73).]

From trichloro-p-benzoquinone. [For formn. of \bar{C} from 2,3,5-trichlorobenzoquinone-1,4 (3:4672) with $Cl_2 + I_2 + aq$. (47), or with $Cl_2 + HCl$ (65), see indic. refs.]

From various amines. [For form. of \bar{C} from aniline in 10% HCl by electrolytic oxidation (23% yield (9)) (74), with HCl + KClO₃ (75) (76), with Na₂Cr₂O₇ + HCl (89), or with aqua regia (60) see indic. refs. — For form. of \bar{C} from diphenylamine, 2,4-dichloroaniline, m-nitroaniline, aniline black, or phenylhydrazine with aqua regia see (60).]

[For form. of \bar{C} from p-phenylenediamine with aqua regia (60) (4), with ClSO₃H (large excess) at 150-160° for 5 hrs. (77), with Cl₂ in AcOH (78), or with HCl + KClO₃ (3) see indic. refs.; from 2,6-dichloro-p-phenylenediamine with HCl + KClO₃ see (79).]

[For formn. of \bar{C} from o-aminobenzoic acid (anthranilic acid) (42) (80), m-aminobenzoic acid (80), p-aminobenzoic acid (80), p-tyrosine (α -amino- β -(p-hydroxyphenyl)propionic acid) (81) with HCl + KClO₃ see indic. refs.; from sulfanilic acid (aniline-p-sulfonic acid) with aqua regia see (60).]

[For form. of \tilde{C} from 2,3,5,6-tetrachloro-p-phenetidine by diazotization and boilg. see (82).]

From miscellaneous sources. [For formn. of \bar{C} from 1,2,4,5-tetrachlorobenzene (3:4115) as by-product of nitration with fumg. HNO₃ see under (3:4115), from hexachlorobenzene (3:4939) on boilg. with mixt. of fumg. HNO₃ + conc. H₂SO₄ see (83); from N-nitro-2,4,6-trichloroaniline in dil. alc. or AcOH soln. with HCl or H₂SO₄ see (84); from N-nitro-acet-2,3,5,6-tetrachloroanilide on bollg. in toluene or xylene see (85); from tetrachlorobenzo-quinone-1,4-mono-(2,4,6-trichlorophenylimide) by H₂SO₄ hydrolysis see (86); from various azo dyes by oxidn. with NaOCl soln. at 0° see (87); from anisolesulfonic acid or phenetolesulfonic acid in aq. soln. with Cl₂ see (88); from nitrobenzene with ClSO₃H (20 wt. parts) at 150° for 20 hrs. (95% yield) see (7).]

CHEMICAL BEHAVIOR OF C

REDUCTION OF C

C upon reduction by a wide variety of reagents gives tetrachlorohydroquinone (3:4941) the text of which should be consulted for details.

OXIDATION OF C

Č is extremely stable to oxidizing agents in neutral or acid soln. and is unaffected by aqua regia or hot conc. HNO₃.

BEHAVIOR WITH CHLORINE

[C with MnO₂ + conc. HCl in s.t. at 180° for 10 hrs. adds 1 mole Cl₂ giving (45) hexachlorocyclohexen-2-dione-1.4 [Beil. VII-574], m.p. 89° (45).]

BEHAVIOR WITH OTHER INORGANIC REACTANTS

In many of the reactions of \bar{C} with other reagents, 2 of the chlorine atoms are often replaced by other groups as exemplified below.

With aqueous alkali. \bar{C} with dil. aq. alk. at 70-80° readily replaces 2 chlorine atoms by hydroxyls giving (16) (3) (90) (91) (92) 2,5-dichloro-3,6-dihydroxybenzoquinone-1,4 (chloranilic acid) (3:4970), m.p. 282-284° s.t. (92).

With ammonia. [C with alc. NH₃ on boilg, replaces 2 chlorine atoms by amino groups giving (75% yield (103)) (93) (94) 2,5-dichloro-3,6-diaminobenzoquinone-1,4 (chloroanilamide) [Beil. XIV-144]. — Note, however, that C with aqueous NH₄OH gives (16) 2,5-dichloro-3-amino-6-hydroxybenzoquinone-1,4 (chloranilamic acid) [Beil. XIV-250].]

With various salts. [\bar{C} with sodium azide as directed (95) (96) gives 2,5-dichloro-3,6-bis-azidobenzoquinone-1,4. — \bar{C} with NaNO₂ (2 moles) in conc. aq. soln. on warming gives (97) cf. (98) 2,5-dihydroxy-3,6-dinitrobenzoquinone-1,4 (nitranilic acid) [Beil. VIII-384, VIII₁-(683)]. — \bar{C} with KCN (2 moles) in 85% MeOH gives (99) 2,5-dihydroxy-3,6-dicyanobenzoquinone-1,4 (cyananilic acid) [Beil. X₁-(520)].]

[\tilde{C} with warm dilute aq. acid KHSO₃ gives mainly (100) (101) the salt of 2,5-dichloro-3,6-disulfohydroquinone [Beil. XI-301], while with conc. solns. (100) or with neutral K₂SO₃ (101) (102) the main prod. is the salt of thiochronic acid [Beil. XI-302, XI₁-(80)], now (102) recognized as cyclohexadien-2,5-ol-4-one-1-pentasulfonic acid-2,3,4,5,6.]

With PCl₅. [C with PCl₅ + PCl₃ in s.t. at 190-200° for 4 hrs. gives (95% yield (104)) cf. (43) hexachlorobenzene (3:4939); note also, however, that C with PCl₅ + PCl₃ at 135-140° followed by treatment with aq. may also yield (45) (105) mono-(pentachlorophenyl)-phosphoric acid (monohydrate), m.p. 224° (105), and other products.]

BEHAVIOR OF C WITH ORGANIC REACTANTS

With aromatic hydrocarbons. [C with various aromatic hydrocarbons yields addition compounds: e.g., C with 1,2,4,5-tetramethylbenzene (durene) (1:7195) in hot AcOH gives (106) (107) a red cpd. C.2 durene; C with hexamethylbenzene (1:7265) gives from hot AcOH (108) violet-brown ndls. of a 1:1 cpd., m.p. 198-202° (108) (for further study of this prod. see (109) (110)); C with acenaphthene (1:7225) gives (111) (112) from AcOH (107) a violet 1:1 addn. cpd.]

With dienes and other unsaturates. \bar{C} with many dienes and other highly unsaturated compounds forms addn. products and/or gives color reactions.

[Č with cyclopentadiene (1:8030) in C₆H₆ in pres. of a little Me₃N gives (113) a 1:1 addn. cpd., yellowish ndls. from abs. alc., m.p. 146-146.5° (113) (corresp. dibromide with Br₂ in CHCl₃ in direct sunlight, lfts. from AcOEt, m.p. 269° (113)); note that in absence of Me₃N yield in 14 days is only 40%, in presence of Me₃N 100% (for study of cat. influence of Me₃N and of CCl₃.COOH see (114)).]

[For study of color reactions of \bar{C} in CHCl₃ soln. with various trienes see (115) cf. (116) (117).]

[For studies of influence of \bar{C} on polymerization of styrene (1:7435) see (118) (119) (120); for study of effect of \bar{C} on polymerization or depolymerization of natural rubber see (121); for use of \bar{C} as vulcanization accelerator see (122).]

With organic OH (or SH) reactants. With alcohols. [C in boilg. MeOH gradually treated with calcd. amt. 1% MeOH/KOH gives (123) (124) a mixt. of 2,5-dichloro-3,6-

dimethoxybenzoquinone-1,4 (chloranilic acid dimethyl ether) [Beil. VIII-380], dark red pr. from C₆H₆, m.p. 141-142° (123), and 2,6-dichloro-3,5-dimethoxybenzoquinone-1,4 (isochloroanilic acid dimethyl ether) [Beil. VIII-387], dark red pr., m.p. 159° (125) (126), 157-158° (123), 155.5° (127). — Note, however, that \tilde{C} with MeOH/NaOMe (5-6 moles) gives 2,5-dichloro-3,6-dimethoxybenzoquinone-1,4-bis (monomethyl acetal) [Beil. VIII-381] accompanied by tetrachlorohydroquinone (3:4941).]

With phenols. [C (1 mole) with phenol (2 moles) in aq. KOH at 100° gives (128) 2,5-dichloro-3,6-diphenoxybenzoquinone-1,4 (chloranilic acid diphenyl ether) [Beil. VIII-380], dark red pr. from C₆H₆, m.p. 243° (128). — C (1 mole) with aq. K p-cresolate (2 moles) at 100° gives (129) 2,5-dichloro-3,6-di-(p-toloxy)benzoquinone-1,4 (chloranilic acid dip-tolyl ether) [Beil. VIII₁-(681)], cryst. from toluene, m.p. 254-255° (129).]

With mercaptans. [Č (1 mole) with EtSH (4 moles) with EtOH/KOH (4 moles) as directed gives (95% yield (130)) 2,3,5,6-tetra-kis-(ethylthio)benzoquinone-1,4 [Beil. VIII-535], dark green ndls. from alc., m.p. 90-91° (131).]

With thiophenols. [Č (1 mole) with C₆H₅SH in alk. soln. might be expected to yield 2,3,5,6-tetra-kis-(phenylmercapto)benzoquinone-1,4, but neither this reaction nor the expected product appears to have been reported. — However, various analogous cases are known: e.g., Č (1 mole) with p-thiocresol (4 moles) in AcOH at 100° for ½ hr. gives (132) 2,3,5,6-tetra-kis-(p-tolylthio)benzoquinone-1,4, cryst. from AcOH, m.p. 203° (132). — Č (1 mole) with o-nitrothiophenol in boilg. EtOH for 1 hr. gives (96) 2,3,5,6-tetra-(o)-nitrophenylmercapto)benzoquinone-1,4, no m.p. given.]

With organic amines. General. The behavior of \bar{C} with aliphatic amines appears to have been little studied from the structural viewpoint. [However, for studies on color reactions of \bar{C} with prim., sec., and ter-amines (or their salts) (133), for use of \bar{C} (in epichlorohydrin soln.) as a test for plasmochin (134) (135), or for use of \bar{C} in detection of MeNH₂, Me₂NH, or Me₃N and differentiation from NH₃ (136) (137), for use in spot test reactions of 38 different amines (147) see indic. refs.]

With primary aliphatic amines. [C with MeNH₂ might be expected to give 2,5-dichloro-3,6-bis-(methylamino)benzoquinone-1,4 or even 2,3,5,6-tetra-kis-(methylamino)benzoquinone-1,4, but the reaction has not been reported and neither product is known.]

With primary aromatic amines. [\bar{C} with aniline in boilg. alc. refluxed 30 min. gives (81% yield (138)) (100) (93) (139) 2,5-dichloro-3,6-dianilinobenzoquinone-1,4 [Beil. XIV-144, XIV₁-(421)], yel.-br. lfts. from C_6H_6 or nitrobenzene, m.p. 292-293° (138), 290° (140), 288-290° (141); note that this product serves as bases for prepn. of many complex dyestuffs which cannot be discussed here. — \bar{C} with many other homologous and analogous primary aromatic amines behaves similarly.

[\bar{C} with phenylhydrazine in absol. alc. evolves N_2 and gives (10) a chlorine-contg. prod., m.p. 229-230°, of undetermined structure.]

With various organometallic reactants. [\tilde{C} (1 mole) in alc. with diethyl sodiomalonate (4 moles) in C_6H_6 gives (10% yield (142)) tetraethyl 2,5-dichloro-p-benzoquinone-3,6-dimalonate [Beil. X-940], yel. ndls. from alc., m.p. 132° (143).]

[For behavior of C with ethyl sodio-acetoacetate see (144) (145), Beil. X-860, and Beil. X-935.]

[For behavior of C with excess C₆H₅MgBr see (146).]

© Color tests for C. Of the large number of color tests shown by C with various reactants, the following have been especially employed as preliminary tests for C itself; note that for details, limitations, etc., the original references should be consulted.

With dimethylaniline. C on warming with dimethylaniline gives intense violet color (Mulliken).

With ethyl cyanoacetate. C with ethyl cyanoacetate (2-3 drops) + excess alc. NH₄OH (2-3 ml. of mixt. of 1 pt. abs. EtOH + 1 pt. conc. NH₄OH) gives intense bluish-violet coloration, changing to blue, green, and finally reddish brown (148). [Note that the reaction is also shown by certain other quinones, e.g., benzoquinone-1,4 (1:9025), o-toluquinone, thymoquinone, and naphthoquinone-1,4 (1:9040), but is not given by anthraquinone (1:9095), phenanthraquinone (1:9086), naphthoquinone-1,2 (1:9062), or 2,5-dichloro-3,6-diaminobenzoquinone-1,4 (chloranilamide) (148)]

With triphenylphosphine. \bar{C} with 20% soln. of $(C_6H_5)_3P$ in CHCl₃ gives (149) a winered color. [Note, however, that a similar behavior is also shown by 2,3,5-trichlorobenzo-quinone-1.4 (3:4672) and certain other quinones (149).]

3:4978 (1) Eller, Lorenz, Ber. 58, 494-497 (1925). (2) Koenigs, Greiner, Ber. 64, 1047 (1931).
(3) Graebe, Ann. 263, 16-31 (1891). (4) Datta, J. Am Chem. Soc. 36, 1011-1013 (1914). (5) Datta, Bhoumik, J. Am. Chem. Soc. 43, 313 (1921). (6) Eller, Klemm, Ber. 55, 219, 223-224 (1922). (7) Pollak, Heimburg-Krauss, Katscher, Lustig, Monatsh. 55, 373 (1930). (8) Pollak, Gebauer-Fülnegg, Monatsh. 47, 115 (1926). (9) Erdélyi, Ber. 63, 1200-1201 (1930). (10) King, McCombie, J. Chem. Soc. 103, 225-226 (1913).

(11) Conant, Fieser, J. Am. Chem. Soc. 45, 2207-2218 (1923). (12) Hall, Conant, J. Am. Chem. Soc. 49, 3052 (1927). (13) Chorghade, Z. Krist. A-101, 418-424 (1939); Cent. 1939, II 2909; C.A. 33, 9078 (1939). (14) Fels, Z. Krist. 37, 477 (1903). (15) Levy, Schultz, Ann. 210, 154-155, 160 (1881). (16) Erdmann, J. prakt. Chem. (1) 22, 279-282 (1841), Ann. 48, 314-315 (1843). (17) Kempf, Moehrke, Ber. 47, 2615-2622 (1914). (18) Kempf, J. prakt. Chem. (2) 78, 236 (1908). (19) A. S. Coolidge, M. S. Coolidge, J. Am. Chem. Soc. 49, 100-104 (1927). (20) Sjöstrom, Svensk Kem. Tid. 48, 121-124 (1936), Cent. 1937, I 58; C.A. 30, 6634 (1936).

(21) Valeur, Ann. chim. (7) 21, 499-500 (1900). (22) Swietoslawski, Starczewska, J. chim. phys. 22, 399-401 (1925). (23) Hilpert, Buochem. Z. 166, 71-88 (1925), Cent. 1926 I, 2011; C.A. 20, 1861 (1926). (24) Staub, Biochem. Z. 178, 167-180 (1926), Cent. 1928, II 2576; C.A. 21, 1310 (1927). (25) Staub, Biochem. Z. 179, 125-143 (1926); Cent. 1928, II 2576, C.A. 21, 2326 (1927). (26) Staub, Biochem. Z. 179, 227-237 (1926); Cent. 1928, II 2576; C.A. 21, 2327 (1927). (27) Felix, Phytopathology, 32, 4 (1942), C.A. 36, 2674 (1942). (28) Middleton, Plant Disease Reptr. 27, 169-170 (1943); C.A. 37, 4518 (1943). (29) McNew, Science 96, 118-119 (1942). (30) Elmer, Plant Disease Reptr. 28, 44-46 (1942); C.A. 36, 3315 (1942).

(31) McNew, Farm Research (Quart. Bull. N. Y. Agr Expt. Sta) 8, No 2, 9-11 (1942); C.A. 36, 3897 (1942). (32) Horsfall, Conn. Vegetable Grovers Assoc., Proc. Ann. Meeting, 28, 72-74 (1940); C.A. 36, 2074 (1942). (33) McGavack, Boyd, Terranova, J. Ind. Hyg. Toxicol, 25, 98-110 (1943). (34) Denis, Bull. soc. chim. Belg. 35, 375-379 (1926), Cent. 1927, I 721; C.A. 21, 905 (1927). (35) Colmant, Ann. soc. sci. Bruxelles B-51, 27-39 (1931); Cent. 1931, I 3705, C.A. 25, 3323 (1931). (36) Michiels, Hinchot, Bull. acad. roy. med. Belg. (5) 5, 213-228 (1935), C.A. 19, 3260 (1925). (37) Gallotti, Ann. chim. applicata 22, 602 (1932), Cent. 1933, I 1432, C.A. 27, 278 (1933). (38) Arnold, Collins, Zenk, J. Am. Chem. Soc. 62, 983 (1940). (39) Eller, Lorenz, Ger. 390,623, Feb. 21, 1924, Cent. 1924, I 1869; not in C.A. (40) Kempf, Mochike, Ger. 256,034, Feb. 4, 1913; Cent. 1913, I 758; C.A. 7, 2096-2097 (1913).

(41) Fichter, Glantzstein, Ber. 49, 2473-2481 (1916). (42) Hofmann, Ann. 52, 57-65 (1844).
(43) Graebe, Ann. 146, 8-18 (1868). (44) Bouveault, Ann. chm. (8) 13, 142-144 (1908). (46) Zincke, Fuchs, Ann. 267, 15-19, (1892). (46) Knapp, Schultz, Ann. 210, 174-176 (1881).
(47) Stenhouse, Ann. Suppl. 6, 208-213 (1868). (48) Chulkov, Parini, Staroselets, Ory Chem. Ind. (U.S.S.R.) 3, 97-101 (1937); Cent. 1938, I 1419, C.A. 31, 4967 (1937). (49) Chulkov, Shvedova, Parini, Orp. Chem. Ind. (U.S.S.R.) 2, 539-542 (1936); Cent. 1937, I 2866; C.A. 32, 8386 (1938). (50) Chulkov, Parini, Chartova, J. Applied Chem. (U.S.S.R.) 9, 1482-1488 (1936); Cent. 1937, I 4408; C.A. 31, 2723 (1937).

(51) Chulkov, Shvedova, Staroselets, Russ. 50,439, Feb. 28, 1937; Cent. 1938, II 593; C.A. 31, 8550 (1937). (52) Chulkov, Chartova, Russ. 50,440, Feb. 28, 1937; Cent. 1938, II 177, C.A. 31, 8550 (1937). (53) Schuloff, Pollak, Chem. Ztg. 56, 569-570 (1932); Cent. 1932, II 1510; [C.A. 26, 5086 (1932)]. (54) Heimberg, Ger. 511,209, Nov. 7, 1930; Cent. 1931, I 1360, C.A. 25, 1266 (1931). (55) Leger, Compt. rend. 146, 696 (1908); Bull. soc. chim. (4) 3, 578-582 (1908). (56) Merz, Weith, Ber. 5, 460 (1872). (57) Biltz, Giese, Ber. 37, 4018 (1904). (58) Barral, Bull. soc. chim. (3) 27, 272, 275-278 (1902). (59) Holliday and Co., Ltd., Shaw, Brit. 274,700, Aug. 18, 1927; Cent. 1927, II 2227; C.A. 22, 2172 (1928). (60) Datta, Chatterjee, J. Am. Chem. Soc. 38, 1817-1821 (1916).

(61) Stenhouse, Ann. 66, 242 (1848). (62) Stenhouse, Ann. 145, 362-364 (1868). (63)

Seyewetz, Chaix, Bull. soc. chim. (4) 41, 197-199 (1927). (64) Pollak, Gebauer-Fülnegg, Monatsh. 46, 513-514 (1925). (65) Schuloff, Austrian, 127,813, April 25, 1932; Cent. 1932, II 924; C.A. 26. 4348 (1932). (66) Pollak, Gebauer-Fulnegg, Monatsh. 47, 543, 558 (1926). (67) Litvay, Riesz, Landau, Ber. 62, 1867 (1929). (68) Biltz, Ber. 37, 4009-4010 (1904). (69) Barri Bull. soc. chim. (3) 11, 705-710 (1894). (70) Barral, Bull. soc. chim. (3) 13, 345-348 (1895). (69) Barral.

(71) Chelintsev, Compt. rend. acad. sci. U.R.S.S. 14, 289-291 (1937), Cent. 1937, II 381; [C.A. 31, 7350 (1937)]. (72) Chelintsev, Compt. rend. acad. sci. U.R.S.S. 2, 244-247 (1935); Cent. 1936, I 2537, [C.A. 29, 6220 (1935).] (73) Oliveri-Tortorici, Gazz. chim. ital. 27, II 584-586 (1897). (74) Erdelyi, Magyar Chem. Folyorrat 35, 15-16 (1929), Cent. 1929, II 2177; C.A. 23, (75) Fritzsche, J. prakt. Chem. (1) 28, 203 (1843). (76) Hofmann, Ann. 4937-4938 (1929). 47, 67 (1843). (77) Lustig, Katscher, Monatsh. 48, 96 (1927). (78) Krause, Ber. 12, 52 (1879). (79) Witt, Toche-Mittler, Ber. 36, 4390-4392 (1903). (80) Widmann, Ann. 193, 234-240 (1878).

(81) Stadeler, Ann. 116, 99-102 (1860). (82) Bures, Kovarovicova, Casopis Českoslov. Lékárnictva 10, 197-202, 233-239 (1930), Cent. 1930, II 2775; [C.A. 25, 1816 (1931)]. (83) Istrati, Bull. soc. chim. (3) 3, 184-186 (1890). (84) Orton, Pearson, J. Chem. Soc. 93, 731 (1908). (85) Peters, Rowe, Stead, J. Chem. Soc. 1943, 372. (86) Bradfield, Cooper, Orton, J. Chem. Soc. 1927, 2859. (87) Seyewetz, Chaix, Bull. soc. chim. (4) 41, 333-335, 337 (1927). (88) Datta, Mitter, J. Am. Chem. Soc. 41, 2030-2032 (1919). (89) Elbs, Brunnschweiler, J. prakt. Chem. (2) 52, 560 (1895). (90) Graebe, Ann. 146, 30-32 (1868).

(91) Stenhouse, Ann. Suppl. 8, 14-18 (1872). (92) Conant, Fieser, J. Am. Chem. Soc. 46, 1866 (1924). (93) Knapp, Schultz, Ann. 210, 183 189 (1881). (94) Laurent, Ann. 52, 347-348 (1844). (95) Korczynski, Bull. soc. chim. (4) 35, 1189-1190 (1924). (96) Fries, Ochwat, Ber. 56, 1302-1304 (1923). (97) Nef, Ber. 20, 2028-2031 (1887). (98) Nef, Am. Chem. J. 11, 17-26 (1889). (99) Richter, Ber. 44, 3472-3473 (1911); 45, 1682 (1912). (100) Hesse, Ann. 114, 306, 324, 327 (1860).

(101) Graebe, Ann. 146, 36-52 (1868). (102) Jackson, Beggs, J. Am. Chem. Soc. 36, 1210-1218 (1914). (103) Fieser, Martin, J. Am. Chem. Soc. 57, 1845, 1847 (1935). (104) Graebe, Ann. 263, 30-31 (1891). (105) Barral, Bull. soc. chim. (3) 13, 419-420 (1895). (106) Pfeiffer. Ann. 404, 17-18 (1914). (107) Pfeiffer, Ber. 55, 418, 427-428 (1922). (108) Pfeiffer, Ann. 412, 293 (1916). (109) Lifschitz, Ber. 49, 2050-2054 (1916). (110) Michaelis, Granick, J. Am. Chem. Soc. 66, 1025, 1028 (1914).

(111) Haakh, Ber 42, 4595 (1909); J. prakt Chem. (2) 82, 548 (1910). (112) Dimroth, Bamberger, Ann. 438, 106-107 (1924). (113) Albrecht, Ann. 348, 45-46 (1906). (114) Wassermann, J. Chem. Soc. 1942, 618-621. (115) Kuhn, Wagner-Jauregg, Helv. Chem. Acta, 13, 11 (1930). (116) Kesting, Ber. 62, 1422-1424 (1929). (117) Skraup, Freundlich, Ann. 431, 262 (118) Price, J. Am. Chem. Soc 65, 2380-2381 (1943). (119) Breitenbach, Schneider, Ber. 76, 1089-1092 (1943). (120) Breitenbach, Taglieber, Ber. 76, 272-280 (1943).

(121) Spence, Ferry, J. Am. Chem. Soc. 59, 1648-1654 (1937). (122) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; Cent. 1933, I 3134; CA. 27, 2845 (1933). (123) Kehrmann, J. prakt. Chem. (2) 40, 368-370 (1889). (124) Kehrmann, J. prakt. Chem. (2) 43, 260-267 (1891). (125) Graebe, Hess, Ann. 340, 239-240 (1905). (126) Kohn, Gurewitsch. Monatsh. 49, 186 (1928). (127) Hunter, Levine, J. Am. Chem Soc. 48, 1614 (1926). (128) Jackson, Grindley, Am. Chem. J. 17, 594-595, 602-603 (1895). (129) Torrey, Hunter, J. Am. Chem. Soc. 34, 711 (1912). (130) Sammis, J. Am. Chem. Soc. 27, 1121-1122 (1905).

(131) Grindley, Sammis, Am. Chem. J. 19, 292 (1897). (132) R. Pollak, E. Riesz, J. Riesz, Monatsh. 58, 133 (1931). (133) Sivadjian, Bull. soc. chim. (5) 2, 623-625 (1935). (134) Slvadjian, J. pharm. chim. (8) 13, 528-529 (1931); CA. 26, 2277 (1932); Cent. 1931, II 475. (135) Schuleman, Schönhöfer, Wingler, Cent. 1928, I 2193; C.A. 23, 2453 (1929). (136) Berthelot, Amoureux, Bull. soc. chim. biol. 18, 649-651 (1936); Cent 1936, II 3707; [C.A. 30, 5532 (1936)]. (137) Tsalpatani, Bul. Soc. Strinte Bucuresci 16, 167 (1907); Cent. 1908, I 299; C.A. 2, 1106 (1908). (138) Shibata, Tech. Repts. Tohoku Imp. Univ. 7, No. 2, 53-71 (1928); Cent. 1928, I 2619; [C.A. 22, 1585 (1928)]. (139) Andresen, J. prakt. Chem. (2) 28, 425-427 (1883). (140) Niemeyer, Ann. 228, 333 (1885).

(141) Schutz, Buschmann, Wissebach, Ber. 56, 1975 (1923). (142) Stieglitz, Am. Chem. J. 13, 38-42 (1891). (143) Grindley, Jackson, Ber. 26, 398 (1893). (144) Ikuta, J. prakt. Chem. (3) 45, 65-66, 71-72 (1892). (145) Graebe, Levy, Ann. 283, 246-252 (1894). (146) Clar, Engler, Ber. 64, 1600-1601 (1931). (147) Frehden, Goldschmidt, Mikrochim. Acta 1, 347-351 (1937). (148) Craven, J. Chem. Soc. 1931, 1605-1606. (149) Schönberg, Ismail, J. Chem. Soc. 1940. 1376-1377.

M.P. 295° (1) 294.5° (2) 293° (3) 290–292° (4) 286° u.c. (5)

Colorless ndls. from hot aq. in which it is very spar. sol. requiring 130 pts. for soln. (4); eas. sol. alc., spar. sol. ether, insol. C₆H₆ or CHCl₃ (2).

[For prepn. of $\bar{\mathbb{C}}$ from 4-chloro-1,3-dimethylbenzene (3:8665) by oxidn. with aq. KMnO₄ (1) in pres. of MgSO₄ (2) see indic. refs.; from 2-chloro-5-methylphenyl methyl ketone (3), 2-chloro-5-methylbenzoic acid (6) (3:4615), or α,β -bis-(2-chloro-5-methylbenzoyl)ethylene (5) by oxidn. with KMnO₄ see indic. refs.; from sodium 1,3-dimethylbenzenesulfonate [Beil. XI-123, XI₁-(34)] with SOCl₂ in s.t. at 230°, followed by treatment with aq. alk., see (7); from 4-chloroisophthaldiamide (see below) by hydrolysis with boilg. aq. KOH see (4).]

- Dimethyl 4-chloroisophthalate: unreported.
- --- Diethyl 4-chloroisophthalate: unreported.
- 4-Chloroisophthaldiamide: ndls., lfts., or pl. from 17 pts. boilg. aq., m.p. 232-233° (4). [From isophthalic acid-4-arsinic acid (1,3-dicarboxybenzenearsinic acid-4, 1,3(HOOC)₂.C₆H₃.As(O)(OH)₂, with PCl₅ at 110° for 3 hrs. followed by treatment in toluene soln. with NH₃ (4).]

3:4980 (1) Davies, Wood, J. Chem. Soc. 1928, 1126. (2) Ullmann, Uzbachian, Ber. 36, 1799 (1903). (3) Mayer, Freund, Ber. 55, 2052 (1922). (4) Gough, King, J. Chem. Soc. 1930, 690-691. (5) Conant, Lutz, J. Am. Chem. Soc. 47, 891 (1925). (6) Scholl, Meyer, Keller, Ann. 513, 298 (1934). (7) Farbwerke Meister Lucius & Brüning, Ger. 282,133, Feb. 15, 1915; Cent. 1915, I 464.

M.P. 306-306.5° (1) 305-306° cor. (2) 305° (3)

Colorless ndls. from hot aq.; sublimes on cautious gradual htg.

[For prepn. of $\bar{\mathbb{C}}$ from 2,5-dichloro-1-methyl-4-isopropylbenzene (2,5-dichloro-p-cymene [Beil. V-423, V_{2} -(326)] by oxidn. with 20 pts. HNO_3 (D=1.15) in s.t. at $180-200^\circ$ for 10-12 hrs. (1) (3) see indic. refs.; from 2,5-dichlorocyclohexadiene-1,4-dicarboxylic acid. 1,4 (2,5-dichloro-3,6-dihydroterephthalic acid) [Beil. IX-785] in 12% yield by short boilgwith 20% HNO_3 (some 2,5-dichloro-3-nitroterephthalic acid is also formed) see (4) (2); from 2,5-dichloro-1,4-bis-(trichloromethyl)benzene (5) by hydrolysis with H_2SO_4 (66° B6) at $70-80^\circ$ see (5).]

 $Ag_2\bar{A}$, insol. aq. (2); $Ba\bar{A}$, $4H_2O$, very eas. sol. aq. (2).

[The acid chloride corresp. to Č, viz., 2,5-dichloroterephthaloyl (di)chloride, cryst. from lgr., m.p. 80.5-81° (6), has been obtd. indirectly (6) from 2,5-dichloro-3,6-dihydroterephthalic acid (above) by actn. of PCl₅.]

[A mononitro- \bar{C} , viz., 2,5-dichloro-3-nitroterephthalic acid [Beil. IX-852], pale yel. ndls. from conc. aq. soln., m.p. 225-226° dec. (2) (corresp. dimethyl ester, m.p. 207-208° dec. (2)), has been obtd. indirectly as stated above.

- Dimethyl 2,5-dichloroterephthalate: lfts. from MeOH, m.p. 137-138° (7) (5), 136° (6) (3). [From C in MeOH with HCl gas (2), or from 2,5-dichloroterephthaloyl dichloride in MeOH (6).]
- --- Diethyl 2,5-dichloroterephthalate: unreported.
- 2,5-Dichloroterephthaldiamide: ndls. from aq., m.p. above 300° (6). [From 2,5-dichloroterephthaloyl dichloride in ether with NH₃ (6).]

3:4985 (1) Bocchi, Gazz. chim. ital. 26, II 406 (1896). (2) Levy, Andreocci, Ber. 21, 1959-1964 (1888). (3) Wheeler, Giles, J. Am. Chem. Soc. 44, 2611 (1922). (4) Levy, Andreocci, Ber. 21, 1467-1468 (1888). (5) I.G., French 663,781, Aug. 26, 1929; Cent. 1929, II 2731-2732. (6) Levy, Curchod, Ber. 22, 2109-2111 (1889). (7) Fels, Z. Krist. 32, 411 (1900).

M.P. 312° (1) 310° (2) (3) 297° (4) (5) (6)

[See also α -benzenehexachloride (3:4410).]

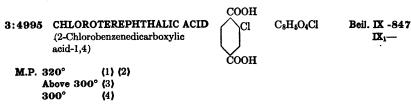
Nine stereoisomeric configurations of benzenehexachloride are possible (cf. (2)) and four are known; of these \bar{C} has definitely been shown (7) to be the *sym.-trans* stereoisomer; α -benzenehexachloride (3:4410) is probably the *sym.-cis* stereoisomer; the configurations of the γ -isomer, m.p. 112–113° (8), and the δ -isomer, m.p. 129–132° (8), are unknown.

 \bar{C} cryst. from C_6H_6 (8), alc. (10), or xylene. — \bar{C} is not volatile with steam (dif. and sepn. (10) from α -isomer) but sublimes after melting. — \bar{C} is sol. in 775 pts. CHCl₈ at 20° or in 213 pts. C_6H_6 at 17.25° (9) (note much less soly. than for α -isomer); 100 g. C_6H_6 at 22° dis. 1.204 g. \bar{C} (10); 100 g. AcOH at 15.6° dis. 0.289 g. \bar{C} (10). — \bar{C} forms with the α -isomer a eutectic, m.p. 155.5° (8), contg. 20.3% \bar{C} (8).

[For prepn. of \bar{C} or its mixt. with the α -benzenehexachloride see the latter (3:4410).]

 \ddot{C} is much more unreactive than the α -isomer; e.g., \ddot{C} is unaffected by boilg. alc. KCN (3) (10) and is only slightly attacked by boilg. pyridine (8). However, \ddot{C} on boilg. 4 hrs. with alc. KOH gives 100% yield (8) of a mixt. of trichlorobenzenes contg. 86.4% 1,2,4-trichlorobenzene (3:6420), 8.3% 1,3,5-trichlorobenzene (3:1400), and 5.3% 1,2,3-trichlorobenzene (3:0990) (8).

3:4990 (1) Klingstedt, Wiese, Rudback, Acta Acad. Aboensis Math. et Phys. 4, No. 2, 1-36 (1927); Cent. 1928, I 504; C.A. 23, 1399 (1929). (2) Williams, Fogelberg, J. Am. Chem. Soc. 53, 2096-2104 (1931). (3) Meunier, Ann. chem. (6) 16, 223-269 (1887). (4) Tei, Komatsu, Mem. Coll. Sci. Kyoto Imp. Unv. 10-A, 325-330 (1927); Cent. 1928, I 2370; C.A. 22, 1086 (1928). (5) Scholl, Nörr, Ber. 33, 726 (1900). (6) van de Vloed, Bull. soc. chem. Belg. 48, 255-256 (1938). (7) Hendrick, Bilicke, J. Am. Chem. Soc. 48, 3007-3015 (1926); 50, 764-770 (1928). (8) van der Linden, Ber. 45, 231-247 (1912). (9) Friedel, Bull. soc. chem. (3) 5, 130-138 (1891). (10) Matthews, J. Chem. Soc. 59, 165-172 (1891).



Cryst. from hot aq. (3), very dil. alc., (3) or 50% alc. (7); sol. in much hot aq., eas. sol. alc. or ether.

[For prepn. of $\bar{\rm C}$ from 2-aminobenzenedicarboxylic acid-1,4 [Bell. XIV-558, XIV₁-(637)] via diazotization and use of Cu₂Cl₂ reactn. see (3); from 3-chloro-1-methyl-4-isopropyl-benzene (3-chloro-p-cymene) (3:8770) by oxidn. with 15 pts. boilg. HNO₃ (D=1.39) for 1 day (other prods. are also formed) see (4); from 3-chloro-4-acetylbenzoic acid (1), from 2-chloro-4-acetylbenzoic acid (2), or from 3-chloro-4-methylphenyl methyl ketone (8) by oxidn. with alk. KMnO₄ see indic. refs.; from 2-chloro-4-carbamidobenzoic acid (5) by hydrolysis with boilg. 25% NaOH see (5); from 2-chloro-4-methylbenzotrichloride (6) by hydrolysis with H₂SO₄ (66° Bé) at 70-80° see (6).]

Ag₂A; pptd. from soln. of (NH₄)₂A by addn. of AgNO₃ (3).

[C with PCl₅(3) or with SOCl₂ in pres. of SbCl₅, AlCl₃, or SnCl₄(7) yields chloroterephthaloyl (di)chloride, b.p. 154-155° at 19 mm. (7).]

[C on nitration with HNO₃/H₂SO₄ at 65° yields (7) 2-chloro-5-nitrobenzenedicarboxylic acid-1,4, cryst. from 50% alc., m.p. 265° (7), 263-264° (8) (this prod. is also obtd. from 2-chloro-4-methyl-5-nitrophenyl methyl ketone (8) by oxidn.).]

- Dimethyl chloroterephthalate: lfts. from MeOH, m.p. 60° (6) (3), 59-60° (4). [From C in MeOH with HCl gas or from Ag₂Ā with MeI (3).]
- --- Diethyl chloroterephthalate: oil (3).
- ---- Chloroterephthaldiamide: cryst. from dil. alc., m.p. above 300° (3). [From chloroterephthaloyl (dı)chloride (above) with (NH₄)₂CO₃ (3).]

3:4995 (1) Ganguly, LeFevre, J. Chem. Soc. 1934, 851. (2) Ganguly, LeFevre, J. Chem. Soc. 1934, 854. (3) Ahrens, Ber. 19, 1637–1639 (1886). (4) Fileti, Cross, Gazz. chim. ital. 18, II 311, 313 (1888). (5) Magidson, Trawin, Ber. 69, 540 (1936). (6) I.G., French 663,791, Aug. 26, 1929; Cent. 1929, II 2731–2732. (7) I.G., French 810,595, March 24, 1937; Cent. 1937, I 5048; C.A. 32, 592 (1938). (8) Mayer, Albert, Schön, Ber. 65, 1296, 1298–1299 (1932).

CHAPTER XII

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 1. D_4^{20} greater than 1.1500

(3:5000-3:5499)

3:5000	PHOSGI (Carbony		oride)		•	COCl ₂	Beil. III - 13 III ₁ -(7) III ₂ -(12)
B.P.				F.P.				
8.2° co	r. at 756.4	mm.	(1)	[-118°	(7)]	$D_4^{186} = 1.392$	(1)	•
8.2°	at 756	mm.	(2)	-126°	(6)	-	-	
8.1°	at 756	mm.	(3)	-127.5°	(5)	See Note 2.		
8.02°	at 760	mm.	(4)	-128°	(6)			
7.95°	at 760	mm.	(5)					
7.89°	at 765.8	mm.	(4)					,
6.96°	at 760	mm.	(6)					

See Note 1.

Note 1. For studies of vap. press. of \bar{C} over range -96.3° (1.1 mm.) to 5.0° (678 mm.) (5); over range -88.94° (0.5 mm.) to $+12.6^\circ$ (889.2 mm.) (3); over range -79° (4.0 mm.) to $+50.0^\circ$ (5.11 atm.) (6); over range -23.42° (191.2 mm.) to $+25.03^\circ$ (1410.9 mm.) (4); over ranges 0° (556.5 mm.) to $+27.9^\circ$ (1540 mm.) and $+147.6^\circ$ (35.6 atm.) to $+182.5^\circ$ (56.4 atm.) (8) see indic. refs.

Note 2. For extensive studies on density of liquid C see (6) (4) (367).

Č at ord. temps. is a colorless gas with highly characteristic odor. It now is sold commercially in metal tanks or dissolved in an organic solvent such as toluene or CCl₄. Iron containers which have been used for long periods for storage of Č may contain small amounts of liquid iron pentacarbonyl.

 \bar{C} was first prepd. by John Davy in 1812 (9); for extensive history see (10). For general surveys on chemistry of \bar{C} (11) (12) from viewpoint of chemical warfare agent (13) (14) (15) (16) (17) (18) (19) see indic. refs.; for a bibliography of \bar{C} and its derivatives see (35).

MISCELLANEOUS PHYSICAL PROPERTIES OF C

[For studies on heat capacity from spectroscopic data (20) and other thermodynamic functions of \tilde{C} (21) (22) see indic. refs.; for studies on dipole moment (23) (24), dielectric const. (25), molecular structure (26) (27), and electron diffraction (28) of \tilde{C} see indic. refs.; for study of refractive index of \tilde{C} as gas see (29); for studies of critical temp. (181.75° (8), 183° (30), 187° (4)) and critical press. (55.3 atm. (8)) see indic. refs.]

 \bar{C} is readily sol. in C_6H_6 , toluene, or AcOH [for studies of solubility of \bar{C} in C_6H_6 at 20° (31), toluene over range 17-31.5° (6), xylene (6), EtOAc at 20° (31), nitrobenzene (6), CCl₄ (3:5100) at 20° (31), 1,1,2,2-tetrachloroethane (3:5750) (6), chlorobenzene (3:7903) (6), or 1-chloronaphthalene (3:6878) (6) see indic. refs.; for soly. of \bar{C} in various org.

solvents at pressures below 1 atm. see (32) cf. (33); for patent on removal of \bar{C} from contaminated drinking water by extraction with org. solvents see (34)].

[For technical papers (36) (37) (38) (39) (40) (41) (42) (43) (44) (45) and patents (46) on adsorption of \bar{C} by various forms of carbon see indic. refs.]

[For influence of \ddot{C} in extinction of H/O flames see (47).]

PHYSIOLOGICAL ASPECTS OF C

Č is more than ten times as toxic as Cl₂. An atmosphere contg. 1 part by vol. of Č in 6000 may cause lung injuries in 2 min., 1 part in 30,000 is very dangerous, and 1 part in 200,000 is probably fatal for exposures of 30 min. The maximum permissible concn. for prolonged exposure is about 1 p.p.m., i.e., 0.004 mg./l. (48).

The least detectable odor of \bar{C} is 5.6 p.p.m., the least conen. that affects the throat is 3.1 p.p.m., the least conen. that causes irritation of the eyes is 4.0 p.p.m., the least conen. that causes coughing is 4.8 p.p.m. (48) (49). A conen. of 0.02-0.05% is lethal to most animals in a short time, a conen. of 0.0025% is dangerous for exposures of 30-60 min., and the maximum conen. to which animals can be exposed for several hours without serious effects is 0.0001% or 1 p.p.m. (48) (50).

[For report of industrial accidents from \bar{C} (51), for legal (British) aspects of industrial poisoning by \bar{C} (52), for toxicology and treatment of poisoning by \bar{C} (53), for immunization against \bar{C} (54), for variations in toxicity of \bar{C} for small animals with duration of exposure (55) see indic. refs.]

[For studies relating to chemical warfare aspects of C with respect to foodstuffs see (56) (57).]

USES OF C

Apart from the uses of \bar{C} as a chemical warfare agent (above), many chemical utilizations are indicated below under its chemical behavior. [In addition will be mentioned here a few further examples as follows: for use of mixt. of \bar{C} + HF for cracking of hydrocarbon oils see (58); for use as dehydrating agent in conversion of amides to corresp. nitriles see (59); for use in sepn. of Pt metals see (60).]

DETECTION OF C

Č may be detected by its characteristic odor (see above) and by various color reactions of which the following represent the more important types.

For detection of \tilde{C} by the yellow or orange color produced by reaction with Harrison's reagent (a soln. in EtOH (100 ml.) of p-dimethylaminobenzaldehyde [Beil. XIV-31, XIV₁-(360)] (5 g.) (for prepn. see (61)) and of diphenylamine [Beil. XII-174, XII₁-(163)] (5 g.)) see (62) (63) (64) (65) (66) (67) (68) (69) (70) (71) (83); note that this test suffers interference from HCl, Cl₂, ClSO₃H, TiCl₄, chloromethyl chloroformate (3:5275), diphosgene (3:5515), and triphosgene (3:1915); for application of this reagent in an absorptive tube see (72) cf. (73).

For detection of C by green color imparted to a test paper impregnated with a xylene soln. of 0.5% 6-nitroso-3-dimethylaminophenol (4-dimethylamino-o-benzoquinoneoxime-1) [Beil. XIV-131] and a xylene soln. of 0.5% m-diethylaminophenol [Beil. XIII-408, XIII₁-(130)] see (74) (75) (76).

For spot test detection of Č by use of phenylhydrazine cinnamate (for prepn. see (77)) in CHCl₃ or CCl₄ followed by treatment with 1% CuSO₄ soln. to give a red-violet color from the 1,5-diphenylcarbohydrazide [Beil. XV-292, XV₁-(72)] produced see (78).

For study of detection of C with resorcinol (1:1530) or vanillin (1:0050) see (79); by

indirect use of the Gilman color test for RMgX compounds see (80) cf. (81); for study of utility of various dyestuffs in detection of \bar{C} see (82).

DETERMINATION OF C

Methods for the quant. detn. of C may be classified under three main types according to whether they are based upon hydrolysis, reaction with alkali iodides, or reaction with aniline.

Detn. by methods based on hydrolysis. [For studies of methods based upon alkaline hydrolysis of \bar{C} and subsequent detn. of resultant chloride ion see (83) (84) (85) (86) (87) (88) (89) (90); for especial criticism of this method see (91).]

Detn. by reaction with alkali iodide. [For studies of methods based upon reaction of \bar{C} with NaI (92) (91) or KI (93) in acetone followed by thiosulfate titration of the liberated I₂ see indic. refs.]

Detn. by reaction with aniline. [For study of methods based upon reaction of \bar{C} with aniline and gravimetric estn. of the resultant N,N'-diphenylurea (carbanilide) (94) (95) cf. (91) or titration of the residual aniline HCl in the filtrate (96) see indic. refs.]

Related topics. [For detn. of small amts. Cl_2 in pres. of \tilde{C} (97), of HCl in \tilde{C} (98) (85), for analysis of mixts. of \tilde{C} + Cl_2 + NOCl (99), for anal. of mixts. of \tilde{C} with CO, CO₂, Cl₂, CCl₄, C₂Cl₆ (88) (86), for anal. of industrial \tilde{C} (89), or for detn. of \tilde{C} in air by means of an ultraviolet photometer (R. + H. Tri-Per Analyzer) (100) see indic. refs.]

PREPARATION OR FORMATION OF C

From CO + Cl₂. The photochemical reaction of CO with Cl₂ to yield \bar{C} was the method by which it was first prepared in 1812 (9) (for extensive history see (10)). Over the years the reaction has been very extensively studied. The more important earlier reports include those of Wilm and Wischin (101), Wildermann (102), Dyson and Hardin (103), Weigert (104), Coehn and Becker (105), Chapman and Gee (106), etc. Since 1920 the number of studies of this reaction has so greatly increased as to preclude in this text any detailed analysis; however, the following references ((107)–(134), incl.) arranged in receding chronology will be found fruitful from one viewpoint or another.

[For studies on formn. of \bar{C} from CO + Cl₂ in dark at 349-452° (135) in liq. medium (145), or over cat. such as Pt at 300-400° (136), activated carbon (6) (137), or AlCl₃ at 30-35°, or in CHCl₃ soln. (138) see indic. refs. — For formn. of \bar{C} from CO + NOCl over activated carbon at 100-250° see (139) cf. (137).]

[For formn. of \bar{C} from CO passed over heated AgCl (140)(141), over CuCl₂, PbCl₃, or NiCl₂ at 450-750° (141), over heated AuCl₃ (142), or through boilg. SbCl₃ (143), or over chlorides of Pt metals (144) see indic. refs.]

From various chlorinated hydrocarbons. From CCl₄. [For studies on formn. of C from CCl₄ (3:5100) during use of latter as fire extinguisher see (146) (84) cf. (147) (368); for patents on repression of formn. of C in such use see (148) (149) (150) cf. (368); for formn. of C from CCl₄ fire extinguishers on Mg see (151); for phosgene content of smoke from Berger mixt. (Zn + chlorohydrocarbons) see (152).]

[For form. of \bar{C} from CCl₄ with O₂ in light of 2537 Å (153) or with atomic oxygen (154) see indic. refs.]

[For formn. of C from CCl₄ by chemical oxidizing agents such as O₂ over white-hot Pt (155), air over CuCl₂ or FeCl₃ at elev. temp. (156), GeO₂ (157), chromic acid (1) (158), pyrosulfuryl chloride (1 mole) + sulfuric acid monohydrate (2 moles) on warming (158) (159) (160) (161) (162) (163) see indic. refs.]

[For formn. of \bar{C} from CCl₄ by passing with CO₂ over pumice at 350° (164), by htg. with

ZnO at 200° (164), with P_2O_5 at 200-220° for 2 days (165), or over gypsum at 900° (166), or even by htg. with a little aq. in s.t. at 250° (220) see indic. refs.]

From CHCl₃. [For an extensive account of formn. of \tilde{C} from CHCl₃ (3:5050) by oxidn. in air and light see (167). Note that such oxidn. is not effected by air in absence of light, nor by light in absence of air (168). With limited air in sunlight CHCl₃ reacts according to equation CHCl₃ + O O COCl₂ + HCl, but with excess air in sunlight in sense 2CHCl₃ + O O COCl₂ + H2O (169). Note that CHCl₃ + air over dry KOH gives some C (170). For studies on photochem. oxidn. of CHCl₃ (171) in tropical sunlight (172) including search for possible intermediate peroxides (173) (174) see indic. refs. For studies of Cl₂-sensitized photochem. oxidn. of CHCl₃ see (175) (176) (177). For oxidn of CHCl₃ by atomic oxygen see (154).]

[For formn. of \bar{C} from CHCl₃ (3:5050) by shaking with siloxen + excess O₂ (178), by action of O₃ (179) (180), by passing over CuO at 350-550° (181) or gypsum at 900° (166), with $K_2Cr_2O_7 + H_2SO_4$ (1) (158), with ClSO₃H at 120° (187), or during explosion of CHCl₃ with alkali metals (182) see indic. refs]

From Cl_2C = CCl_2 . [For form of \bar{C} from tetrachloroethylene (3:5460) during Cl_2 -sensitized photochem. oxidn. see (183) (184) (185)]

From Cl_2C =CHCl. [For form. of \tilde{C} from trichloroethylene (3:5170) with air or O_3 see (186).]

From various compounds containing the trichloromethyl group. [For formn. of \tilde{C} from trichloroacetaldehyde (chloral) (3:5210) by Cl₂-sensitized (188) or Br₂-sensitized (189) photochem. oxidn. with O₂ at 70–90°, with Cl₂ in sunlight (190), or with AlCl₃ on warming (191) see indic. refs.]

[For formn. of \tilde{C} from trichloroacetic acid (3:1150) on htg. with ZnCl₂ (192), on illuminating dry acid in pres. of air (193), or on electrolysis of aq. soln. (194) see indic. refs.; from trichloroacetyl chloride (3:5420) at 600° (195); from trichloroacetonitrile in air (196); from trichloroacetyl hydrogen peroxide on warming (200); from trichlorobromomethane + Br₂ + O₂ in light (197) see indic. refs.]

[For formn. of \tilde{C} from di-(trichloromethyl) carbonate (triphosgene) (3:1915) on distn. (198), htg. at 200° in s.t. (199), or on mixing with charcoal and htg. just above m.p. (78°) (198) see indic. refs.; from trichloromethyl chloroformate (diphosgene) (3:5515) on htg. above 300° (200) (209) or on contact with activated carbon, charcoal, or iron oxide at ord. temp. (198); from methyl trichloromethyl carbonate [Beil. III-17, III_I-(8), III₂-(15)], b.p. 57-58° at 17 mm. (204), $D_4^{17}=1.5228$ (204), $n_D^{17}=1.4487$ (204), on boilg. at ord. press. (202) or on warming with AlCl₃ (203) (204); from ethyl trichloromethyl carbonate, b.p. 78° at 19 mm. (204), $D_4^{20}=1.4205$ (204), $n_D^{20}=1.4450$ (204), or from n-propyl trichloromethyl carbonate, b.p. 93° at 12 mm. (204), $D_4^{20}=1.359$ (205), $n_-^{20}=1.4451$ (205), on warming with AlCl₃ (203); from isoamyl trichloromethyl carbonate, b.p. 120° at 23 mm. (204), $D_4^{20}=1.2644$ (204), $n_D^{20}=1.4466$ (204), phenyl trichloromethyl carbonate [Beil. VI₁-(88)], m.p. 70.5° (204), or p-tolyl trichloromethyl carbonate (206) on warming with aq. (but not with aq. NaOH) (206); from bis-(trichloromethyl) oxalate [Beil. III-17] at 350-400° (207); or from trichloromethyl perchlorate (208) see indic. refs.]

[For form. of C from trichloronitromethane (chloropicrin) [Beil. I-76, I₁-(20), I₂-(41)] in u.v. light (210), on boilg. (at 112°) under ord. press. (211), on passing with HCl over pumice at 400° (212), or on treatment with fuming H₂SO₄ (20% SO₃) at 100° (213) see indic. refs.]

From miscellaneous sources. [For formn. of \tilde{C} from $CO_2 + CCl_4$ (3:5100) + cat. at elevated temp. (225), from CS_2 with aqua regia (214) or Cl_2O (215); from COS with Cl_2 at red heat (1); from COS over fused $CuCl_2$ (1) or through boiling $SbCl_5$ (1); from thiophosgene with air or O_2 under various conditions (216); from anhydrous Na_2CO_3 with

PCl₅ (217); from pentachloropropionyl chloride (3:0470) with AlCl₃ at 60° (218); from oxalyl (di)chloride (3:5060) at 600° or with AlCl₃ in CS₂ on warming (219) see indic. refs.]

CHEMICAL BEHAVIOR OF C

Pyrolysis of \tilde{C} . \tilde{C} on heating above 300° decomposes in two ways: (1) into CO + Cl₂ (CO equilibrium) and (2) into CO₂ + CCl₄ (CO₂ equilibrium). The extent of these reactions together with the influence of various factors has been extensively studied. [For a concise summary of earlier work see the review of Dyson (11); for many important details see the original references represented by (225) (221) (222) (5) (135) (6) (223) (224).]

Photochemical decompn. of \bar{C} . [\bar{C} on exposure to short-wave u.v. light decomposes yielding (105) (226) CO + Cl₂; for more recent studies of this photochem. decompn. see (227) (228) (229) (230) (231); for application to problem of separation of isotopes of Cl₂ see (232).]

Electrolysis of C. [C or a soln. of AlCl₃ in C upon electrolysis gives (233) CO + Cl₂.]

BEHAVIOR OF C WITH INORGANIC REACTANTS

Reduction of \bar{C} . $[\bar{C} + H_2 \text{ in u.v. light at } 10^{\circ} \text{ gives CO} + \text{HCl} + \text{traces of formaldehyde} (1:0145) but at <math>80^{\circ}$ gives CO + CO₂ + CH₄ + HCl (234). $-\bar{C}$ + H₂ over Pd or Ni on pumice, or over vanadium carbide, at $300-450^{\circ}$ gives (235) cf. (236) CO + HCl + small amts. formaldehyde (1:0145) cf. (229).]

Oxidation of C. [For study of photochem. oxidn. of C see (230).]

Hydrolysis of \bar{C} . Contrary to earlier reports \bar{C} with aq. is almost instantly hydrolyzed but the rate is influenced by the manner in which contact is effected and whether the aq. is in vapor or liquid state. [For studies on the hydrol. of \bar{C} see (237) (4) (96) (238); for study of rate of hydrolysis in dioxane at 25° (239) or in toluene at 25° and at 45° (240) see indic. refs.]

Behavior of \bar{C} with metal oxides, sulfides, or phosphates. [\bar{C} with metallic oxides on htg. at 250-600° (depending upon the metal) gives the corresp. metal chloride which in some cases, e.g., FeCl₃, ThCl₄, readily sublimes in pure form; for examples of this reaction see (241) (242) (243); for use in prepn. of AlCl₃ see (249).]

[C on htg. with metal sulfides gives (246) COS [Beil. III-131, III₁-(61), III₂-(104)], b.p. -50.2° (244), f.p. -138.2° (244) (use with CdS in prepn. (245)), and the metal chloride cf. (241).]

 $[\bar{C} \text{ on htg. with certain phosphates (247) gives } CO_2 + POCl_3 + metal chloride (use in prepn. of POCl_3 (248)).]$

Analogs of \bar{C} . Carbonyl fluoride. [This compound, b.p. -83.1° (250), m.p. -114.0° (250), has been prepd. from AgF₂ + CO (250), F₂ + CO (251) cf. (250), or from acetone with F₂ (252), but has not been reported from \bar{C} . Note that \bar{C} with HF at 80° and 280 lb./sq. in. in Cu bomb gives (25-50% yield (253)) carbonyl chlorofluoride, COCIF, b.p. -42° , m.p. 138° (253).]

Carbonyl bromide. [C with BBr₃ at 150° (254) or with AlBr₃ (255) gives carbonyl bromide Beil. III-20, III₁-(9), III₂-(7)], but this prod. is better prepd. from CBr₄ by oxidn. with conc. H₂SO₄ (256) (257) (258) (for study of photochemical oxidn. see (259)); for studies of structure (26) and pyrolysis (260) (261) (262) see indic. refs.]

Carbonyl cyanide. [This compound, b.p. 65.0-65.5° (263), $D_4^{20} = 1.124$ (263), $n_2^{20} = 1.3919$ (263), has been prepd from acetone- α,α' -dicarboxylic acid (1:0485) by conversion (264) to di-isonitrosoacetone [Beil. I-806, I₂-(413)], thence to diacetyl-di-isonitrosoacetone (263), then acetoximinoacetyl cyanide (263) which was then pyrolyzed at 160-180° and

210-220 mm. (263) cf. (265). For formn. using propionyl (instead of acetyl) derivatives see (266).]

Behavior of \tilde{C} with inorganic acids. [\tilde{C} with HF as directed (250) (see analogs of \tilde{C} above) gives carbonyl chlorofluoride. — \tilde{C} with HBr does not react even at 200° (267). — \tilde{C} as liq. does not react with HI, but \tilde{C} as gas reacts with HI gas even at room temp. with sepn. of I_2 (267).]

Behavior of \tilde{C} with inorganic salts. [\tilde{C} with KI or NaI in acetone solns, gives $CO + I_2$ (use in detn. of \tilde{C} (91) (92) (93)).]

[The behavior of AlCl₃ with \bar{C} has been extensively studied; for studies of solns, of AlCl₃ in liq. \bar{C} from viewpoint of vapor pressure (268), density (269), and conductance (270) see indic. refs. — For general studies of liq. \bar{C} as solvent (271) (272) including studies on system \bar{C} + Cl₂ (273) and on phosgeno salts such as calcium phosgeno-aluminate (274) (275) and others (276) see indic. refs.]

Behavior with various inorganic nitrogen compounds. With NH_3 . [\bar{C} in lgr. (277) or C_6H_6 (278) gives urea, biuret, cyanuric acid, cyamelide, ammelide, etc.; \bar{C} as gas with NH_3 as gas gives urea (279) cf. (280) (143), guanidine, cyanuric acid (281), and cyamelide (282). — For reaction of \bar{C} in toluene soln. with aq. NH_4OH as a source of isocyanic acid see (283). — Note also that \bar{C} with sodamide reacts in cold in sense $COCl_2 + 3NaNH_2 \rightarrow NaNCO + 2NaCl + 2NH_3$, but at about 250° in sense $COCl_2 + 5NaNH_2 \rightarrow Na_2N - C = N + 2NaCl + NaOH + 3NH_3$ (284).]

[Č with NH₄Cl at elevated temps., e.g., 200–400°, gives (285) (286) carbamyl chloride, NH₂.CO.Cl [Beil. III-31, III₁-(15)], b.p. 61–62° dec. (285). — For study of analogous carbamyl fluoride and carbamyl bromide (previously unknown) see (287).]

With hydroxylamine. [For studies on behavior of C with NH₂OH see (288) (289).]

With hydrazine. [C with 1 mole hydrazine would be expected to give N-aminocarbamyl chloride, NH₂.NH.CO.Cl, but this compound appears to be unknown; C with 2 moles hydrazine should yield N,N'-diaminourea (carbohydrazide) [Beil. III-121, III₁-(57), III₂-(96)], but this compound has not been reported as prepd by this method.]

BEHAVIOR OF C WITH ORGANIC REACTANTS

With hydrocarbons. [For studies on photochem. reaction of \bar{C} with alkanes (290) or with cycloalkanes (291) or with aliphatic or alicyclic acid chlorides (292) as a means of replacement of hydrocarbon H atoms by the CO.Cl group see indic. refs. — For reaction of \bar{C} with satd. nonaromatic hydrocarbons in pres. of cat. yielding ketones see (293). — Note also that \bar{C} with $CH_4 + H_2 + CH_2$ cat. is claimed (236) to give acetaldehyde (1:0100).]

Č with aromatic hydrocarbons in pres. of a Friedel-Crafts' type cat. condenses according to conditions with either one or two moles of hydrocarbon yielding, respectively, the corresp. acid chloride or ketone. No attempt can be made here to collect the reported cases of these types since the many acid chlorides contained in this book afford numerous examples.

|C with ethylene + AlCl₃ in CS₂ adds to the unsatd. linkage giving (295) (296) (297) (298)
β-chloropropionyl chloride (3:5690) although the method has been questioned (299) (300).
- C with propylene + AlCl₃ as directed (301) gives β-chloroisobutyryl chloride (3:9101).]
|C with acetylene (302) or acetylene homologs (303) gives complex condensation products suitable for molding.

With alcohols. \bar{C} with alcohols reacts according to circumstances with either 1 mole alcohol giving the corresponding chloroformate (chlorocarbonate) esters, or with 2 moles alcohol giving the corresponding carbonate ester. The countless known cases cannot here be cited in detail but the following examples are given; see also the summary of Dyson (308).

Č with MeOH (1:6120) gives (304) methyl chloroformate (3:5075) q.v. and/or dimethyl carbonate (1:3046); Č with EtOH (1:6130) gives ethyl chloroformate (3:7295) q.v. and/or diethyl carbonate (1:3150); Č with n-PrOH (1:6150) gives n-propyl chloroformate (3:7540) q.v. and/or di-n-propyl carbonate (1:3373); Č with isopropyl alcohol (1:6135) gives isopropyl chloroformate (3:7405) q.v. and/or di-isopropyl carbonate (1:3261); Č with n-butyl alcohol (1:6180) gives n-butyl chloroformate (3:7980) q.v. and/or di-n-butyl carbonate (1:3626); Č with isobutyl alcohol (1:6165) gives isobutyl chloroformate (3:7760) q.v. and/or di-isobutyl carbonate (1:3501); Č with n-AmOH (1:6205) presumably gives n-amyl chloroformate (3:9380) q.v., but di-n-amyl carbonate appears to be unreported; Č with isoamyl alcohol (1:6200) gives isoamyl chloroformate (3:8215) q.v. and/or di-isoamyl carbonate (1:3937).

 $\ddot{\mathbf{C}}$ with allyl alcohol (1:6145) gives allyl chloroformate (3:7487) q.v. and/or diallyl carbonate; $\ddot{\mathbf{C}}$ with cyclohexanol (1:6415) gives cyclohexyl chloroformate (3:5770) q.v.; $\ddot{\mathbf{C}}$ with benzyl alcohol (1:6480) gives benzyl chloroformate (3:9565) q.v. — [For analogous reaction of $\ddot{\mathbf{C}}$ with unsatd. monohydric alcohols such as methallyl alcohol, crotyl alcohol, etc., see (305).]

 \bar{C} with monohydroxyethers gives analogous products: e.g., \bar{C} with β -methoxyethanol (1:6405) gives β -methoxyethyl chloroformate (3:9140) q.v.; \bar{C} with β -ethoxyethanol (1:6410) gives β -ethoxyethyl chloroformate (3:9280) q.v. — [For reaction of \bar{C} with polyhydroxyethers such as diethylene glycol (1:6525), triethylene glycol (1:6538), tetra-ethylene glycol, etc., giving corresp. bis-(chloroformates), see (306).]

[For study of behavior of C toward various alkali alkoxides see (307).]

[Note that \tilde{C} as liq. reacts with enol form of acetone (1:5900) in $\frac{1}{2}$ hr. at room temp. giving (330) isopropenyl chloroformate (3:7358).]

With phenols. The reaction of \bar{C} with phenols is more sluggish than with alcohols, and the corresp. diaryl carbonates are usually obtained from \bar{C} with 2 moles of the corresponding sodium phenolate cf. (308).

[\bar{C} (as liquid) with phenol (1:1420) in s.t. at 140–150° (309), or \bar{C} in toluene (310) or trichloroethylene (3:5170) (311) with aq. phenol (311) or aq. Na phenolate (310), or \bar{C} with Na phenolate in toluene (312), or \bar{C} with 10% aq. Na phenolate at 30° (313) gives (yields: 45% (312), 44% (313)) phenyl chloroformate [Beil. VI-159, VI₁-(88), VI₂-(157)], b.p. 97–98° at 25 mm. (310), 83–84° at 12 mm. (313), $n_D^{11} = 1.5180$ (313); for use as acylating agent see (314).]

[C in toluene shaken with a soln. of o-cresol (1:1400) in aq. NaOH (310) (315) gives o-tolyl chloroformate [Beil. VI-356], b.p. 119° at 35 mm. (310), 114° at 25 mm. (310). — C in toluene shaken with a soln. of m-cresol (1:1730) in aq. NaOH (315) gives m-tolyl chloroformate [Beil. VI-379], b.p. 103° at 22 mm. (315). — C in toluene shaken with a soln. of p-cresol (1:1410) in aq. NaOH (315), or C passed as gas into aq. Na p-cresolate below 10° (316), gives (78–80% yield (316)) p-tolyl chloroformate [Beil. VI-398, Vl₂-(380)], b.p. 108° at 30 mm. (315) (316).]

Countless other phenois behave with $\tilde{\mathbf{C}}$ in generally similar fashion but cannot be detailed here.

With carboxylic and sulfonic acids. Č with carboxylic acids or sulfonic acids or their salts at elevated temps, or in pres. of tertiary bases effects conversion to the corresponding carboxylic acid chlorides or sulfonyl chlorides.

[E.g., Č with AcOH (1:1010) at 110-120° (317), or at 160° over MgCl₂ on diatomaceous earth (318) cf. (319) (320), or Č with NaOAc at 120° under press. (321), or Č with Ac₂O (1:1015) + cat. (322) gives acetyl chloride (3:7065). — Č with chloroacetic acid (3:1370) over activated carbon at 200° gives (323) chloroacetyl chloride (3:5235). — Č with anhydrous oxalic acid (1:0535) in pres. of tertiary amines yields (324) oxalyl (di)chloride

(3:5060). — \bar{C} with cinnamic acid (1:0735) in pres. of tertiary amines yields (324) cinnamoyl chloride (3:0330). — \bar{C} with phenoxyacetic acid (1:0680) in pres. of tertiary amines yields (324) phenoxyacetyl chloride (3:8790). — \bar{C} with lauric acid (1:0605) at 140–150° gives (85–90% yield (325)) lauroyl chloride (3:9858). — \bar{C} with palmitic acid (1:0650) at 140–150° gives (70–75% yield (325)) palmitoyl chloride (3:9912). — \bar{C} with stearic acid (1:0660) at 140–150° gives (70–75% yield (325)) stearoyl chloride (3:9960). — \bar{C} with oleic acid (1:0565) gives (325) oleoyl chloride (3.9940).]

[\bar{C} with benzoic acid (1:0715) at 140-200° (326), or in pres. of tertiary bases or their salts (324), or \bar{C} with AgOBz in s.t. at 100° (327) gives benzoyl chloride (3:6240). — \bar{C} with salicylic acid (1:0780) in toluene (328) or in C_6H_6 in presence of tertiary bases (324) gives salicyloyl chloride (3:0085). — \bar{C} with furoic acid (1:0475) under press. at not above 100° gives (329) furoyl chloride (3:8515).]

[Many other cases including sulfonic acids, e.g., (324), cannot be detailed here.]

With amines. With primary amines. \bar{C} with primary amines reacts in various ways according to conditions to yield N-alkyl (or aryl) carbamyl chlorides, N-alkyl (or aryl) isocyanates, or N,N'-dialkyl (or aryl) ureas. Examples of these types of reaction are included below.

 $|\bar{C}|$ with CH₃NH₂.HCl at 250–300° gives (285) (331) N-methylcarbamyl chloride [Beil. IV-64]; for stabilization of this prod. by formn. of insol. compds. with AlCl₃, etc., see (332); note that treatment with CaO causes loss of HCl giving (285) methyl isocyanate [Beil. IV-77, IV₁-(337), IV₂-(578)], best prepd. by other means, e.g., from NaN₃ with Ac₂O (333) or AcCl (334) (335). — \bar{C} with CH₃NH₂ in C₆H₆ + aq. alkali, however, gives N,N'-dimethylurea [Beil. IV-65, IV₁-(331), IV₂-(568)], m.p. 106°.]

[Č with $C_2H_5NH_2$.HCl at 250-300° gives (285) N-ethylcarbamyl chloride [Beil. IV-114]; note that treatment of this prod. with CaO causes loss of HCl giving (285) ethyl isocyanate [Beil. IV-122, IV₁-(357), IV₂-(613)], b.p. 60°.]

[Č with other primary aliphatic or cycloaliphatic amine hydrochlorides under conditions such that HCl is removed from reaction mixt. gives corresp. isocyanates (336) cf. (337).]

[C with aniline hydrochloride presumably yields N-phenylcarbamyl chloride [Beil. XII-346, XII₁-(230)], m.p. 58-59°, but this compound is usually prepd. by other means (338) (339) since it readily loses HCl at 90-100° or by action of aq. or aq. alk. (340) giving phenyl isocyanate; for stabilization of N-phenylcarbamyl chloride by formn. of molecular compound with AlCl₃ see (332). — C in dry aniline (341) or aq. aniline (342) (96) gives N,N'-diphenylurea (carbanilide) [Beil. XII-352, XII₁-(233)], m.p. 238°; for use of this reaction as method of quant. detn. of C see (94) (95) cf. (91). — C with fused aniline HCl or carbanilide (343), or C with aniline HCl in C₆H₆ at 120° under press. (344) cf. (337), gives phenyl isocyanate [Beil. XII-437, XII₁-(259)], b.p. 166°.]

 \bar{C} with countless other arom. prim. amines behaves in generally similar fashion but details cannot be included here [however, for reaction of \bar{C} with p-nitroaniline in EtOAc soln. giving N-p-nitrophenylcarbamyl chloride which on recrystn. from CCl₄ loses HCl yielding p-nitrophenyl isocyanate see (345) (346) (347)].

With secondary amines. [\bar{C} with $(CH_3)_2NH$ in C_6H_6 at 0° (348) (349), or \bar{C} over fused $(CH_3)_2NH$.HCl (350) (351), gives N,N'-dimethylcarbamyl chloride [Beil. IV-73], b.p. 167°, which with dimethylamine in C_6H_6 yields (349) N,N,N',N'-tetramethylurea [Beil. IV-74, IV₁_(335), IV₂-(574)], liquid, b.p. 177°.]

[$\bar{\mathbf{C}}$ with $(\mathbf{C}_2\mathbf{H}_5)_2\mathbf{NH}$.HCl at elev. temp. (350), or with $(\mathbf{C}_2\mathbf{H}_5)_2\mathbf{NH}$ in $\mathbf{C}_6\mathbf{H}_6$ (352), gives N,N-diethylcarbamyl chloride [Beil. IV-120, IV₂-(611)], liquid, b.p. 186-190°, which with diethylamine gives (353) cf. (354) N,N,N',N'-tetraethylurea [Beil. IV-120, IV₂-(611)], liquid, b.p. 210-215°.]

[C with piperidine HCl would be expected to give N-piperidylformyl chloride ("penta-

methylenecarbamyl chloride") [Beil. XX-54], b.p. 237-238°, but this compound has been reported only by other means.]

Č with aromatic secondary amines behaves in generally analogous fashion but cannot be detailed here.

With tertiary amines. [\bar{C} with N,N-dimethylaniline at ord. temp. is claimed (355) (356) to give 4,4'-bis-(dimethylamino)benzophenone ("Michler's ketone") [Beil. XIV-89; XIV₁-(391)], m.p. 174°. However, \bar{C} passed into boilg. N,N-dimethylaniline evolves CH₂Cl (3:7005) and gives (almost quant. yield (357)) N,N'-dimethyl-N,N'-diphenylurea [Beil. XII-418, XII₁-(251)], m.p. 121° — Similarly, \bar{C} with boilg. N,N-diethylaniline evolves C₂H₅Cl (3:7015) and gives N,N'-diethyl-N,N'-diphenylurea [Beil. XII-422], m.p. 79°.]

[For use of \bar{C} in sepn. of a mixture of aniline, N-ethylaniline, and N,N-diethylaniline see (361).]

With arylhydrazines. [C in toluene added to cold ether soln of phenylhydrazine gives (358) 1,5-diphenylcarbohydrazide ("diphenylcarbazide") [Beil. XV-292, XV₁-(72)], m.p. 175-175.5° u.e. when pure (359). For use of this reaction, followed by CuSO₄ treatment of the resultant product, as a delicate test for C see (78).]

With other nutrogenous organic reactants. [For a concise review of behavior of $\bar{\mathbf{C}}$ with other nitrogenous classes such as amides, amidoximes, thioureas, thiosemicarbazides, etc., see the review of Dyson (360).]

With hexamethylenetetramine \bar{C} with hexamethylenetetramine in CHCl₃ gives (362) (363) (364) a compound of compn $\bar{C}.2C_6H_{12}N_4$, mp 187–190° dec., (363) 196–197° from MeOH (364). — [For use of hexamethylenetetramine in paints protective against \bar{C} see (365); for use of alumina or silica gels contg. hexamethylenetetramine as absorbents for \bar{C} see (366).]

3:5000 (1) Emmerling, Lengyel, Ann. Suppl 7, 101-107 (1870); Ber. 2, 546-548 (1869). (2) Beckmann, Z anorg. Chem. 55, 370-379 (1907). (3) Nikitin, J. Russ. Phys.-Chem. Soc. 52, 235-249 (1920); Cent. 1923, III 1557; C.A. 17, 1357 (1923). (4) Paterno, Mazzucchelli, Gazz. chim. ital. 50, 1 30-53 (1920), Cent. 1920, III 43; C.A. 14, 2921-2922 (1920). (5) Stock, Wustrow, Z. anorg. allgem. Chem. 147, 245-255 (1925). (6) Atkinson, Heycock, Pope, J. Chem. Soc. 117, 1410-1426 (1920). (7) Erdmann, Ann. 362, 148 (1908). (8) Germann, Taylor, J. Am. Chem. Soc. 48, 1154-1159 (1926). (9) Davy, Phil. Trans. Roy. Soc. 102, 144-151 (1812). (10) Dobbin, Ann. Sci. 5, 270-287 (1945), C.A. 39, 4781 (1945).

(11) Dyson, Chem. Revs. 4, 109-165 (1927). (12) Melnikov, J. Chem. Ind. (Moscow) 1932, No. 9, 20-25; [Cent. 1933, I 652]; [C.A. 27, 708 (1933)] (13) Shiver, J. Chem. Education 7, 98-100 (1930). (14) Jackson, J. Chem. Education 10, 622-626 (1933). (15) Labat, Bull. trav. soc. pharm. Bordeaux 72, 106-113 (1934); [Cent. 1934, II 2209]; not in C.A. (16) Fries, West, "Chemical Warfare," McGraw-Hill Book Co., 1921, pp. 126-136. (17) Prentiss, "Chemicals in War," McGraw-Hill Book Co., 1937, pp. 154-157. (18) Sartori, "The War Gases," D. Van Nostrand Co., 1940, pp. 59-74. (19) Jacobs, "War Gases," Interscience Publishers, 1942, pp. 48-49, 103-104. (20) Spender, Flannagan, J. Am. Chem. Soc. 64, 2511-2513 (1942).

(21) Thompson, Trans. Faraday Soc. 37, 251-260 (1941). (22) Stevenson, Beach, J. Chem. Phys. 6, 27-28, 341 (1938). (23) C. G. Le Fevre, R. J. W. Le Fevre, J. Chem. Soc. 1935, 1700-1701. (24) Smyth, McAlpine, J. Am. Chem. Soc. 56, 1697-1700 (1934). (25) Schlundt, Germann, J. Phys. Chem. 29, 353-355 (1925). (26) Dornte, J. Am. Chem. Soc. 55, 4126-4130 (1933). (27) Henri, Howell, Proc. Roy. Soc. (London) A-128, 177-189, 190-191, 192-214 (1930). (28) Brockway, Beach, Pauling, J. Am. Chem. Soc. 57, 2693-2704 (1935). (29) Lowery, Proc. Roy. Soc. (London) A-133, 195-196 (1931). (30) Hackspill, Mathieu, Bull. soc. chim. (4) 25, 482-485 (1919).

(31) Baskerville, Cohen, J. Ind. Eng. Chem. 13, 333-334 (1921). (32) Kireev, Kaplan, Vasneva, J. Gen. Chem. (U.S.S.R.) 6, 799-805 (1936); Cent. 1937, II 755; C.A. 30, 7013 (1936). (33) Kireev, Kaplan, Zlobin, J. Applied Chem. (U.S.S.R.) 8, 949-951 (1935); Cent. 1937, I 3474; C.A. 30, 5484 (1936). (34) Soc. anon. des produits chimiques du centre, French 802,573, Sept. 8, 1946; Cent. 1936, II 3750-3751, C.A. 31, 1923 (1937). (35) Berolzheimer, J. Ind. Eng. Chem. 11, 263-266 (1919). (36) Ramat, Bull. soc. chim. (5) 7, 492-495 (1940); C.A. 36, 3413 (1942).

- (37) Arii, Huzita, Bull. Inst. Phys. Chem. Research (Tokyo) 20, 209-217 (1941); C.A. 35, 3504 (1941).
 (38) Bardan, Scarlatescu, Bull. soc. chem. (5) 6, 46-55 (1939).
 (39) Bardan, Popa, Compt. rend. inst. sci. Roumanie 3, 675-682 (1939); C.A. 36, 6695 (1942).
 (40) Engelhard, Stiller, Z. Elektrochem 49, 833-836 (1934); Cent. 1935, I 3257; C.A. 29, 2046 (1935).
- (41) Remy, Hene, Kolloid-Z. 61, 313-322 (1932). (42) Nielsen, Z. ges. Schiess- u. Sprengstoffw. 27, 136-139, 170-173, 208-211, 244-248, 280-284 (1932); Cent. 1932, II 3281-3282, [C.A. 26, 4658, 6035 (1932)]. (43) Engel, Z. ges. Schiess- u. Sprengstoffw. 24, 451-454, 495-497 (1929); Cent. 1936, I 1281; C.A. 24, 1265 (1930). (44) Herbst, Biochem. Z. 118, 103-119 (1921); Cent. 1932, I 163; C.A. 15, 3009 (1921). (45) Bunbury, J. Chem. Soc. 121, 1525-1528 (1922). (46) Comp. Française de Produits Organo-chimiques, French 742,153, March 1, 1933; Cent. 1933, I 3612; C.A. 27, 3568 (1933): French addition 42,779, Oct. 10, 1933; Cent. 1934, I 537; C.A. 28, 867 (1934). (47) Valkenburg, Rec. trav. chim. 57, 1286-1289 (1938). (48) Jacobs, "Analytical Chemistry of Industrial Poisons, Hazards and Solvents," Interscience Publishers, 1941, p. 304. (49) Fieldner, Katz, Kinney, U.S. Bur. Mines, Tech. Paper 248 (1921). (50) Sayers, Dallavalle, Yant, Ind. Eng. Chem. 26, 1251-1255 (1934).
- (51) Wilkes, Matheson, Chemistry & Industry 1939, 316-323; C.A. 33, 4696 (1939). (52) Hunter, Pharm. J. 137, 514-515, 539 (1936); C.A. 31, 6582 (1937). (53) Rothlin, Schweiz. med. Wochschr. 71, 1526-1532 (1941); C.A. 36, 6244 (1942). (54) Gwan, Proc. Acad. Sci. Amsterdam 44, 205-216 (1941); C.A. 37, 464 (1943). (55) Boyland, McDonald, Rumens, Brit. J. Pharmacol. 1, 81-89 (1946); C.A. 40, 6661 (1946). (56) Plucke, Z. Untersuch. Lebensm. 68, 313-320 (1934). (57) Schoofs, J. pharm. Belg. 21, 793-802 (1939); Cent. 1943, I 1010; C.A. 38, 5984 (1944). (58) Linn, Ipatieff (to Universal Oil Products Co.), U.S. 2,381,828, Aug. 7, 1945; C.A. 39, 4748, 5465, (1945). (59) Greenhalgh and Imperial Chem. Ind., Ltd., British 488,036, June 29, 1938; C.A. 33, 178 (1939). (60) Robertson, J. S. African Chem. Inst. 12, 39-49 (1929); Cent. 1930, I 2774-2775; C.A. 25, 3282-3283 (1931).
- (61) Adams, Coleman, Org. Syntheses, Coll. Vol. 1 (2nd ed) 214-217 (1941); (1st ed.), 208-211 (1932); 2, 17-21 (1922). (62) Fenton, J. Chem. Education 21, 488-489 (1944). (63) Zais, J. Chem. Education 21, 489-490 (1944). (64) Fenton, J. Chem. Education 20, i.64 (1943). (65) Claffin, Hickey, J. Chem. Education 20, 351-357 (1943). (66) Hoogeveen, Chemistry & Industry 1940, 550-556. (67) Vallender, Chemistry & Industry 1939, 330-333. (68) Patty, Am. J. Pub. Health 30, 1191-1198 (1940). (69) Grogg, Protar 4, 144-150, 164-170, 184-192 (1938); C.A. 33, 263 (1939). (70) Rosenthaler, Pharm. Acta Helv. 12, 6-7 (1937); C.A. 31, 2358 (1937).
- (71) Suchier, Z. anal. Chem. 79, 183-185 (1929).
 (72) Chema, Ltd., and Sigmund, Brit. 519,957, April 10, 1940; C.A. 36, 589 (1942).
 (73) Schröter (to O. H. Drager), U.S. 2, 103,187, Dec. 21, 1937; C.A. 32, 1214 (1938).
 (74) Kretov, J. Applied Chem. (U.S.S.R.) 2, 483-501 (1929); [Cent. 1929, II 2230]; C.A. 24, 313-314 (1930).
 (75) Studinger, Chemistry & Industry 56, 225-227 (1937); Mitt. Lebensm. Hyg. 27, 8-20 (1936).
 (76) Cox, Analyst 64, 807-813 (1939).
 (77) Liebermann, Ber. 24, 1106-1107 (1891).
 (78) Anger, Wang, Mikrochim. Acta 3, 24-26 (1938); C.A. 32, 3295 (1938).
 (79) Allport, Analyst 56, 706-710 (1931).
 (80) Gilman, Sweeney, Heck, J. Am. Chem. Soc. 52, 1604-1607 (1930).
- (81) Gilman, Heck, J. Am. Chem. Soc. 52, 4953 (1930). (82) Pu, Lo, J. Chinese Chem. Soc. 8, 140-142 (1941); C.A. 37, 6053 (1943). (83) Fieldner, Oberfell, Teague, Lawrence, J. Ind. Eng. Chem. 11, 523,527 (1919). (84) Fieldner, Katz, Kinney, Longfellow, J. Frankin Inst. 196, 543-565 (1920); C.A. 15, 294 (1921). (85) Delépine, et al., Bull. soc. chim. (4) 27, 283-295 (1920). (86) Bredig, von Goldberger, Gas- u. Wasserfach 67, 490-491 (1924); Cent. 1924, II 2307; C.A. 19, 1112 (1925). (87) Reeves, J. Soc. Chem. Ind. 43, 279-280T (1924); Cent. 1924, II 2065-2066; C.A. 19, 24 (1925). (88) Stock, Wustrow, Z. anorg. allgem. Chem. 195, 129-139 (1931). (89) Nenitzescu, Pana, Bul. Soc. Chim. România 15, 45-48 (1933); Cent. 1933, II 3890; C.A. 28, 73 (1934). (90) Matuszak, Ind. Eng. Chem., Anal. Ed. 6, 374-375 (1934).
- (91) Olsen, Ferguson, Sabetta, Scheflan, Ind. Eng. Chem., Anal. Ed. 3, 189-191 (1931). (92) Jahresber. der Chem.-Techn. Reichsanstatt 5, 11-20 (1926). (93) Matuszak, Ind. Eng. Chem., Anal. Ed. 6, 457-459 (1934). (94) Kling, Schmutz, Compt. rend. 168, 773,891 (1919). (95) Yant, Olsen, Storch, Littlefield, Scheflan, Ind. Eng. Chem., Anal. Ed. 8, 20-25 (1936). (96) Vles, Rec. trav. chim. 53, 962-964 (1934). (97) Martin, Oettingen, Kuhn, Z. anal. Chem. 117, 305-317 (1939); C.A. 34, 47 (1940). (98) Berthelot, Bull. soc. chim. (2) 13, 15-16 (1870). (99) Steacie, Smith, Can. J. Research 16-B, 1-5 (1938); C.A. 32, 2866 (1938). (100) Hanson, Ind. Eng. Chem., Anal. Ed. 13, 119-123 (1941).
- (101) Wilm, Wischin, Ann. 147, 150-157 (1868). (102) Wildermann, Phil. Trans. Roy. Soc. London A-199, 337-397 (1902); Z. physik. Chem. 42, 257-335 (1902). (103) Dyson, Harden, J. Chem. Soc. 83, 201-205 (1903). (104) Weigert, Ann. Physik (4) 24, 55-67, 243-266 (1907). (105) Coehn, Becker, Ber. 43, 130-133 (1910). (106) Chapman, Gee, J. Chem. Soc. 99, 1726-1739 (1911). (107) Fye, Beaver, J. Am. Chem. Soc. 63, 2395-2400 (1941). (108) Brenschede,

Z. physik. Chem. B-41, 254-286 (1938). (109) Brenschede, Z. physik. Chem. B-41, 237-253 (1938). (110) Bodenstein, Brenschede, Schumacher, Z. physik. Chem. B-49, 121-134 (1938).

(111) Franke, Schumacher, Z. physik. Chem. B-40, 115-120 (1938). (112) Bodenstein, Brenschede, Schumacher, Z. physik. Chem. B-35, 382-402 (1937). (113) Rollefson, Z. physik. Chem. B-37, 472-473 (1937). (114) Bodenstein, Brenschede, Schumacher, Z. physik. Chem. B-28, 81-94 (1935). (115) Rollefson, J. Am. Chem. Soc. 56, 579-583 (1934). (116) Rollefson, J. Am. Chem. Soc. 55, 148-152 (1933). (117) Warming, Z. physik. Chem. B-18, 156-158 (1932). (118) Rollefson, Trans. Faraday Soc. 27, 465-468 (1931). (119) Kistiakowsky, Z. angew. Chem. 44, 602-605 (1931). (120) Schumacher, Stieger, Z. physik. Chem. B-13, 169-189 (1931).

(121) Schumacher, Stieger, Z. physik. Chem. B-13, 157-168 (1931). (122) Bodenstein, Chem. Revs. 7, 225-229 (1930). (123) Schumacher, J. Am. Chem. Soc. 52, 3133-3136 (1930). (124) Alyea, Lind, J. Am. Chem. Soc. 52, 1853-1868 (1930). (125) Lenher, Rollefson, J. Am. Chem. Soc. 52, 500-506 (1930). (126) Schultze, Z. physik. Chem. B-5, 368-384 (1929). (127) Bodenstein, Lenher, Wagner, Z. physik. Chem. B-3, 459-478 (1929). (128) Bodenstein, Onoda, Z. physik. Chem. 131, 153-174 (1928). (129) Cathala, J. chim. phys. 25, 190-194 (1928). (130) Cathala, J. chim. phys., 24, 663-711 (1927).

(131) Bodenstein, Z. physik. Chem. 130, 422-448 (1927). (132) Schumacher, Z. physik. Chem. 129, 241-261 (1927). (133) Cathala, Bull. soc. chim. (4) 33, 576-581 (1923). (134) Bodenstein, Rec. trav. chim. 41, 585-591 (1921). (135) Bodenstein, Plaut, Z. physik. Chem. 110, 399-416 (1924). (136) Schutzenberger, Ann. chim. (4) 21, 350-362 (1870); Ann. Suppl. 8, 242-254 (1872). (137) Chem. Fabrik Schering, Ger. 369,369, Feb. 17, 1923; Cent. 1923, II 909; not in C.A. (138) Plotnikow, J. Russ. Phys.-Chem. Soc. 48, 457-458 (1916); Cent. 1923, I 1490; C.A. 11, 764 (1917). (139) Williams (to du Pont Ammonia Corp.), U.S. 1,746,506, Feb. 11, 1930; Cent. 1930, I 2629; [C.A. 24, 1710 (1930)]. (140) Gobel, J. prakt. Chem. (1) 6, 388 (1835).

(141) Belladen, Noli, Sommariva, Gazz. chim. ital 58, 443-449 (1928). (142) Diemer, J. Am. Chem. Soc. 35, 555 (1913). (143) Hofmann, Ann. 70, 139 (1849). (144) Manchot, Lehmann, Ber. 63, 1221-1224 (1930). (145) Martin-Wedard, French 487,617, Oct. 12, 1939; C.A. 35, 5509 (1941). (146) Hamilton, Ind Eng. Chem. 25, 539-541 (1933). (147) Fieldner, Katz, U.S. Bur. Mines, Rept. Investigations 2262 (1921). (148) Hofmann, Rohr, Ger. 571,693, April 29, 1933; Cent. 1933, I 4003; C.A. 27, 4365 (1933). (149) I.G., French 676,753, Feb. 27, 1930; Cent. 1930, I 2936; C.A. 24, 3093 (1930): Brit 319,320, Nov. 13, 1929; Cent. 1930, I 719; C.A. 24, 2849 (1930). (150) Minimax, A. G., Ger. 645,137, May 24, 1937; Cent. 1937, II 1864; C.A. 31, 6382 (1937).

(151) Pearce, Scheflan, Schienk, Ferguson, Brown, U.S. Bur. Mines, Rept. Investigations 3686 (18 pp.) (1943); C.A. 37, 2578-2579 (1943). (152) Esser, Gasschutz u. Luftschutz 8, 266-269, 297-298 (1938); C.A. 33, 777 (1939). (153) Lyons, Dickinson, J. Am. Chem. Soc. 57, 443-446 (1935). (154) Harteck, Kopsch, Z. physik. Chem. B-12, 327-347 (1931). (155) Bodenstein, Günther, Hofmeister, Z. angew. Chem. 39, 875-880 (1926). (156) Biesalski, Z. angew. Chem. 37, 315-317 (1924). (157) Dede, Russ, Ber. 61, 2462 (1928). (158) Erdmann, Ber. 26, 1990-1994 (1893). (159) Lepin, J. Russ. Phys.-Chem. Soc. 52, 1-17 (1920); Cent. 1923, III 823; C.A. 17, 1395 (1923). (160) Oddo, Sconzo, Gazz. chim. ital. 57, 91, 99-102 (1927).

(161) Armstrong, J. prakt. Chem. (2) 1, 245-248 (1870). (162) Schutzenberger, Bull. soc. chim. (2) 12, 198-200 (1869). (163) Grignard, Urbain, Compt. rend. 169, 17-20 (1919). (164) Schutzenberger, Compt. rend. 66, 748-749 (1868). (165) Gustavson, Ber. 5, 30 (1872). (166)Budnikov, Voznesenskii, J. Russ. Phys.-Chem. Soc. 56, 73-79 (1925); C.A. 19, 3148 (1925): Budnikov, Chem. Ztg. 49, 430-431 (1925); Cent. 1925, II 533-534. (167) Baskerville, Hamor, J. Ind. Eng. Chem. 4, 281-288, 362-364 (1912). (168) Schoorl, van der Berg. Pharm. Weekblad 43, 8-10 (1906); Cent. 1906, I 442. (169) Schoorl, van der Berg, Pharm. Weekblad 42, 877-888 (1905); Cent. 1905, II 1623. (170) Mossler, Monatsh. 29, 573-581 (1908).

(171) Hill, J. Am. Chem. Soc. 54, 32-40 (1932). (172) Chatterji, Dhar, Z. anorg. allgem. Chem. 191, 155-160 (1930). (173) Clover, J. Am. Chem. Soc. 45, 3133-3138 (1923). (174) Chapman,
 J. Am. Chem. Soc. 57, 419-422 (1935). (175) Chapman, J. Am. Chem. Soc. 57, 416-419 (1935). (176) Schumacher, Sundhoff, Z. physik. Chem. B-34, 300-308 (1936). (177) Schumacher, Wolff, Z. physik. Chem. B-26, 453-462 (1934). (178) Kautsky, Thiele, Z. anorg. allgem. Chem. 144, 213 (1925). (179) Harries, Ann. 343, 340 (1905). (180) Erdmann, Ann. 362, 147-148

(181) Biosalski, Z. angew. Chem. 37, 314-317 (1924). (182) Davis, McLean, J. Am. Chem. Soc. 60, 720-722 (1938). (183) Schott, Schumacher, Z. physik. Chem. B-49, 107-125 (1941); Cent. 1941, II 2549; C.A. 38, 3551 (1944). (184) Dickinson, Carrico, J. Am. Chem. Soc. 56, 1473-1480 (1934). (185) Dickinson, Leermakers, J. Am. Chem. Soc. 54, 3852-3862 (1932). (186) Erdmann, J. prakt. Chem. (2) 85, 78-89 (1912); cf. Staudinger, ibid. 330-333 (1912). (187) Dewar, Cranston, Chem. News 20, 174 (1869). (188) Alexander, Schumacher, Z. physik. Chem. B-44, 313-326 (1939). (189) Stauff, Schumacher, Z. physik. Chem. B-48, 154-175 (1941). (190) Gauthier, Bull. soc. chim. (2) 45, 86-88 (1886).

(192) Underwood, Baril, J Am. Chem. (191) Böeseken, Rec. trav. chim. 29, 104-108 (1910). Soc. 57, 2730 (1935). (193) Benrath, Ann. 382, 224 (1911). (194) Jaeger, Cent. 1912, I 1817. (195) Simons, Sloat, Meunier, J. Am. Chem. Soc. 61, 435-436 (1939). (196) Gassner, Z. hyg. Zool. Schädlingsbekämpf. 32, 225 (1940); C.A. 36, 3293 (1942). (197) Gruss, Z. Elektrochem. 29, 147 (1923). (198) Hood, Murdock, J. Phys. Chem. 23, 498-514 (1919). (199) Marotta, Gazz. chim. ital. 59, 959 (1929). (200) Hentschel, J. prakt. Chem. (2) 36, 99-113, 209-218, 305-317, 468-480 (1887).

(201) Fichter, Fritsch, Muller, Helv. Chim. Acta 6, 504-505 (1923). (202) Hentschel, J. prakt. Chem. (2) 36, 103, 314 (1887). (203) Melnikov, J. Russ. Phys.-Chem. Soc. 62, 2019-2022 (1930); Cent. 1931, I 2864; [C.A. 25, 4228 (1931)]. (204) Nekrasov, Melnikov, J. prakt. Chem. (2) 126 81-96 (1930). (205) Nekrasov, Melnikov, J. prakt. Chem. (2) 127, 210-218 (1930). Melnikov, J. Gen. Chem. (U.S.S.R.) 4, 1057-1060 (1936); Cent. 1936, I 3131; not in C.A. (207) Cahours, Ann. chim. (3) 19, 344-349 (1847); Ann. 64, 313-314 (1848). (208) Birckenbach, Goubeau, Ber. 64, 218-227 (1931). (209) Ramsperger, Waddington, J. Am. Chem. Soc. 55, 214-220 (1933). (210) Piutti, Mazza, Gazz. chim. ital. 57, 612-614 (1927); Cent. 1927, I 240; C.A. 22, 356 (1928).

(211) Gardner, Fox, J. Chem. Soc. 115, 1188-1194 (1919). (212) Silberrad, Chem. News 123, 271 (1921); Cent. 1922, I 403; C.A. 16, 1073 (1922). (213) Secareano, Bull. soc. chim. (4) 41, 630-631 (1927). (214) Berzelius, Marcet, Gilbert's Annalen 48, 161 (1814). (215) Schutzenberger, Ber. 2, 219 (1869). (216) Delépine, Bull. soc. chim. (4) 31, 775, 781-782 (1922). (217) Gustavson, Ber. 3, 990 (1870). (218) Boeseken, Rec. trav. chim. 32, 11-12 (1913). (219) Staudinger, Ber. 41, 3565-3566 (1908). (220) Goldschmidt, Ber. 14, 928-929 (1881).

(221) Stock, Wustrow, Lux, Ramser, Z. anorg. allgem. Chem. 195, 140-148 (1931). (222) Ingleson, J. Chem. Soc. 1927, 2244-2254. (223) Christiansen, Z. physik. Chem. 103, 99-138 (1922). (224) Bodenstein, Dunant, Z. physik. Chem. 61, 437-446 (1908). (225) Fink, Bonilla, J. phys. Chem. 37, 1152-1167 (1933). (226) Berthelot, Gaudchon, Compt. rend. 156, 1245 (1913). (227) Montgomery, Rollefson, J. Am. Chem. Soc. 56, 1089-1092 (1934). (228) Kassel, J. Am. Chem. Soc. 56, 243 (1934). (229) Montgomery, Rollefson, J. Am. Chem. Soc. 55, 4025-4035 (1933). (230) Rollefson, Montgomery, J. Am. Chem. Soc. 55, 142-147 (1933).

(231) Almasy, Wagner-Jauregg, Z. physik. Chem. B-19, 405-419 (1932); Naturwissenschaften 19, 270 (1931). (232) Kuhn, Martin, Z. physik. Chem. B-19, 93-137 (1933); Naturwissenschaften 20, 772 (1932). (233) Germann, Science 61, 70-71 (1925). (234) Bredig, von Goldberger, Z. physik. Chem. 110, 521-546 (1924). (235) von Wartenberg, Muchlinski, Riedler, Z. angew. Chem. 37, 458 (1924). (236) Fohlen, French 680,586, May 2, 1930, Cent 1930, II 2829; [C.A. 24, 3799 (1930)]. (237) Delépine, Douris, Ville, Bull. soc. chim. (4) 27, 286-288 (1920). (238) Rona, Z. ges. exptl. Med. 13, 16-30 (1921); Cent. 1921, III 374; C.A. 15, 1933 (1921). (239) Böhme, Ber. 74, 248-256 (1941). (240) Velasco, Anales soc. españ. fís. quím. 37, 254-262 (1941); C.A. 37, 4614 (1943).

(241) Ref. 11, pp. 128-132. (242) Chauvenet, Compt. rend. 147, 1046-1048 (1908); 152, 87, 89 (1911). (243) Matignon, Cathala, Compt. rend. 181, 1066-1068 (1925); 182, 601 (1926). (244) Stock, Kuss, Ber. 50, 161 (1917). (245) Nuricsau, Ber. 24, 2967-2974 (1891). (246) Chauvenet. Compt. rend. 152, 1250-1252 (1911). (247) Barlot, Chauvenet, Compt. rend. 157, 1153-1155 (1913). (248) Dunn, Briers (to Imperial Chem. Ind., Ltd.), Brit. 337,123, Nov. 20, 1930; Cent. 1931, I 665; C.A. 25, 1956 (1931). (249) Brode, Wursten (to I.G.), Ger. 502,884, July 18, 1930; Cent. 1930, II 1753; not in C.A. (250) Ruff, Miltschitzky, Z. anorg. allgem. Chem. 221, 154-158 (1934).

(251) Li, J. Chinese Chem. Soc. 11, 14-24 (1944); C.A. 39, 1099 (1945). (252) Fukuhara, Bigelow, J. Am. Chem. Soc. 63, 788-791 (1941). (253) Simons, Herman, Pearlson, J. Am. Chem. Soc. 68, 1672-1673 (1946). (254) Besson, Compt. rend. 120, 190-192 (1895); Bull. soc. chim. 13, 444-445 (1895). (255) von Bartal, Z. anorg. Chem. 55, 152-158 (1907). (256) Schumacher, Lenher, Ber. 61, 1671-1675 (1928). (257) von Bartal, Ann. 345, 334-353 (1906). (258) Rosenmund, Döring, Arch. Pharm. 266, 279 (1928). (259) Koblitz, Meissner, Schumacher, Ber. 70, 1080-1086 (1937). (260) Schumacher, Bergmann, Z. physik. Chem. B-13, 269-284 (1931).

(261) Lenher, Schumacher, Z. physik. Chem. 135, 85-101 (1928). (262) Reerink, Rec. trav. chim. 47, 989-999 (1928). (263) Malachowski, Jurkiewicz, Wojtowicz, Ber. 70, 1012-1016 (1937). (264) Koessler, Hanke, J. Am. Chem. Soc. 40, 1717-1718 (1918). (265) Malachowski, Ger. 666,394, Oct. 19, 1938; Cent. 1939, I 1061; C.A. 33, 2152 (1939). (266) Malachowski, Pisarska, Ber. 71, 2239-2240 (1938). (267) Staudinger, Anthes, Ber. 46, 1426 (1913). (268) Germann, McIntyre, J. Phys. Chem. 29, 102-105 (1925). (269) Germann, J. Phys. Chem. 29, 138-141 (1925). (270) Germann, J. Phys. Chem. 29, 1148-1154 (1925).

Germann, J. Phys. Chem. 28, 879-886 (1924). (272) Germann, Gagos, J. Phys. Chem.
 98, 965-972 (1924). (273) Germann, Jersey, Science 53, 582 (1921). (274) Germann, Timpany,
 J. Phys. Chem. 29, 1423-1431 (1925). (275) Germann, Timpany,
 J. Am. Chem. Soc. 47, 2275-2278 (1925). (276) Germann, Birosel,
 J. Phys. Chem. 29, 1469-1476 (1929). (277) Hantssch;
 Stuer, Ber. 38, 1042 (1905). (278) Werner, Carpenter,
 J. Chem. Soc. 113, 694-697 (1918).
 Natanson, Ann. 98, 287-291 (1856). (280) Regnault, Ann. chem. (2) 69, 180-193 (1838).

(281) Bouchardat, Compl. rend. 69, 961 (1859); Ann. 154, 354-356 (1870). (282) Stuer, Ber. 38, 2326 (1905). (283) Fosse, DeGraeve, Thomas, Compl. rend. 202, 1544-1547 (1936). (284) Ferret, Perrot, Compl. rend. 199, 955-957 (1934). (285) Gattermann, Schmidt, Ann. 244, 30-38 (1888). (286) Theis (to I.G.), U.S. 1,937,328, Nov. 28, 1933; not in Cent., [C.A. 28, 1053 (1934)]: Brit. 396,870, Aug. 17, 1933; not in Cent.; C.A. 28, 488 (1934): Ger. 580,140, July 6, 1933; not in Cent.; C.A. 27, 4887 (1933): French 746,596, June 1, 1933; Cent. 1933, II 1761; C.A. 27, 4636 (1933). (287) Linhard, Betz, Ber. 73, 177-185 (1940). (288) Hantzsch, Sauer, Ann. 299, 91-94 (1898). (289) Jones, Neuffer, J. An. Chem. Soc. 39, 657-659 (1917). (290) Brown, Record

Chem. Progress (Kresye-Hooker Sci. Lib.) 6, 15-20 (1945); [C.A. 39, 3247 (1945)].

(291) Kharasch, Brown, J. Am. Chem. Soc. 62, 454 (1940). (292) Kharasch, Eberly, Kleiman, J. Am. Chem. Soc. 64, 2975-2977 (1942). (293) Antares Trust, Registered, Swiss 165,822, Feb. 16, 1934; Cent. 1934, II 3181; C.A. 28, 2724 (1934). (294) Hochstetter, Ger 292,089, May 22, 1916; Cent. 1916, II 39; [C.A. 11, 1520 (1917)]. (295) Lippmann, Ann. 129, 85-87 (1864). (296) Pace, Gazz. chim. ital. 59, 580-582 (1929). (297) Klebanskii, Chevuichalova, J. Gen. Chem. (U.S.S.R.) 5, 535-548 (1935); Cent. 1935, II 3090, C.A. 29, 6879 (1935); Compt. rend. acad. sci. U.R.S.S. 2, 42-47 (1935); Cent. 1936, I 4895]; C.A. 29, 5814 (1935). (298) Klebanskii, Chevuichalova, Trans. State Inst. Applied Chem. 1937, No. 31, 46-62; Cent. 1938, I 1335; C.A. 34, 6222 (1940). (299) Frolich, Wiezevich, Ind. Eng. Chem. 24, 16 (1934). (300) Varshavskii, Doroganyevskaya, Gazz. chim. ital. 64, 53-59 (1934); Cent. 1934, I 3848; C.A. 28, 5043 (1934).

(301) Reid (to du Pont Co.), U.S. 2,028,012, Jan. 14, 1936, Cent. 1936, II 866; C.A. 39, 1387 (1936). (302) Armour and Co., Brit. 525,184, Aug. 22, 1940; C.A. 35, 6694 (1941). (303) Ralston (to Armour and Co.), U.S. 2,196,445, April 9, 1940, C.A. 34, 5569 (1940). (304) Izard (to du Pont Co.), U.S. 2,020,685, Nov. 12, 1935; Cent. 1936, I 2430; [C.A. 30, 485 (1936)]. (305) Muskat (to Pittsburgh Plate Glass Co.), U.S. 2,370,570, Feb. 27, 1945; C.A. 39, 4087 (1945). (306) Muskat, Strain (to Pittsburgh Plate Glass Co.), U.S. 2,370,568, Feb. 27, 1945; C.A. 39, 4087 (1945). (307) Bowden, J. Chem. Soc. 1939, 310-314. (308) Ref. 11, pp. 149-152. (309) Kempf, J. prakt Chem. (2) 1, 402-407 (1870). (310) Barral, Morel, Compt. rend. 128, 1578-1581 (1899); Bull. soc. chrm. (3) 21, 722-727 (1899).

(311) Hochstetter, Ger. 282,314, Feb. 16, 1915; Cent. 1915, I 464; C.A. 9, 2425 (1915). (312) von Auwers, Shaich, Ber. 54, 1769 (1921). (313) Hoeflake, Rec. trav. chim. 40, 517 (1921). (314) Raiford, Dudley, Proc. Iowa Acad. Sci. 51, 313-317 (1944), C.A. 40, 5179 (1946). (315) Pickard, Littlebury, J. Chem. Soc. 91, 302 (1907). (316) Copisarow, J. Chem. Soc. 1929, 253. (317) Kempf, J. prakt. Chem. (2) 1, 414 (1870). (318) Eggert, Grimm (to I.G.), Ger. 655,683, Jan. 25, 1938; Cent. 1938, I 2445; C.A. 32, 3773, 6672 (1938). (319) I.G., French 754,986, Nov. 17, 1933; Cent. 1934, I 942; C.A. 28, 1361 (1934). (320) I.G., French 755,052, Nov. 18, 1933; Cent. 1934, I 942-943; C.A. 28, 1361 (1934).

(321) Hochstetter, Ger. 284,617, May 31, 1915; Cent. 1915, II 215; C.A. 10, 94 (1916). (322) Stellmann, French 785,075, Aug. 1, 1935; Cent 1935, II 3301, C.A. 30, 490 (1936). (323) Hochstetter, Ger. 283,896, April 27, 1915; Cent. 1915, I 1190; C.A. 10, 93-94 (1916). (324) Soc. Chem. Ind. Basel, Brit. 401,643, Dec. 14, 1933; Cent. 1934, II 2133-2134, not in C.A.: French 732,078, Sept. 12, 1932; Cent. 1934, I 287; C.A. 27, 734 (1933). (325) Prat. Étienne, Bull. soc. chim. (5) 11, 30-34 (1944); C.A. 38, 6274 (1938). (326) Uvarov, Stepanov, Russian 56,693, March 31, 1940; C.A. 36, 2869 (1942). (327) Meyer, Ann. 156, 271, Note (1870). (328) Kopetschni, Karczag, Ger. 266,351, Oct. 21, 1913; Cent. 1913, II 1715; [C.A. 8, 790 (1914)]. (329) Meuser (to Dominion Rubber Co.), Canadian 373,516, May 3, 1938, Cent. 1938, II 3609; C.A. 32, 5003 (1938). (330) Matuszak, J. Am. Chem. Soc. 56, 2007 (1934).

(331) Hamilton, Simpson, J. Am. Chem. Soc. 51, 3160 (1929). (332) I.G., French 797,771, May 4, 1936; C.A. 30, 7292 (1936). (333) Colucci, Can. J. Research 23-B, 111-112 (1945); C.A. 39, 4317 (1945). (334) Pacilly, Rec. trav. chim. 55, 103 (1936). (335) Schroeter, Ber. 42, 3367-3358 (1909). (336) I.G., Brit. 462,182, April 1, 1937; Cent. 1937, I 4882; C.A. 31, 5383 (1937): French 809,233, Feb. 26, 1937; Cent. 1937, I 4882; C.A. 31, 6676 (1937). (337) Greenhalgh, Piggott, and Imperial Chem. Ind., Ltd., Brit. 483,308, May 19, 1938; Cent. 1938, II 1676-1677; C.A. 32, 7056 (1938). (338) Hentzschel, Ber. 18, 1178 (1885). (339) Lengfeld, Stiegler, Am. Chem. J. 16, 73 (1894). (340) Brady, Dunny, J. Chem. Soc. 123, 1790, 1802-1803 (1923).

(341) Hofmann, Ann. 70, 140 (1849).
 (342) Hentzschel, J. prakt. Chem. (2) 27, 499 (1883).
 (343) Hentzschel, Ber. 17, 1284-1285 (1884).
 (344) Vereinigte Chininfabriken Zimmer und Co.,

Ger. 133,760, July 29, 1902; Cent. 1902, II 553-554. {345} Shriner, Cox, J. Am. Chem. Soc. 53, 1603-1604 (1931). {346} Horne, Shriner, J. Am. Chem. Soc. 53, 3186 (1931). {347} Shriner, Horne, Cox, Org. Syntheses, Coll. Vol. 2 (1st ed.), 453-455 (1943); 14, 72-74 (1934). {348} Franchimont, Rouffser, Rec. trav. chem. 13, 333-335 (1894). (349) Michler, Escherich, Ber. 12, 1162-1164 (1879). {350} Hantzsch, Sauer, Ann. 299, 85-86, 90 (1898).

(351) Stollé, J. prakt. Chem. (2) 117, 201 (1927). (352) Lumière, Perrin, Bull. soc. chim. (3) 31, 689 (1904). (353) Wallach, Ann. 214, 275 (1882). (354) Michler, Ber. 8, 1664-1666 (1875). (355) Michler, Ber. 9, 716-718 (1876). (356) Michler, Dupertuis, Ber. 9, 1899-1901 (1876). (357) Wahl, Bull. soc. chim. (5) 1, 244-246 (1934); C.A. 28, 5430 (1934). (358) Heller, Ann. 263, 277 (1891). (359) Noller, J. Am. Chem. Soc. 52, 1132-1134 (1930). (360) Ref. 11, pp. 156-160. (361) Gershzon, Lastovskii, J. Applied Chem. (U.S.S.R.) 9, 2058-2064 (1936); C.A. 31, 2589 (1937); Russian 44,556, Oct. 31, 1935; Cent. 1936, I 3576; C.A. 32, 2955 (1938). (362) Puschin, Mittle, Ann. 532, 300-301 (1937). (363) Puschin, Zivadinovic, Bull. soc. chim. roy. Yougoslav. 6, 165-168 (1936), Cent. 1936, II 794; C.A. 30, 4422 (1936). (364) Dominikiewicz, Arch. Chem. Farm. 3, 248-254 (1937); Cent. 1938, II 321; C.A. 32, 4522 (1938). (365) Evans, Paint Manuf. 8, 153-168 (1938); C.A. 32, 5529 (1938). (366) Patrick, U.S. 2,400,709, May 21, 1946; C.A. 40, 5507 (1946). (367) Davies, J. Chem. Phys. 14, 48-49 (1946). (368) Biesalski, Angew. Chem. 47, 149-151 (1934).

B.P. 31.7° at 760 mm. (1) F.P. -122.1° (1) $D_4^{20} = 1.2129$ (1) $n_D^{20} = 1.4249$ (1)

Care must be taken to avoid confusion of \bar{C} with vinyl chloride (3:7010), with 1,2-dichloroethane (ethylene (di)chloride) (3:5130), or especially with the isomeric compounds cts-1,2-dichloroethylene (3:5042), trans-1,2-dichloroethylene (3:5028), or their ordinary mixture (3:5030).

 \bar{C} when pure is colorless liq. with mild and characteristic odor; note, however, that at temps. above 0° and especially in pres. of oxygen or other cat. \bar{C} polymerizes to a white powder insoluble in the monomeric \bar{C} . (For much further comment on polymerization see below.)

PREPARATION OF C

[For prepn. of \bar{C} from 1,1,2-trichloroethane (3:5330) by elimination of 1 HCl with alc. KOH (2) (by this process \bar{C} was initially prepared (3)), or with excess aq. Ca(OH)₂ at 70-80° (90% yield (4)) (5), or with aq. or alc. NH₃ at ord. temp. (100% yield (7)), or with Na in dry ether (36) see indic. refs.; from 1,1,1-trichloroethane (3:5085) with excess aq. Ca(OH)₂ at 70-80° see (4) (5); for formn. of \bar{C} (as by-product of the isomeric 1,2-dichloroethylenes (3:5030)) from trichloroethane by catalytic pyrolytic dehydrochlorination see (6).

[For prepn. of C from 1,1,1,2-tetrachloroethane (3:5555) by loss of HCl by actn. of aq. + Fe, Zn, or Cd on warming under reflux see (8); from 1-bromo-1,1,2-trichloroethane by loss of Br-Cl with Zn dust + boilg. alc. see (37).]

[For formn. of C (together with vinyl chloride) from ethyl trichloroacetate (3:5950) by actn. of Zn in alc. see (9).]

[For formn. of \bar{C} (20% yield) from 1,2-dichloroethane (ethylene (di)chloride (3:5130) with Cl_2 in pres. of $AlCl_3/NaCl/FeCl_3$ at 400-480° see (10); note that some 22% 1,2-dichloroethylenes (3:5030) + 29% trichloroethylene (3:5170) + 29% higher chlorination prods. are also formed.]

PURIFICATION AND STABILIZATION OF MONOMERIC C

[For purification of Č by distn. as an azeotrope with MeOH, followed by removal of the latter by extraction with aq., see (11).]

Many compds. recommended as stabilizers or polymerization inhibitors for monomeric C have been described in patents: e.g., see (12) (13) (14) (15) (16).

CHEMICAL BEHAVIOR OF MONOMERIC Č

 $\ddot{\mathbf{C}}$ + chlorine. [$\ddot{\mathbf{C}}$ with Cl₂ at 25-35° in pres. of absence of cat. adds 1 mole halogen giving (85-92% yield (17)) 1,1,1,2-tetrachloroethane (3:5555).]

 $\ddot{\mathbf{C}}$ + bromine. $\ddot{\mathbf{C}}$ with Br₂ adds 1 mole halogen yielding (18) 1,1-dichloro-1,2-dibromoethane [Beil. I-93], oil, b.p. 175° at 760 mm. decg., 65° at 13 mm., f.p. -66.85°, D_4^{25} = 2.2203, D_4^{20} = 2.2449, D_4^{15} = 2.2695, n_D^{15} = 1.55930 (18).

 $\ddot{\mathbf{C}}$ + hydrogen chloride. $\ddot{\mathbf{C}}$ with dry HCl gas at 25-35° in pres. of AlCl₃ or FeCl₃ adds 1 mole HCl giving (85-90% yields (19) (20)) 1,1,1-trichloroethane (3:5085).

 $\ddot{\mathbf{C}}$ + hydrogen bromide. The addition to $\ddot{\mathbf{C}}$ of HBr appears to be unreported.

Polymerization of Č. Polymerization of Č either with itself or with other cpds. (especially other substituted ethylene derivs.) leads to a large group of industrially important materials broadly designated as "vinylidene polymers." Certain plasticized and stabilized copolymer compositions have been named "Saran." [For extremely valuable comprehensive reviews of this general field see (1) (21) (22); in view of the comprehensive surveys and prior literature (including patents) references given (especially in (1)), the following text will in general include only citations since 1942.]

 \bar{C} when carefully purified and free from oxygen polymerizes only very slowly; however, in the pres. of various catalysts, notably peroxides, polymerization readily occurs (for amplification see {1}).

[For patents involving polymeric \bar{C} from viewpoint of purification (23), storage of supercooled material (24), heat treatment to increase tensile strength (25), improvement of stability to light and heat (26) (27) (28) (29), or coloring (30) see indic. refs. — For studies on structure of fibers of polymeric \bar{C} see (1) (31). — For identification of common comml. plastics (including "Saran" and "Velon") see (32).]

[For review of copolymerization of \bar{C} see (1); for copolymerization with butadiene (33), with vinyl chloride or vinyl acetate (34), with styrene, acrylonitrile, various methacrylates, etc. (35), see indic. refs.]

3:5005 (1) Reinhardt, Ind. Eng. Chem. 35, 422-428 (1943). (2) Brockway, Beach, Pauling, J. Am. Chem. Soc. 57, 2695 (1935). (3) Regnault, J. prakt. Chem. (1) 18, 82-85 (1839); Ann. chim. (2) 69, 155-159 (1838). (4) I.G., Brit. 349,872, July 2, 1931, Cent. 1931, II 1191; C.A. 26, 5314 (1932): French 702,361, April 7, 1931; Cent. 1931, II 1191; C.A. 25, 4285 (1931); Ger. 529,604, July 4, 1929; not in Cent.; C.A. 25, 5178 (1931). (5) Howell (to Imperial Chem. Ind., Ltd.), Brit. 534,733, March 17, 1941; C.A. 36, 1336 (1942). (6) Hermann, Baum (to Consortium für Elektrochem. Ind.), U.S. 1,921,879, Aug. 8, 1933; not in Cent.; [C.A. 27, 5086 (1933)]: Ger. 570,954, Feb. 22, 1933; not in Cent.; C.A. 27, 4252 (1933): French 694,054, Nov. 28, 1930; Cent. 1931, I 1514; [C.A. 25, 1843 (1931)]. (7) Engel, Bull. soc. chim. (2) 48, 87 (1887). (8) Compagnie des Products Chim. d'Alais, etc., French 786,803, Sept. 10, 1935; Cent. 1936, I 175; C.A. 30, 737 (1936): Brit. 436,133 Oct. 4, 1935; C.A. 30, 1394 (1936), not in Cent. (9) Jocitsch, Favorsky, J. Russ. Phys.-Chem. Soc. 30, 998-1003 (1898); Cent. 1899, I 777-778. (10) Reifly (to Dow Chem. Co.), U.S. 2,140,548, Dec. 20, 1938; Cent. 1939, I 3625; C.A. 33, 2540 (1939).

(11) Taylor, Horsley (to Dow Chem. Co.), U.S. 2,293,317, Aug. 18, 1942; C.A. 37, 889 (1943). (12) The Distillers Co. & Galitzenstein, Brit. 551,584, March 2, 1943; C.A. 38, 2969 (1944). (13) Coleman, Zemba (to Dow Chem. Co.), U.S. 2,160,944, June 6, 1939; Cent. 1939, II 3751; C.A. 33, 7318 (1939). (14) Coleman, Zemba (to Dow Chem. Co.), U.S. 2,136,333 & 2,136,334, Nov. 8, 1938; Cent. 1939, I 1653; C.A. 33, 1346 (1939). (15) Wiley (to Dow Chem. Co.), U.S. 2,136,347, & 2,136,348 & 2,136,349, Nov. 8, 1938; Cent. 1939, I 1653; C.A. 33, 1346 (1939). (16) Britton, LeFevre (to Dow Chem. Co.), U.S. 2,121,009, & 2,121,010 & 2,121,011 & 2,121,012, Jan. 21, 1938; Cent. 1938, II 2497; C.A. 32, 5856 (1938). (17) I.G., Ger. 530,649, July 31, 1931; Cent. 1931, II 1920; C.A. 26, 155 (1932). (18) van de Walle, Bull. acad. roy. Belg. (5) 10, 99 (1924); Cent. 1924, II 303: Bull. soc. chim. Belg. 34, 10-21 (1925); C.A. 19, 1856 (1925). (19) Nutting, Huscher (to Dow Chem. Co.), U.S. 2,209,000, July 23, 1940; Cent. 1940,

II 3703; C.A. 35, 140 (1941). (20) I.G., Ger. 523,436, April 23, 1931; Cent. 1931, I 3607; C.A. 25, 3362 (1931).

(21) Goggin, Lowry, Ind. Eng. Chem. 34, 327-332 (1942). (22) Goggins, Ind. Eng. Chem., News Ed. 18, 923-924 (1940). (23) Britton, Taylor (to Dow Chem. Co.), U.S. 2,235,796, March 18, 1941; C.A. 35, 4040 (1941). (24) Wiley (to Dow Chem. Co.), U.S. 2,320,112, May 25, 1943; C.A. 37, 6378 (1943). (25) Williams (to Dow Chem. Co.), U.S. 2,309,370, Jan. 26, 1943; C.A. 37, 3860 (1943). (26) Matheson, Boyer, Stone (to Dow Chem. Co.), U.S. 2,258,188, Oct. 7, 1941; C.A. 36, 857 (1942). (27) Hanson, Goggin (to Dow Chem. Co.), U.S. 2,273,262, Feb. 17, 1941; C.A. 36, 3809 (1942). (28) Matheson, Boyer, Coleman (to Dow Chem. Co.), U.S. 2,287,189, June 23, 1942; C.A. 37, 201 (1943). (29) Boyer, Matheson, Moyle (to Dow Chem. Co.), U.S. 2,344,489, March 21, 1944; C.A. 38, 3293 (1944). (30) Hanson (to Dow Chem. Co.), U.S. 2,251,486, Aug. 5, 1941; C.A. 35, 7070 (1941).

(31) Fuller, Baker, J. Chem. Education 20, 9 (1943). (32) Nechamkin, Ind. Eng. Chem., Anal. Ed. 15, 40-41 (1943). (33) Hopff, Rautenstrauch (to I.G.), Ger. 731,982, Jan. 28, 1943; C.A. 38, 894 (1944). (34) Scott, Seymour (to Wingfoot Corp.), U.S. 2,328,748, Sept. 7, 1943; C.A. 38, 1051 (1944). (35) Arnold (to du Pont Co.), U.S. 2,278,415, April 7, 1942; C.A. 36, 4939 (1942). (36) Brunner, Brandenburg, Ber. 10, 1497-1499 (1877); 11, 61-62 (1878). (37)

Kharasch, Norton, Mayo, J. Org. Chem. 3, 53 (1933).

B.P. F.P. 32-33° at 748 mm. (1) (2) (3)
$$-66$$
 to -64.2 ° (1) $D_4^{20} = 1.261$ (9) $n_D^{20} = 1.42790$ (9)

Colorless oil which ignites in air and explodes even on stirring; however, its 5-10% soln. in ether is safely handled (4).

[For prepn. of \bar{C} from acetylene + aq. alk. KOCl soln. under N₂ see (1) (2) (3); from 1,1,2-trichloroethylene (3:5170) in N₂ at 130° over solid granular KOH (65% yield (4)) see (4) (5) (9); from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) with KOH in xylene under N₂ (can be carried out as a lect. expt.) see (6) (9); for formn. of \bar{C} from barium salt of α,β,β -trichloroacrylic acid (3:1840) by htg. in H₂ see (13).]

 $\bar{\mathbf{C}}$ forms with diethyl ether a molecular cpd., $\bar{\mathbf{C}}.\bar{\mathbf{C}}_4\mathbf{H}_6\mathbf{O}$, eas. decomposed by aq. into its components (5); for D and n of ether solns. of $\bar{\mathbf{C}}$ see (9).

C on combusion yields CO, CO₂, COCl₂ (4) together with other products (5).

[For use of C in extraction of coffee see (7).]

 \bar{C} in CCl₄ treated 9 hrs. with strong Cl₂/CCl₄ soln. gives (1) on evapn. hexachloroethane (3:4835), m.p. 187° in s.t. (1).

 \bar{C} on passing into Br₂/aq. yields (1) a heavy oil which on stdg. under the excess reagt. solidifies to cryst. of 1,2-dichloro-1,1,2,2-dibromoethane; after recrystn. from alc., m.p. 209-210° dec., with yellowing at 200° (1). [Note that \bar{C} in CCl₄ treated with Br₂/CCl₄ can add 1 mole Br₂ giving (65% yield (4)) 1,2-dichloro-1,2-dibromoethylene, b.p. 172° at 760 mm. (8), $D_1^{45} = 2.3036$ (8), $n_1^{15} = 1.57984$ (8), m.p. +4.40° (8), 4.9° (4).]

C with I₂ in ether (4) or CCl₄ (5) gives slowly 1,2-dichloro-1,2-dicodoethylene, cryst. from ether or pet. eth., m.p. 70° (4). [Another stereoisomer, m.p. 5-7°, is formed only to extent of 10% and is removed by the solvent (5).]

[For studies on behavior of Č on polymerization (10), and its reactions with NH₃ (10), amines (10) (11), alcoholates (10), diethyl sodio-malonate (10), organic Mg compds. (12), ethyl diazoacetate (12), and NO₂ (12) see indic. refs.]

3:5010 (1) Straus, Kollek, Heyn, Ber. 63, 1873-1876 (1930). (2) Straus, Kollek (to I.G.), Ger. 495,787, April 17, 1930; Cent. 1930, II, 1439. (3) I.G., Brit. 333, 946, Sept. 18, 1930; Cent. 1931, I 523. (4) Ott, Ottenmeyer, Packendorff, Ber. 63, 1941-1944 (1930). (5) Ott, Packendorff, Ber. 64, 1324-1329 (1931). (6) Metz, J. prakt. Chem. (2) 135, 142-144 (1932). (7)

French 725,338, May 11, 1932; Cent. 1932, II 1713. (8) van der Walle, Bull. soc. chim. Belg. 29, 307-308 (1920). (9) Ott, Ber. 75, 1517-1522 (1942). (10) Ott, Dittus, Ber. 76, 80-84 (1943). (11) Ott, Dittus, Weissenberger, Ber. 76, 84-88 (1943). (12) Ott, Bossaller, Ber. 76, 88-91 (1943). (13) Böeseken, Carriere, Verslag Akad. Wetenschappen 22, 1186-1188 (1914); C.A. 8, 3296 (1914).

```
METHYLENE (DI)CHLORIDE
3:5020
                                                                    CH<sub>2</sub>Cl<sub>2</sub>
                                                                                       Beil. I - 60
            (Dichloromethane)
                                                                                             I_{1}-(8)
                                                                                             I<sub>2</sub>-(13)
 B.P.
                                     F.P.
  41.4-42.2° at 760 mm.
                                                    (17) D_4^{30} = 1.30777 (12)
                               (1)
                                     -96.0^{\circ}
                                               (10) (18)
  41.6° cor. at 760 mm.
                                       -96.5°
                                                    (19)
                                                   (168)
  41.5°
                                     -96.7^{\circ}
                                                    (19) D_4^{25} = 1.3181
                at 760 mm.
                               (3)
                                                                               (23)
                                               (11) (20)
                                                                  1.31678 (12)
                                      -96.8° (12) (19)
                                                                              n_{\rm D}^{24.8} = 1.4220 (23)
  41.5°
                                (4)
  41.5°
                at 680 mm.
                                     -97.0° (21) (22)
                               (5)
                                                                             n_{5462}^{234} = 1.43239 (5)
                                                          D_{23}^{23}\stackrel{4}{4}=1.3612
  41.3-41.5°
                               (6)
                                                                                (5)
  40.67° cor. at 760 mm.
                               (7)
                                     Note 2. For in-
                                                           D_4^{20} = 1.3361
  40.4°-42°
                               (8)
                                     fluence of very
                                                                              (15)
  40.1-40.3° at 769 mm.
                               (9)
                                     high press. on
                                                                               (24)
                                     f.p. of C see
  40.1°
                at 760 mm. (10)
                                                                   1.326
                                                                              (25)
  40.0°
                                     (20).
                                                                  1.32578 (12)
                              (11)
                                                                               n_{\rm D}^{20} = 1.4253 \ (25)
  39.95°
                at 760 mm. (12)
  39.93-40.12° cor.
                              (13)
                                                                                       1.4249 (13)
  39.9
                at 736 mm. (14)
                                                                                       1.4237 (26)
  39.8°
                at 760 mm. (15)
                                                                                       1.4234 (15)
  39.5-40.1°
                                                          D_4^{15} = 1.33479 \quad (12)
                              (16)
                                                                       n_{\text{He(yellow)}}^{15} = 1.42721 (12)
  Note 1. For study of vap.
                                                           D_4^0 = 1.3620
  press. of \bar{C} over range -87^{\circ}
                                                                                n_{\rm D}^0 = 1.4361 (23)
  to +38^{\circ} see (7).
                                                           For D_4^t over range
                                                           t = -100^{\circ} \text{ to } +40^{\circ}
                                                           see (25); -273 to
                                                           -194° see (10).
```

MISCELLANEOUS PHYSICAL PROPERTIES OF C

VARIOUS SOLUBILITY RELATIONS

With water. $ildе{C}$ is only slightly soluble in aq. and readily volatile with steam. E.g., 100 g. water dissolves following amts. of $ildе{C}$: 2.363 g. at 0° (27), 2.122 g. at 10° (27), 2.000 g. at 20° (27) (15), 1.969 g. at 30° (27). — For study of soly. of water in $ildе{C}$ at 0°, 25°, and 30° see (28) (29); for study of reciprocal soly. of $ildе{C}$ and water see (30) (68). — $ildе{C}$ with H₂O is claimed (35) to form a hydrate stable up to +2°.

With organic compounds. [For studies on soly. of \bar{C} in 35 org. solvents of various types see (31); for soly. of \bar{C} in cellosolve acetate (33), carbitol acetate (32) (33), diethylene glycol diethyl ether (32), tetraethylene glycol dimethyl ether (32), and tetraethylene glycol diethyl ether (33) see indic. refs.]

(4).

BINARY SYSTEMS CONTAINING C (See also azeotropes containing C)

 $C + Cl_2$: for f.p./compn. data and diagram (various compounds and eutectics are formed) see (21).

 $\bar{C} + C_2 H_5 Cl$ (3:7015); for f.p./compn. data and diag. (eutectic, f.p. -149.7°, conts. 31.7 wt. % \ddot{C}) see (17). — \ddot{C} + $CHCl_3$ (3:5050): for f.p./compn. data and diag. (eutectic, f.p. -108.4° , conts. 70.5 wt. % \bar{C}) see (17); for data on b.p., D_4^{20} , and liq./vapor equilibria see (34). $-\bar{C} + CCl_4$ (3:5100): for data on b.p., D_4^{20} , and liq./vapor equilibria see (34). $-\bar{C}$ $ar{C}+1$,1,-dichloroethane (3:5035): for f.p./compn. data see (19). — $ar{C}+2$,2-dichloropropane (3:7140): for f.p./compn. data see (22).

C + isobutyl bromide: for f.p./compn. data see (19). — C + methylene (di)bromide: for f.p./compn. data see (19).

 \ddot{C} + methylene (di)iodide: for f.p./compn. data see (19).

 \bar{C} + dimethylaniline: for D_4^{25} and $n_D^{24.8}$ for 0-100% \bar{C} see (23); for f.p./compn. data and diagram (eutectic, m.p. -97.2° , conts. 91 wt % \overline{C}) see (168).

TERNARY SYSTEMS CONTAINING C (See also azeotropes containing C)

 $\ddot{C} + CHCl_3 + CCl_4$: system forms ternary eutectic, f.p. -111.4°, contg. 60 wt. % \ddot{C} + 27.0 wt. % CHCl₃ (3:5050) + 13.0 wt. % CCl₄ (3:5100) (17).

BINARY AZEOTROPES CONTAINING C

 $\vec{C} + H_2O$: \vec{C} forms with aq. a const.-boilg. mixt., b.p. 38.1°, contg. 98.5 wt. % \vec{C} (68). $\overline{C} + MeOH$: \overline{C} forms with MeOH (1:6120) a const.-boilg. mixt., b.p. 39.2° (4) at 760 mm. (3), contg. 92 wt. % (3), 94 wt. % (4) \ddot{C} . $-\ddot{C}$ + EtOH: \ddot{C} forms with EtOH (1:6130) a const.-boilg. mixt., b.p. 41.0° at 760 mm. (3), contg. 96.5 wt. % (3) C. — C forms with formaldehyde dimethylacetal (1:0105) a const.-boilg. mixt., b.p. 45.0° (36), contg. (36) 41 wt. % \bar{C} , cf. (37). — \bar{C} + acetone: note that this system forms no azeotrope; note also that C is the only known liquid which with MeOH (see above) gives a const.-boilg. mixt.

boilg. lower than acetone and at the same time not forming a binary azeotrope with acetone TERNARY AZEOTROPES CONTAINING Č

 $C + H_2O + EtOH$: forms no ternary azeotrope (68).

C + MeOH + acetone: this system forms no ternary azeotrope; for discussion see (4) (38).

 $\bar{C} + CHCl_8 + acetone$: for discussion see (4).

OTHER PHYSICAL PROPERTIES OF C

[For study of thermal conductivity of C see (39); for studies of heat capacity of C (40) as calculated from spectroscopic data (41) see indic. refs.; for studies of critical temp. of C (7) (15) (6) and method for its microdetermination (6) see indic. refs.; for ebullioscopic const., viz., 2.6° for 1000 g. Č, see (43).]

[For studies of adsorption of C on wood charcoal at 25° and 50° (44) or on cocoanut charcoal over range -31.5° to 184° (45), on Al(OH)₈ gel (46), on Fe(OH)₃ gel (47), on Cr₂O₃ (48) see indic. refs.; Č is preferentially adsorbed (42) by silica gel from its mixt. with CHCl₃ (3:5050).]

[For study of attempt to separate isotopes of Cl₂ by reversible fractional distn. of Č see (49).]

PHYSIOLOGICAL ASPECTS OF C

 \tilde{C} has low toxicity compared to other chlorinated hydrocarbon solvents; the maximum allowable conc. for 8 hrs. daily exposure is 500 p.p.m. (50). [For study of relative toxicity of \tilde{C} see (51); for extensive study of industrial hygiene and toxicity of \tilde{C} (together with 12 other chlorinated solvents (52)) (53) (50) see indic. refs.; for study of \tilde{C} upon running activity of male rat see (54).]

USES OF C

Č is widely used as a solvent, as a fluid for refrigeration processes, and for removing water from other organic materials; examples of all these aspects are cited below.

[For study of utility of \bar{C} as solvent for the ozonization of org. compds. see (10); for use of \bar{C} as solvent for the extraction of vitamin A (55) or of soy-bean oil (56) see indic. refs.; for general studies (15) (57) (58) and patents (59) (60) (61) (62) (63) (64) (65) on use of \bar{C} in refrigerating machines and systems see indic. refs.; for use of \bar{C} in detn. of water content of liquids (66) (67) or for prepn. of abs. EtOH (68) (69) (70) see indic. refs.]

DETECTION OR DETERMINATION OF C

[For detection of \bar{C} in pres. of acetone (by means of Fujiwara color test with pyridine + NaOH) see (71); for distinction of \bar{C} from CHCl₃ (3:5050) and from CCl₄ (3:5100) by color tests see (72) (73) (also under \bigcirc below).]

[For detn. of \bar{C} in blood by removal through aeration, pyrolytic decompn. of \bar{C} , and alk. absorption of resultant HCl as directed see (74); for detn. of C, H, and Cl in \bar{C} by combustion see (75). Note that the R. + H. Tri-Per Analyzer, a recording ultra-violet photometer very useful for detn. of trichloroethylene (3:5170) and tetrachloroethylene (3:5460), is insensitive (76) to \bar{C} .]

PREPARATION OR FORMATION OF C

From methane. [The chlorination of CH₄ under various conditions to yield $\bar{\mathbf{C}}$ (accompanied by more or less CH₃Cl (3:7005), CHCl₃ (3:5050), and CCl₄ (3:5100)) has been extensively studied and no attempt will be made here to sift out details. For examples of leading scientific papers ((77)–(88), incl.) and patents ((89)–(96), incl.) see indic. refs.]

From methyl chloride. [The chlorination of MeCl to \bar{C} has also been extensively studied; many of the relevant data are included in the papers and patents on the chlorination of methane (see preceding paragraph), to which should be added the following patents (91) (97) (98) (99) (100). Note patent (98) on separation of MeCl (3:7005) from \bar{C} by hydrolysis of former to MeOH (1:6120) with Ca(OH)₂ under press.]

From chloroform. [For formn. of \bar{C} from CHCl₃ (3:5050) by replacement of 1 chlorine by hydrogen using Zn + alc. HCl (101), Zn + AcOH (103), Zn dust + alc. NH₃ (102) (8) (2), Al/Hg + aq. (103), Fe + AcOH (103), or Si₃H₈ + AlCl₃ in absence of air (104) see indic. refs.]

From carbon tetrachloride. [For prepn. of C from CCl₄ (3:5100) using aq. FeSO₄ + NaOH see (105).]

From miscellaneous sources. [For prepn. or formn. of \bar{C} from CH_2I_2 with Cl_2 (first prepn. of \bar{C}) (106) cf. (158); from polyoxymethylene with PCl_5 in s.t. (107); from MeOH + S_2Cl_2 + Cl_2 (108); or from chloroacetic acid (3:1370) by electrochem. oxidn. (109) see indic. refs.]

CHEMICAL BEHAVIOR OF C

Oxidation of \tilde{C} . [\tilde{C} with air at ord. temps. and press. does not give inflammable mixts.; at high temps. vapor of \tilde{C} becomes inflammable and ignites at 642° in air, at 606° in O_2 ;

limiting concns. of \bar{C} for inflammability in O_2 are 15.5-66.4%; N_2 does not greatly affect the lower limit of inflammability in O_2 but greatly reduces the upper limit (110). — For study of inflammability of mixts. of \bar{C} with O_2+,N_2 , air + CO, or O_2+N_2+ MeBr see (111). — For effect of \bar{C} on flash point of solvents see (115).]

[C with atomic O gives (112) COCl₂ (3:5000), Cl₂, HCl, CO₂ + H₂O; C with air over CuO at 450° gives (113) little COCl₂ (3:5000); for study of Cl₂-sensitized photochem. oxidn. of C see (114).]

Fluorination of \tilde{C} . [\tilde{C} with SbF₃ + cat. readily gives (126) (127) CH₂F₂, b.p. -51.6°, + CH₂ClF, b.p. -9.0°.]

Chlorination of \tilde{C} . [\tilde{C} with Cl_2 as directed (116) (117), or \tilde{C} with HCl gas + air over CuCl₂ at 440° (118), gives CHCl₃ (3:5050) and CCl₄ (3:5100).]

Bromination of \tilde{C} . [\tilde{C} with Br₂ cf. (158) in pres. of Al gives (128) cf. (129) CH₂BrCl + CH₂Br₂ [Beil. I-67, I₁-(16), I₂-(32)], b.p. 96.95° at 760 mm., f.p. -52.7°, $D_4^{25} = 2.48417$, $D_4^{20} = 2.49702$ (130). — For an alternative synthesis of CH₂Br₂ (88–90% yield) from CHBr₃ with Na₃AsO₃ + NaOH see (138).]

Hydrolysis of \bar{C} . \bar{C} on suitable hydrolysis yields formaldehyde (1:0145). [E.g., \bar{C} with aq. in pres. of weakly alk. reacting salts such as NaHCO₃, Na₂HPO₄, NaOAc, etc., at 165° under press. (119), or $\bar{C} + N_2$ over dry Na₂CO₃ at 310-320° (120), \bar{C} with steam over activated carbon at 260-270° (121), \bar{C} with aq. at 140-170° under press. (122), \bar{C} with steam at 550-850° over cat. (123), or \bar{C} with steam over tin phosphate at 460° (124) gives formaldehyde (1:0145) + HCl. Note that \bar{C} on protracted htg. with aq. at 180° gives (125) formic acid (1:1005), MeCl (3:7005), MeOH (1:6120) HCl + CO.]

Behavior with inorganic salts. [C with NaI in acetone htd. in press. bottle for 20 hrs. as directed (131), or \tilde{C} with NaI in acetone, McOH, or EtOH at 120–130° under press. (132), gives (60% yield (131)) methylene (d1)iodide [Beil. I-71, I₁–(18), I₂–(37)], b.p. 151–153° cor. at 330 mm. (133), 88° at 39 mm. (134), 66–67° at 11–12 mm. (24); exists in two crystn. forms, stable form, m.p. + 5.85° (135), metastable form, m.p. 40° (136); $D_4^{25} = 3.3078$ (130); $D_4^{20} = 3.3212$ (130); $D_4^{15} = 3.3345$ (130); $n_D^{15} = 1.74428$ (130). — For an alternative synthesis of CH₂I₂ (90–97% yield) from iodoform by treatment with Na₃AsO₃ + NaOH see (137).]

[Č with 2 moles K₂SO₃ in aq. at 150-160° under press. gives (85% yield (139)) the dipotassium salt of methanedisulfonic acid (methionic acid) [Beil. I-579, I₁-(303), I₂-(644)] [Č with alc. AgNO₃ does *not* react even on stdg. for several days; note that while neither CHCl₃ (3:5050) nor CCl₄ (3:5100) reacts either, CH₃Cl (3:7005) gives a ppt. within 3 hrs. (140).]

[For form. of polymeric prods. from reaction of \bar{C} with metal sulfides or polysulfides see (141); for study of photochem. reaction of \bar{C} with H₂S see (149).]

Behavior with metals. \bar{C} (like many other polyhalogenated hydrocarbons) in presence of metallic K, Na, K/Na alloy, or even of certain other active metals explodes under the influence of mechanical or thermal shock. [For study of this characteristic (142), especially with regard to sensitivity toward Li, Na, K, Ca, Sr, Ba (143), see indic. refs.]

[Note that \bar{C} with molten sodium at 260-300° gives (144) C, H, and CH₄, together with smaller amts. of ethane, ethylene, and acetylene; note that \bar{C} with Na vapor in pres. of H₂ gives (145) 92% CH₄ + 8% ethylene, while \bar{C} with Na vapor in N₂ gives (145) almost 100% ethylene; for further studies of behavior of \bar{C} with Na vapor see (146) (147). Note that attempts to obtain a free methylene radical (CH₂) with \bar{C} + Na vapor have been unsuccessful (148).]

[For study of stability of various metals with respect to corrosion by \bar{C} under various conditions see (15).]

Behavior with various organic reactants. [C with CO + AlCl₃ at 260° and 800 atm. press. for 8 hrs. gives (150) chloroacetyl chloride (3:5235); but C with CO, COS, or COCl₂ (3:5000) + cat. at 700° gives (151) malonyl (di)chloride (3:9030).]

[$\bar{\mathbf{C}}$ with $\mathbf{C}_6\mathbf{H}_6$ + AlCl₃ gives (152) cf. (153) diphenylmethane (1:7120); $\bar{\mathbf{C}}$ with toluene + AlCl₃ gives (152) di-p-tolylmethane [Beil. V-615, V₁-(289), V₂-(518)], m.p. 28° (154), b.p. 302° cor. at 768 mm. (154), accompanied by considerable (152) (155) 2,7-dimethylanthracene, m.p. 241° cor. (155); $\bar{\mathbf{C}}$ with o-xylene (1:7430) + AlCl₃ in acetylene tetrachloride (3:5750) as solvent gives (156) 2,3,6,7-tetramethylanthracene, m.p. 299° (156); for behavior of $\bar{\mathbf{C}}$ in pres. of AlCl₃ with m-xylene (1:7420) or with pseudocumene (1:7470) see (152).]

[$\bar{\rm C}$ with CH₂Br₂ + 5-10% KCl in pres. of moistened AlCl₃ at 180° in s.t. for 16 hrs. undergoes a redistribution reaction giving (157) a mixt. contg. 33% $\bar{\rm C}$ + 18% CH₂Br₂ + 50% ClCH₂Br; $\bar{\rm C}$ with CH₂I₂ similarly treated at 114° for 18 hrs. gives (157) a mixt. contg. 33% $\bar{\rm C}$ + 21% CH₂I₂ + 46% ClCH₂I.]

[\tilde{C} with NaOMe in s.t. at 100° (158), or vapor of \tilde{C} over NaOMe + pumice at 200° (37), gives formaldehyde dimethylacetal (1:0105); \tilde{C} + NaOEt in s.t. at 100° (158), or \tilde{C} with excess EtOH + calcd. amt. NaOH at 100-125° under press. (159), gives formaldehyde diethylacetal (1:0135); for analogous behavior of other alcoholates (158) (159) or phenolates (158) see indic. refs.]

[\tilde{C} with alc. NH₃ at 125° in s.t. gives (160) hexamethylenetetramine [Beil. I-583, I₁-(306)]. — \tilde{C} with Me₂NH in s.t. at 70° gives (161) bis-(dimethylamino)methane. — \tilde{C} with Me₃N in 90% acctone at 55° or more slowly in ether undergoes a quaternization reaction giving trimethyl-chloromethyl-ammonium chloride (constants not detd.) (162).]

- P Beilstein test for halogen. Note that because of its low b.p. C often appears to fail in Beilstein copper gauze test for halogen compds.; in such cases use the modification described by (163) (164).
- P Hydrolysis to formaldehyde. C (2 g.) in 10% MeOH/alk. (20 ml.) boiled 20 min. under good reflux, subsequently acidified with dil. H₂SO₄, gives soln. containg. Cl and formaldehyde (1:0145).
- ② Color reaction with α-naphthol/cyclohexanol. C

 (1 drop) with 2 ml. of a 2% soln. of α-naphthol (1:1500) in cyclohexanol (1:6415) + 1 pellet of solid NaOH, boiled 25 seconds and cooled, gives (72) blue color; one portion of this blue soln. underlaid with equal volume 85% H₂SO₄, stood 1 minute and shaken, turns green-blue; a second portion of the alkaline blue soln. acidified with equal volume of AcOH (1:1010) stood 1 minute and shaken becomes yellow. [Note that the alkaline boiling also gives a blue color with CHCl₃ (3:5050) and with CCl₄ (3:5100) while other chlorinated solvents (72) give yellow-brown, gray, or brown; in the H₂SO₄ acidification both CHCl₃ and CCl₄ give blue rather than green-blue; in the AcOH acidification CHCl₃ gives an orange-yellow, CCl₄ a red color.]
- P Color test with 2,7-dihydroxynaphthalene/cyclohexanol. C (1 drop) with 2 ml. pure cyclohexanol (1:6415) + 1 pellet NaOH + a few mgms. 2,7-dihydroxynaphthalene htd. at 197° (b.p. of ethylene glycol) for 45 seconds, decanted from undissolved NaOH, cooled, and shaken with 2 ml. AcOH + 4 ml. 96% EtOH, gives steel-blue color (73). [Note that under these conditions CHCl₃ (3:5050) gives a deep-red color while CCl₄ (3:5100) gives a pale yellow brown.]
- Color test with cyclopentanol. Č (1 drop) in cyclopentanol (1 ml.) with 1 pellet NaOH boiled 25 seconds, then shaken vigorously for 35 seconds, gives deep red color; upon addition of 4 ml. 96% EtOH and shaking color intensifies or becomes reddish brown (73). [Note that after addn. of alc. CHCl3 gives only a pale citron-yellow or

yellowish brown and that as little as 20% of \bar{C} can be detected by this means in CHCl₃ (73); CCl₄ gives (73) after addn. of alc. an intense nut-brown.]

Formaldehyde di- α -naphthylacetal (methylene di- α -naphthyl ether): unreported. Formaldehyde di- β -naphthylacetal (methylene di- β -naphthyl ether): m.p. 134° (165), 133-134° (166). [From CH₂I₂ with Na β -naphtholate refluxed in alc. (165) (166) (167); not actually reported from \bar{C} but presumably resulting by above method if some KI be added to refluxing mixture of \bar{C} + Na β -naphtholate in acetone. Note that this ether fails (165) (167) to form any PkOH addition compound.]

3:5020 (1) Mathews, J. Am. Chem. Soc. 48, 569 (1926). (2) Thorpe, J. Chem. Soc. 37, 194 (1880). (3) Lecat, Rec. trav. chrm. 46, 242 (1927). (4) Ewell, Welch, Ind. Eng. Chem. 37, 1224—1231 (1937). (5) Ramaswamy, Proc. Indian Acad. Sci. A-4, 111 (1936). (6) Harand, Monatsh. 65, 153—184 (1935). (7) Perry, J. Phys. Chem. 31, 1737—1741 (1927). (8) Perkin, Chem. News 18, 106 (1868). (9) Walker, Trans. Faraday Soc. 31, 1434 (1935). (10) Biltz, Sapper, Z. anorg. allgem. Chem. 203, 283, 285 (1932).

[11] Timmermans, Bull. soc. chrm. Belg. 25, 300 (1911); Cent. 1911, II 1015. [12] Timmermans, Hanaut-Roland, J. chrm. phys. 29, 531-533 (1932). [13] Maryott, Hobbs, Gross, J. Am. Chem. Soc. 63, 660 (1941). [14] Greenwood, J. Org. Chem. 10, 414-418 (1943). [15] Carlisle, Levine, Ind. Eng. Chem. 24, 146-147 (1932). [16] Sutton, Brockway, J. Am. Chem. Soc. 57, 474 (1935). [17] Kanolt, Sci. Papers U. S. Bur. Standards 20, 619-633 (1926). [18] Stock, Stiebler, Ber. 56, 1089 (Note) (1923). [19] Timmermans, Bull. soc. chrm. Belg. 43, 631-632 (1934). [20] Bridgman, J. Chem. Phys. 9, 795 (1941); Proc. Am. Acad. Arts Scr. 74, 425-440 (1942).

Wheat, Browne, J. Am. Chem. Soc. 62, 1575-1576 (1940). (22) van de Vloed, Bull. soc. chim. Belg. 48, 260 (1939). (23) Davies, Evans, Whitehead, J. Chem. Soc. 1939, 645. (24) Patterson, Thomson, J. Chem. Soc. 93, 369-370 (1908). (25) Morgan, Lowry, J. Phys. Chem. 34, 2401-2402, 2413 (1930). (26) Gorke, Kóppe, Staiger, Ber. 41, 1163 (1908). (27) Rex, Z. physik. Chem. 55, 365 (1906). (28) Staverman, Rec. trav. chim. 60, 836-841 (1941). (29) van Arkel, Vles, Rec. trav. chim. 55, 407-411 (1936). (30) Niini, Suomen Kemistilehti 11-A 19-20 (1938); Cent. 1939, II 614; C.A. 32, 486 (1938).

(31) Copley, Zellhoefer, Marvel, J. Am. Chem. Soc. 60, 2714-2716 (1938). (32) Zellhoefer, Copley, Marvel, J. Am. Chem. Soc. 60, 1338 (1938). (33) Zellhoefer, Ind. Eng. Chem. 29, 548 (1937). (34) Kaplan, Monakhova, J. Gen. Chem. (U.S.S.R.) 7, 2499-2512 (1937), Cent. 1938, II 1572; C.A. 32, 2404 (1938). (35) Villard, Ann. chim. (7) 11, 386 (1897) (36) Lecat, Compt. rend. 222, 733-734 (1946). (37) Loberring, Fleischmann, Ber. 70, 1680-1683 (1937). (38) Ewell, Harrison, Berg, Ind. Eng. Chem. 36, 874 (1944). (39) Bates, Hazzurd, Palmer, Ind. Eng. Chem. 33, 375-376 (1941). (40) Glockler, Edgell, Ind. Eng. Chem. 34, 532-534 (1942).

(41) Vold, J. Am. Chem. Soc. 57, 1192-1195 (1935). (42) Grimm, Raudenbusch, Wolff, Z. angew. Chem. 41, 105 (1928). (43) Walden, Bull. acad. sci. Petrograd (6) 1915, 1485-1514; Cent. 1925, I 1676; C.A. 10, 2425 (1916). (44) Pearce, Reed. J. Phys. Chem. 35, 905-914 (1931). (45) Pearce, Johnstone, J. Phys. Chem. 34, 1260-1279 (1930). (46) Perry, J. Phys. Chem. 29, 1462-1468 (1925). (47) Perry, Ind. Eng. Chem. 19, 746-748 (1927). (48) Harbard, King, J. Chem. Soc. 1940, 19-29. (49) Urban, White, J. Phys. Chem. 37, 397-399 (1933). (50) Heppel, Neal, Perrin, Orr, Porterfield, J. Ind. Hyg. Toxicol. 26, 8-16 (1944).

(51) Barsoun, Saad, Quart. J. Pharm. Pharmacol. 7, 205-214 (1934); Cent. 1934, II 2550; C.A. 28, 6194 (1934). (52) Lehman, Schmidt-Kehl, Arch. Hyg. Bakt. 116, 131-268 (1936); C.A. 31, 477 (1937). (53) von Oettingen, J. Ind. Hyg. Toxicol. 19, 357-359 (1937). (54) Heppel, Neal, J. Ind. Hyg. Toxicol. 26, 17-21 (1944). (55) Tompkins, Bolomey, Ind. Eng. Chem., Anal. Ed. 15, 437-439 (1943). (56) Arnold, Proc. Iowa Acad. Sci. 51, 309-311 (1944); C.A. 40, 3009 (1946). (57) Churchill, Chem. Markets 25, 587-592 (1929). (58) Waterfill, Ind. Eng. Chem. 24, 616-619 (1932). (59) Carrier (to Carrier Eng. Corp.), U.S. 1,781,051, Nov. 11,1930; Cent. 1931, II 2192; C.A. 25, 155 (1931): Brit. 276,887, Sept. 8, 1927; Cent. 1931, II 2192; [C.A. 22, 2421 (1928)]. (60) Davenport (to Chicago Pneumatic Tool Co.), U.S. 1,803,098, April 28, 1931; Cent. 1932, I 1935; [C.A. 25, 3746 (1931)].

(61) Braun (to Sartain, Fessracht, Schwoerer), U.S. 1,966,881, July 17, 1934; Cent. 1935, II 3805; C.A. 28, 5904 (1934). (62) Davenport (to Chicago Pneumatic Tool Co.), U.S. 1,986,959, Jan. 8, 1935; Cent. 1936, II 147; C.A. 29, 1294 (1935). (63) Kenney, Jordan, Threlkeld (to General Household Utilities Co.), U.S. 2,010,547, Aug. 6, 1935; Cent. 1937, I 145; C.A. 29, 6477 (1935). (64) Kenney (to General Household Utilities Co.), U.S. 2,021,691, Nov. 19, 1935; Cent. 1937, I 145; C.A. 39, 336 (1936). (65) Ernst (to I.G.), Ger. 534,530, Sept. 26, 1931; Cent. 1932, I 428; not in C.A. (66) Bakowski, Treszczanowicz, Przemysl Chem. 21, 204-208 (1937):

Cent. 1938, I 2758; C.A. 31, 8438 (1937). (67) Bakowski, Treszczanowicz, Przemsyl Chem. 22, 239-240 (1938); Cent. 1939, I 2040; C.A. 33, 6755 (1939). (68) Bakowski, Treszczanowicz, Przemsyl Chem. 22, 211-227 (1938); Cent. 1939, I 1878; C.A. 33, 6518 (1939). (69) Bakowski, Treszczanowicz, Przemsyl Chem. 22, 266-278 (1938); Cent. 1939, II 4607; C.A. 33, 3517 (1939). (70) Bakowski, Treszczanowicz (to Chemiczny Instytut Badawczy), Polish 26,192, Apr. 14, 1938; Cent. 1939, I 1880; not in C.A.: Polish 26,769, Sept. 6, 1938; Cent. 1939, II 729; not in C.A.: French 831,536, Sept. 7, 1938; Cent. 1938, II 3996; C.A. 33, 1758 (1939).

(71) Webb, Kay, Nichol, J. Ind. Hyg. Toxicol. 27, 249-255 (1945); C.A. 40, 1116 (1946). (72) Weber, Chem. Zig. 57, 836 (1933); Cent. 1933, II 3889; C.A. 28, 727 (1934). (73) Weber, Chem. Zig. 61, 807-808 (1937); Cent. 1938, I 950; C.A. 32, 74 (1938). (74) Moran, J. Ind. Hyg. Toxicol. 25, 243-248 (1943), C.A. 39, 4110 (1945). (75) Balis, Liebhafsky, Bronk, Ind. Eng. Chem., Anal. Ed. 13, 119 (1941). (77) McBee, Hass, Neher, Strickland, Ind. Eng. Chem. 34, 296-300 (1942). (78) Padovani, Magaldi, Gron. chim. ind. applicata 15, 1-7 (1933); Cent. 1933, I 3056; C.A. 27, 3443 (1933); Inst. Ind. Chem. Fuels, Polytechnicum, Milan 4, 193-208 (1932/1933); [C.A. 29, 1229 (1935)]. (79) Mason, Wheeler, J. Chem. Soc. 1931, 2282-2293. (80) Egloff, Schaad, Lowry, Chem. Revs. 8, 6-25 (1931).

(81) Coehn, Cordes, Z. physik. Chem. B-9, 1-24 (1930).
(82) Schleede, Luckow, Ber. 55, 3710-3726 (1922).
(83) Whiston, J. Chem. Soc. 117, 183-190 (1920).
(84) Martin, Fuchs, Z. Elektrochem. 27, 150-162 (1921); C.A. 15, 2375 (1921).
(85) Jones, Allison, Meighan, U.S. Bur. Mines, Tech. Paper 255, 44 pp. (1921); C.A. 15, 1983-1984 (1921).
(86) Baskerville, Riederer, J. Ind. Eng. Chem. 5, 5-8 (1913).
(87) Bedford, Ind. Eng. Chem. 8, 1090-1094 (1916).
(88) Pfeifer, Mauthner. Reitlinger, J. prakt. Chem. (2) 39, 239-242 (1919).
(89) Martin, Lux (to Dow Chem. Co), U.S. 1,801,873, Apr. 21, 1931; Cent. 1931, II 1631; C.A. 25, 3357 (1931).
(90) McKee, Salls, U.S. 1,765,601, June 24, 1930; Cent. 1930, II 1439, C.A. 24, 4051 (1930).

(91) Carter, Coxe, to S Karpen and Bros., U.S. 1,572,513, Feb. 9, 1926; Cent. 1926, I 2838; [C.A. 20, 1243 (1926)]: Brit. 245,991, Sept. 11, 1926; Cent. 1926, I 2838; C.A. 21, 415 (1927); Ger. 472,421, Feb. 28, 1929; Cent. 1929, I 2818; [C.A. 23, 2448 (1929)]. French 597,678, Nov. 26, 1925; Cent. 1926, I 2838; not in C.A. Canadian 251,763, July 14, 1925; C.A. 19, 3272 (1925). (92) I.G., French 816,957, Aug. 21, 1937; Cent. 1937, II 3380, C.A. 32, 2142 (1938). (93) Söll, Runkel (to I.G.), Ger. 491,316, Dec. 20, 1932, Cent. 1933, I 1013; C.A. 27, 991 (1933). (94) Ernst, Wahl, Ger. 486,952, Nov. 30, 1929; Cent. 1930, I 3829; C.A. 24, 1393 (1930). (95) Pfeifer, Szarvasy, Ger. 242,570, Jan. 13, 1912; Cent. 1912, I 384, [C.A. 6, 2211 (1912)]; U.S. 1,012,149, Dec. 19, 1911; [C.A. 6, 459 (1912)]. (96) Walter, Ger. 222,919, June 9, 1910; Cent. 1910, II 255; [C.A. 4, 2866 (1910)]. (97) I.G., Brit. 283,119, Feb. 29, 1928; Cent. 1928, II 1034; C.A. 22, 3893 (1928): French 646,661, Nov. 14, 1928; Cent. 1929, I 803; [C.A. 23, 2191 (1929)]. (98) Weber, Erasmus (to T. Goldschmidt, A.G.), U.S. 1,565,345, Dec. 15, 1925, Cent. 1926, I 2051; [C.A. 20, 424 (1926)]. (99) Wheeler, Mason (to Imperial Chem. Ind., Ltd.), U.S. 1,918,624, July 18, 1933; not in Cent.; C.A. 27 4816 (1933): Brit. 342,329, Feb. 26, 1931; Cent. 1931, II 629, C.A. 25, 4890 (1931). (100) Carlisle (to du Pont Co.), U.S. 1,939,292, Dec. 12, 1933; Cent. 1934, I 1883; not in C.A.

(101) Greene, Jahresber. 1879, 490. (102) Perkin, Zett. für Chem. 1868, 714. (103) Bachrach, Oel. u. Fett. Ind. 10, No. 4, 42 (1934); Cent. 1935, II 1872; not in C.A. (104) Stock, Stiebler, Ber. 56, 1091 (1923). (105) Soc. chim. des Usines du Rhone, Ger. 416,014, July 7, 1925; French 586,006, March 13, 1925; Cent. 1925, II 1795, not in C.A. (106) Butlerow, Ann. 111, 251-252 (1859); Zett. für Chem. 1869, 276. (107) Henry, Bull. acad. roy. Belg. 1900, 48-56; Cent. 1900, I 1122. (108) Dreyfus, Brit. 341,878, Feb. 19, 1931; Cent. 1931, II 120; C.A. 25, 4890 (1931). (109) Panizzon, Helv. Chem. Acta 15, 1187-1194 (1932). (110) Huff, U.S. Bur. Mines, Rept. Investigations 3794 (1945); C.A. 39, 1291 (1945): Jones, Kennedy, Scott, U.S. Bur. Mines, Rept. Investigations 3727 (1943); C.A. 38, 487 (1944).

(111) Langen van der Valk, Rec. trav. chim. 48, 201-219 (1929). (112) Harteck, Kopsch, Z. physik. Chem. B-12, 345-347 (1931); Z. Elektrochem. 36, 714-716 (1930). (113) Biesalski, Z. angew Chem. 37, 317 (1924). (114) Brenschede, Shumacher, Z. physik. Chem. A-177, 245-262 (1936). (115) Zeidler, Meyer, Farben-Zig. 46, 464-465 (1941); Cent. 1941, II 1686; C.A. 39, 4487 (1945). (116) Levine (to du Pont Co.), U.S. 1,975,727, Oct. 2, 1934; Cent. 1935, I 1934; C.A. 28, 7268 (1934). (117) Söll, Runkel (to I.G.), Ger. 518,166, Jan. 14, 1933; Cent. 1933, I 2171; C.A. 27, 1364 (1933). (118) "Polmin" Panstwowa Fabryka Olejow Mineralnych, E. Sucharda, Polish 11,909, June 25, 1930; Cent. 1931, II 2512; not in C.A. (119) Rhenania Verein Chem. Fabriken, A.G., Ger. 362,746, Oct. 30, 1922; Cent. 1923, II 477; not in C.A. (120) Leopold, Michael (to M.L.B.), Ger. 382,391, Oct. 1, 1923; Cent. 1924, I 1710; not in C.A.

(121) M.L.B., Ger. 426,670, Mar. 17, 1926; [Cent. 1926, I 3184], not in C.A.: Brit. 189,432, Jan. 17, 1923; Cent. 1923, II 743; C.A. 17, 2428 (1923). (122) Roka (to Holzverkohlungs-Ind.,

A.G.), Austrian 94,305, Sept. 25, 1923; Cent. 1924, I 2542; not in C.A.: Ger. 467,234, Aug. 29, 1922; [Cent. 1939, I 1396]; C.A. 23, 2191 (1929). (123) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994; [C.A. 26, 2747 (1932)]. (124) Abkin, Medvedev, J. Chem. Ind. (Moscow) 1934, No. 1, 30-34; Cent. 1935, I 2801; C.A. 28, 3051 (1934) Russian 34,551, Feb. 28, 1934: Cent. 1935, I 2894; C.A. 29, 2973 (1935). (125) André, Compt. rend. 102, 1474 (1886). (126) Henne, J. Am. Chem. Soc. 59, 1400-1401 (1937). (127) Henne, Renoll, Leicester, J. Am. Chem. Soc. 61, 938 (1939). (128) Scherer, Dostal, Dachlauer (to I.G.), U.S. 2,347,000, April 18, 1944; [C.A. 39, 89 (1945)]: Ger. 727,690, Oct. 8, 1942; C.A. 37, 6676 (1943). French 870,965, April 1, 1942; Cent. 1942, II 1180: Italian 389,972, March 18, 1941; Cent. 1942, II 2849. (129) Pouret, Compt. rend. 130, 1192 (1900); Bull. soc. chim. (3) 25, 193 (1901). (130) Timmermans, Hennaut-Roland, J. chim. phys. 29, 533-536 (1932).

(131) Perkin, Scarborough, J. Chem. Soc. 119, 1408 (1921). (132) Fragner, Czechoslovak 46,929, Mar. 10, 1934; Cent. 1934, II 331; not in C.A. (133) Perkin, J. prakt. Chem. (2) 31, 505 (1885). (134) Berthelot, Compt. rend. 130, 1095 (1900). (135) Gross, Saylor, J. Am. Chem. Soc. 53, 1749 (1931). (136) Beckmann, Z. physik. Chem. 46, 853 (1903). (137) Adams, Marvel, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 358-360 (1941); (1st ed.), 350-351 (1932); 1, 57-59 (1921). (138) Hartmann, Dreger, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 357-358 (1941); (1st ed.), 349 (1932); 9, 56-57 (1929). (139) Backer, Rcc. trav. chim. 48, 950-951 (1929). (140) Tchakıran,

Compt. rend. 196, 1026-1028 (1933).

(141) Patrick, Martin, Trans. Faraday Soc. 32, 347-358 (1936). (142) Staudinger, Z. Elektrochem. 31, 549-552 (1932). (143) Lenze, Metz, Z. ges. Schress-u. Sprengstoffw. 27, 294, 337 (1932). (144) Saffer, Davis, J. Am. Chem. Soc. 67, 641-645 (1945). (145) Bawn, Milstead, Trans. Faraday Soc. 35, 894 (1938). (146) von Hartel, Meer, Polanyi, Z. physik. Chem B-19, 139-163. (1932). (147) Haresnape, Stevels, Warhurst, Trans. Faraday Soc. 36, 465-472 (1940). (148) Paneth, Lausch, J. Chem. Soc. 1935, 380-383. (149) Avery, Forbes, J. Am. Chem. Soc. 60, 1005-1011 (1938). (150) Theobald (to du Pont Co.), U.S. 2,378,048, June 12, 1945; C.A. 39, 4085 (1945).

(151) Wiezevich, Fröhlich (to Standard Oil Development Co.), U.S. 2,062,344, Dec. 1, 1936; Cent. 1937, I 4863, C.A. 31, 708 (1937). (152) Friedel, Crafts, Bull. soc. chm. (2) 41, 322-327 (1884); Ann. chim. (6) 11, 263-277 (1887). (153) Schwarz, Ber. 14, 1576 (1881). (154) Sommelet, Compt. rend. 180, 1349-1350 (1925). (155) Morgan, Coulson, J. Chem. Scc. 1929, 2205-2208, 2212-2213. (156) Barnett, Goodway, Watson, Ber. 66, 1879, 1887 (1933). (157) Forbes Anderson, J. Am. Chem. Soc. 67, 1912 (1945). (158) Arnhold, Ann 240, 197-208 (1887). (159) Carter (to S. Karpen and Bros.), U.S. 1,566,819, Dec. 22, 1925, Cent. 1926, I 2510; C.A. 20, 423 (1926): Brit. 249,039, Oct. 23, 1925; not in Cent., C.A. 21, 745 (1927): Ger. 495,020, April 3, 1930; Cent. 1930, I 3485; [C.A. 24, 3251 (1930)]. (160) Delepine, Bull. soc. chim. (3) 11, 556-557 (1894); Ann. chim. (7) 15, 476-477 (1898).

(161) Jones, Whalen, J. Am. Chem. Soc. 47, 1351 (1925). (162) Davies, Evans, Hulbert, J. Chem. Soc. 1939, 416. (163) Piccard, de Montmollin, Helv. Chim. Acta 6, 1020 (1923). (164) Ruigh, Ind. Eng. Chem., Anal. Ed. 11, 250 (1939). (165) Wang, J. Chinese Chem. Soc. 1, 61-62 (1933). (166) Koelle, Ber. 13, 1953 (1880). (167) V. H. Dermer, O. C. Dermer, J. Org. Chem. 3, 289-293 (1939). (168) Hrynakowski, Szmyt, Z. physik. Chem. A-182, 405-408 (1938).

3:5025 1,1,3-TRICHLORO-2-METHYLPROPENE-1 $C_4H_5Cl_3$ Beil. S.N. 11 CH₂ ClCH₂—C=CCl₂

B.P. 45-46° (1)

Note: C readily undergoes allyl transposition so that in reactions of C products derived from the isomeric 1,1,1-trichloro-2-methylpropene-2 (3:5605) may be expected (1) (2) (3) [For prepn. of \bar{C} (57% yield (1)) from β,β,β -trichloro-ter-butyl alc. ("Chloretone") (3:2662) by htg. to 200° with P2O5 and dimethylaniline see (1).] [A 15% yield of the isomeric 1,1,1-trichloro-2-methylpropene-2 (3:5605) together with some α -chloroisobutyric acid (3:0235) are separated from \bar{C} by redistillation (1).

C on hydrolysis by boilg. 2 days with AgOH at 100° under pressure gives (22% yield (2)) 3,3-dichloro-2-methylpropen-2-ol-1, b.p. 78-79°, $D_{-}^{20} = 1.298$, $n_{-}^{20} = 1.493$. [The corresp. ether, b.p. 129° at 11 mm., $D_{-}^{20} = 1.330$, $n_{-}^{20} = 1.5108$, is also formed in 22% yield (2).] The alc. may be characterized by its p-nitrobenzoate, m.p. 91°, or its N-phenylcarbamate, m.p. 64° (2).

 $\bar{\mathbf{C}}$ on htg. with NaOAc + AcOH gives (2) 3,3-dichloro-2-methylpropen-2-yl acetate, b.p. 79° at 12 mm., $D_{-}^{20} = 1.257$, $n_{-}^{20} = 1.4718$ (2). [With boilg. NaOH this ester regenerates the corresp. alc. (2).]

 \bar{C} with NaOEt gives in the cold 70% yield (2) of 3,3-dichloro-2-methylpropen-2-yl ethyl ether, b.p. 56° at 12 mm., $D_{-}^{20} = 1.1285$, $n_{-}^{20} = 1.4610$ (2).

 \bar{C} in CHCl₃, treated with O₃, then hydrolyzed gives α -chloroacetone (3:5425), b.p. 60-62° at 50 mm. (1).

[For reactns. of C with CaI2 and with CH3MgBr see (2).]

- D 1,1,1,2,3-Pentachloro-2-methylpropane (3·1265): m.p. 59.5° (2). [From $\ddot{\textbf{C}}$ by direct treatment with Cl₂ (2).]
- (2). [From C on warming 1 day with excess Br₂, then distg. at 12 mm. (2).]
- 3,3-Dichloro-2-methylpropen-2-yl p-nitrobenzoate: m.p. 91° (2). [From C on boilg. with dil. alc. soln. of K p-nitrobenzoate (2).]

3:5025 (1) Jacob, Bull. soc. chim. (5) 7, 581-586 (1940). (2) Kirrmann, Jacob, Bull. soc. chim. (5) 7, 586-593 (1940). (3) Kirrmann, Jacob, Compt. rend. 203, 1528-1529 (1936).

3:5028 trans-1,2-DICHLOROETHYLENE
$$Cl-C-H$$
 $C_2H_2Cl_2$ Beil. I — (trans-Acetylene dichloride) $H-C-Cl$ $I_1-(78)$ $I_2-(159)$

B.P.
$$[48.8-50.2^{\circ}]$$
 $(35)]$ -53.1° (34) $D_{4}^{25} = 1.2489$ (1) $48.8^{\circ}]$ at 763 mm. (1) -53.0° (12) $n_{D}^{25} = 1.43969$ (7) $48.4-49.4^{\circ}]$ at 741 mm. (2) -50.0° (13) $D_{4}^{20} = 1.2569$ (1) $48.35^{\circ}]$ at 760 mm. (3) (4) (13) $n_{D}^{18} = 1.44662$ (6) $48.2-48.4^{\circ}]$ at 769 mm. (6) $47.85-47.87^{\circ}$ at 769.5 mm. (7) (7) (8) (7) (7) (8) (7) (8) (7) (8) (7) (8) (7) (8) (9) (10) (10) (10) (10) (10) (11) (10) (11) (11) (11) (11) (12) (12) (13) (13) (14) (15)

See also both cis-1,2-dichloroethylene (3:5042) and ordinary (mixt. of cis and trans) 1,2-dichloroethylene (3:5030); the following text is restricted to studies on substantially pure trans stereoisomer.

Note carefully that 1,2-dichloroethylene is not the same as ethylene (di)chloride (3:5130) (there are an almost incredible number of errors in the literature involving this point); neither is it the same as the now very important 1,1-dichloroethylene (vinylidene (di)chloride) (3:5005).

GENERAL DATA ON C

Note that substantially pure \bar{C} is comml. solvent in U.S.A. under designation "Di 48" (referring to the two chlorine atoms and the b.p.). [For study of thermal conductivity and for tabulation of constants of comml. \bar{C} see (14). — For toxicity of \bar{C} see (36) (15). — For use of \bar{C} in extraction of caffeine from coffee see (16).]

[For data on vap. press. of C over range 23-48.8° see (1).]

Binary systems contg. $\bar{\mathbf{C}}$. (See also below under azeotropes.) — $[\bar{\mathbf{C}} + cis-1,2\text{-dichloro-ethylene} (3:5042);$ for use of n_D^{25} in detn. of compn. of mixt. see (7); for f.p./compn. data (eutectic, f.p. -91° contg. about 29% $\bar{\mathbf{C}}$) see (12). — For f.p./compn. data on binary systems $\bar{\mathbf{C}}$ + ethylene dichloride (3:5130), $\bar{\mathbf{C}}$ + 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750), or $\bar{\mathbf{C}}$ + ethylene dibromide see (12). — For f.p./compn. data on system $\bar{\mathbf{C}}$ + $\mathbf{C}_6\mathbf{H}_6$ (1:7400) see (34). — For study of soly. of various other cis-trans isomers in $\bar{\mathbf{C}}$ see (5).]

Azeotropes contg. Č. Binary azeotropes. Č with aq. forms a const.-boilg. mixt., b.p. 45.3°, contg. 98.1% Č (38) (39). — Č with EtOH (1:6130) forms a const.-boilg. mixt., b.p. 46.5° at 760 mm. (17) (38) (39), contg. 94.5% (38) (39) 88.2 mole % (17) Č.

Ternary azeotropes. \tilde{C} with EtOH (1:6130) + aq. forms a const.-boilg. mixt., b.p. 44.4°, contg. 94.5% \tilde{C} + 4.4% EtOH + 1.1% aq. (38) (39).

PREPARATION OF C

Pure \tilde{C} is usually obtd. by careful fractional distillation at ord. press. of the mixt. of the cis and trans stereoisomers comprising ord. 1,2-dichloroethylene (3:5030) [for brief comments on this mode of sepn. see (1) (2) (3) (5) (6) (7) (8) (9) (11); note that some workers (11) recommend distn. in atmosphere of CO_2 . — For detn. of % compn. of mixts. of \tilde{C} with its stereoisomer by means of $n_2^{D_5}$ see (7); by means of dielectric constant see (7) (19).] [For study of possibility of sepn. of \tilde{C} from its stereoisomer by differential adsorption

[For study of possibility of sepn. of C from its stereoisomer by differential adsorption on silica gel see (18).]

[For prepn. of \tilde{C} from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) by splitting out 2 adjacent chlorine atoms with Zn + EtOH (followed by fractionation of crude \tilde{C}) see (19); for prepn. of \tilde{C} from 3,4-dichloro-2-methylbuten-3-ol-2 by slow addn. to 85% KOH at 175-180° (acetone is also formed) see (37).]

[For patents on prepn. of almost pure \bar{C} from acetylene with Cl_2 by controlled reaction over pumice contg. $CuCl_2$ at 200–240° (20) or over activated carbon at 40° (21) see indic. refs.]

ISOMERIZATION OF C

 $\bar{\rm C}$ under the influence of heat, light, or various catalysts in part isomerizes to cis-1,2-dichloroethylene (3:5042). — [For study of thermal isomerization of $\bar{\rm C}$ in vapor phase at 185–275° (22), up to 350° (19), up to 975° (23), in liq. phase or in various solns. (11) see indic. refs.; note that the equilibrium mixt. at 300° conts. 39.2 \pm 0.7% $\bar{\rm C}$, at 350° conts. 40.6 \pm 0.3% $\bar{\rm C}$ (19), at 975° conts. 47.7% $\bar{\rm C}$ (23). — For study of kinetics of thermal isomerization of $\bar{\rm C}$ see (7) (24).]

[For patent on isomerization of pure \tilde{C} to a mixt. contg. 65-70% of the *cis* stereoisomer (3:5042) by means of a small amt. Br₂ at 30° or above in pres. of cat. or in vapor phase at not over 300° see (25) cf. (7). — For patent on thermal isomerization of \tilde{C} see (26).]

CHEMICAL BEHAVIOR OF C

Reactions with inorganic compds. \tilde{C} (in vapor phase at 80–95° in light of 4360 Å (27)) with Cl_2 adds 1 mole halogen yielding 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750).

Č with Br₂ in light adds 1 mole halogen yielding (28) (3) (29) 1,2-dibromo-1,2-dichloro-ethane [Beil. I-93, I₂-(29), I₂-(64)], b.p. 195° at 760 mm. (13) (30), b.p. 79.0-79.5° at 15 mm. (3). — [For extensive study of the resultant equilibrium see (28); for study of influence of O₂ and other factors see (28); for study of kinetics in CCl₄ soln. see (31) (32).

— Note that rate of addn. of Br_2 either directly or in CCl₄ soln. is twice as great for \tilde{C} as for the stereoisomeric cis form (3:5042) (3).]

[\bar{C} with alc. KOH splits out 1 HCl yielding chloroacetylene (3:7000); note, however, that rate of reactn. with \bar{C} is only about $\frac{1}{20}$ as fast as for its cis stereoisomer (3:5042) (3).]

 \bar{C} with aq. NaOH/Hg(CN)₂ behaves quite differently from its *cis* stereoisomer (3:5042): on shaking at room temp. with specified (8) concns. of reagt. \bar{C} shows signs of reactn. only after 3 hrs. (instead of $\frac{1}{2}$ hr. as for the stereoisomer) and suffers replacement of 1 H atom per mole by mercury forming mercury *bis*-(α , β -dichloroethylenide) Hg(CCl = CHCl)₂, m.p. 50.3°, insol. aq., but very sol. CHCl₃, ether, or acetone, together with other, more complex derivatives. — Cf. the entirely different behavior of the *cis* stereoisomer (3:5042).

Č with PtCl₄ in C₆H₆ at 40-50° for 3 hrs. evolves HCl and on cooling separates amber cryst. of trans-1,2-dichloroethylene platinous chloride, Cl.CH = CH.Cl.PtCl₂, m.p. 155-160° (33); note that the cis stereoisomer by similar treatment gives only gums (33).

Reactions with organic compds. [\bar{C} with C_6H_6+Al/Hg at 0° gives same prods. as does the ord. (mixture) 1,2-dichlorocthylene (3:5030) (presumably indicating partial isomerization of \bar{C}); these prods. include dibenzyl, triphenylethane, tetraphenylethane, etc. (6).]

3:5028 (1) Herz, Rathmann, Chem. Ztg. 37, 622 (1913). (2) Walker, Trans. Fara ay Soc. 31, 1434 (1935). (3) Chavanne, Compt. rend. 154, 776-777 (1912), Cent. 1912, I 1539; Bull. soc. chim. Belg. 26, 289-294 (1912); Cent. 1912, II 1006; Bull. soc. chim. Belg. 28, 234-240 (1914); Cent. 1914, II 1144. (4) Bonino, Bruhl, Gazz. chim. ital. 59, 648-649 (1929); Z. Physik 58, 195 (1929). (5) Lebrun, Bull. soc. chim. Belg. 39, 423-433 (1930). (6) Böeseken, Bastet, Rec. trav. chim. 32, 197-203 (1913). (7) Jones, Taylor, J. Am. Chem. Soc. 62, 3480-3485 (1940). (8) FitzGibbon, J. Chem. Soc. 1938, 1218-1222. (9) Ebert, Bull, Z. physik. Chem. A-152, 451-452 (1931). (10) Mahncke, Noyes, J. Chem. Phys. 3, 536 (1935).

(11) Wood, Dickinson, J. Am. Chem. Soc. 61, 3259-3263 (1939). (12) Timmermans, Bull. soc. chim. Belg. 36 184-187 (1927). (13) Timmermans, Bull. soc. chim. Belg. 27, 334-343 (1913); Cent. 1914, I 618 (14) Bates, Hazzard, Palmer, Ind. Eng. Chem. 33, 375-376 (1941). (15) Ferguson, Nature 137, 361-362 (1936). (16) Coffex, A. G., Swiss 162,725, Sept. 1, 1933; Cent. 1933, II 3636. (17) Lecat, "L'Azeotropism," Brussels, 1918, Lecat No. 339. (18) Hesse, Tschachotin, Naturwissenschaften 30, 387-392 (1942); Cent. 1942, II 1325; C.A. 37, 6211 (1943). (19) Olson, Maroney, J. Am. Chem. Soc. 56, 1320-1322 (1934). (20) Consortium für Elektrochem. Ind., Brit. 366,348, Feb. 25, 1932; French 714,995, Nov. 23, 1931; Cent. 1932, I 3345; C.A. 26, 1624 (1932); Ger. 555,373, May 10, 1930; C.A. 26, 5106 (1932).

(21) Ruppert, Fischer, Voigt, Hennig (to I G), U.S. 1,868,077, July 19, 1932; C.A. 26, 5106 (1932); Brit. 310,964, June 26, 1929; Cent. 1930, II 2957; Ger. 553,149, Sept. 30, 1932; Cent. 1932, II 3303. French 674,254, Jan. 27, 1930; Cent. 1930, I 3829; Swiss 141,529; Cent. 1931, 1823. (22) Wood, Stevenson, J. Am. Chem. Soc. 63, 1650-1653 (1941). (23) Maroney, J. Am. Chem. Soc. 57, 2397-2398 (1935). (24) Tamamuri, Akiyama, Z. Elektrochem. 47, 340-345 (1941); C.A. 35, 6859 (1941). (25) Mugdan, Rost (to Consortium für Elektrochem. Ind.), Ger. 595,464, April 11, 1934; Cent. 1935, I 2599; C.A. 28, 4072 (1934). (26) Fertsch (to I.G.), Ger. 510,576, Oct. 20, 1930; Cent. 1931, I 151; C.A. 25, 965 (1931). (27) Muller, Schumacher, Z. physik. Chem. B-35, 285-297 (1935). (28) Müller, Schumacher, Z. physik. Chem. B-42, 327-345 (1939). (29) Verhoogen, Bull. soc. chim. Belg. 34, 434-456 (1925). (30) van der Walle, Bull. soc. chim. Belg. 28, 307 (1914).

(31) Herz, Rathmann, Ber. 46, 2589 (1913). (32) Bruner, Fischler, Z. Elektrochem. 20, 84 (1914). (33) Kharasch, Asford, J. Am. Chem. Soc. 58, 1737-1738 (1936). (34) Band, Jay, Compt. rend. 150, 1687-1690 (1910); Bull. soc. chim. (4) 9, 119 (1911); Ann. chim. (8) 27, 96 (1912). (35) Awberry, Griffiths, Proc. Phys. Soc. (London) 48, 379 (1936). (36) Lehman, Schmidt-Kehl, Arch. Hyg. Bakt. 116, 131-268 (1936); C.A. 31, 477 (1937); not in Cent. (37) Petrov, J. Gen. Chem. (U.S.S.R.) 13, 331-338 (1943); C.A. 38, 1468 (1944). (38) Chavanne, Bull. soc. chim. Belg. 27, 205-209 (1913); Cent. 1913, II 1376; C.A. 8, 1105 (1914). (39) Gowing-Scopes. Analyst 39, 6 (1914).

3:5030 1,2-DICHLOROETHYLENE ord.
$$C_2H_2Cl_2$$
 Beil. I - 187 (Acetylene dichloride) mixt. $HC-Cl + Cl-C-H + Cl$ $I_1-(77)$ $I_2-(158)$ $HC-Cl + H-C-Cl$ $Cis trans$ (3:5042) (3:5028)

The text under this heading refers to the ordinary mixt. of the two individual stereoisomeric forms, viz., cis-1,2-dichloroethylene (3:5042) and trans-1,2-dichloroethylene (3:5028). Since the proportion of the two stereoisomers differs according to conditions and previous treatment no definite physical constants can be given, and those for each pure stereoisomer should be consulted.

Note carefully that 1,2-dichloroethylene is *not* the same as ethylene (di)chloride (3:5130) (there are an almost incredible number of errors in the literature involving this point); neither is it the same as 1,1-dichloroethylene (vinylidene (di)chloride) (3:5005).

Furthermore note that some confusion exists in the literature on the relationship between the two isomers; the high-boilg. stereoisomer (3:5042) is now definitely regarded as the cis form and the lower-boilg. stereoisomer (3:5028) as the trans; however, some records (including "International Critical Tables") have inverted these designations.

PHYSICAL DATA ON Č

General. Ordinary comml. \bar{C} consists of a mixt. of the two stereoisomers; by careful fractional distn. the two stereoisomers can be separated (for references see text of the two pure stereoisomers). — An equilibrium mixt. contg. about 20% of the lower-boilg. (trans) (3:5028) and 80% of the higher-boilg. (cis) (3:5042) forms can be obtd. from either by treatment at ord. temp. in sunlight with 1-2% Br₂ (for data on thermal isomerization see text of both individual stereoisomers). — Note also that the two pure stereoisomers (q.v.) form a eutectic. f.p. -91° , contg. about 29% trans +71% cis forms.

Solubility relationships of \tilde{C} . Soly, of \tilde{C} in aq. is 0.8 ml. per 100 ml. aq. at ord, temp. (1). — [For soly, of I_2 in \tilde{C} over range $11-25^\circ$ (2) and use of such solns, in detn. I_2 number of oils and fats (3) (4) see indic. refs. — For solv, power of \tilde{C} for various org. epds. see (5) (6).

Inflammability of \bar{C} . \bar{C} with air forms explosive mixt. in range contg. 3.3–15.3% \bar{C} (7); 9.7–12.8% \bar{C} (8). [For studies of influence of vapors of \bar{C} on mixts. of air with CH₄ (8), acetylene (10), CO (10) (12), or H₂ (10) see indic. refs.]

Miscellaneous data. [Ebullioscopic const. of \tilde{C} (for 1 mole solute in 100 g. \tilde{C}) = 29.6 (14).]

USES OF C

[For use of \bar{C} as solv. for fats and oils (15), as refrigerating liquids (16) (17) (18) (19) (20) (21), for extraction of caffeine from coffee (22), for dehydration (concentration) of propionic acid from aq. solns. (23), for sepn. of o- and p-isomers of various phenols (24), in dewaxing of mineral lubricating oils (25), for pretreatment in dyeing of cellulose esters and ethers (26) see indic. refs.]

PHYSIOLOGICAL BEHAVIOR OF C

Č acts as an anesthetic and narcotic, but full treatment of this aspect is beyond the scope of this work; for lead references, however, see below.

Toxicity of C. [For studies on toxicity of C see (27) (28) (29) (30) (31); for studies of narcotic action (31) (33) (34) (35) (36) see indic. refs.]

Antiseptic and disinfectant props. of \tilde{C} . [For studies of \tilde{C} from this viewpoint see (37) (38) (1).]

DETERMINATION OF C

Č is detd. by conversion of its halogen by pyrolytic or by chem. means completely to chloride ion followed by either volumetric or gravimetric detn. of the latter.

[For detn. of \bar{C} by methods involving pyrolytic decompn. of \bar{C} see (39) (40) cf. (41).] [For detn. of \bar{C} by methods involving decompn. of \bar{C} with Na + ethanolamine in dioxane see (42) cf. (43).]

[For detn. of Č by means of HgSO₄ catalyzed addn. of Br₂ (from bromide/bromate soln.) to its unsatd. linkage see (44).]

PREPARATION OF C

From various polychloroethanes. From 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750). [For prepn. of \bar{C} from acetylene tetrachloride by removal of 2 chlorine atoms with H_2 over Ni at 300-320° (45), with Fe or Al + aq. (46) (47) or Zn + aq. (47) (48), with acetylene over hydrogenating cat. (such as Ni) on activated carbon at 350° (49) preferably in pres. of aq. vapor (50), or by electrolytic reduction in pres. of ZnCl₂ (51) cf. (52) see indic. refs. — Note that \bar{C} is also one of the prods. of pyrolysis of acetylene tetrachloride over pumice at 700° (53).]

From 1,1,1,2-tetrachloroethane (3:5555). [For prepn. of Č from unsym.-tetrachloroethane with acetylene over hydrogenating cat. (such as Ni) on activated carbon at 350° (49) preferably in pres. of aq. vapor (50) see indic. refs.; note that mechanism yielding this result is unknown.]

From 1,1,2-trichloroethane (3:5330). [For prepn. of C from 1,1,2-trichloroethane (by loss of HCl) over CuCl₂ on pumice at 400° (54) or with MeOH over Al₂O₃ at 290° (MeCl (3:7005) is also formed) (55) see indic. refs.]

From 1,2-dichloroethane (3:5130). [For formn. of \bar{C} (22% yield) together with other prods. from ethylene (dı)chloride with Cl₂ in pres. of AlCl₃/NaCl/FeCl₃ at 400–480° see (56).]

From various mixed-halogenated ethanes. [For formn. of \tilde{C} from 1,2-dibromo-1,2-dichloroethane [Beil. I-93, I₁-(29), I₂-(64)] by removal of 2 Br with Zn in alc. (57) or with H₂ over Ni at 300-320° (45) see indic. refs.; from 2-bromo-1,1,2-trichloroethane (by elimination of Br-Cl) with Zn dust in boilg. alc. (58) (59) or from 2-iodo-1,1,2-trichloroethane on distn. at atm. press. (60) see indic. refs.]

From acetylene. With chlorine. [Starting from acetylene the addition of 1 mole of Cl_2 yields \bar{C} to which further addn. of Cl_2 gives 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750); for this reason most of the processes for prepn. of the latter cpd. by this method yield (or may be made to yield) \bar{C} as a by-product. Since the patents on the addn. of chlorine to acetylene have been extensively cited under the text of 1,1,2,2-tetrachloroethane (3:5750) (prepn. from acetylene), refer to that compound; however, see also (61) (62) (63).]

With other reagents. [For formn. of \bar{C} from acetylene with SbCl₅ (64) (65) cf. (57), with SbCl₅ + SbCl₃ (66), or with aq. ICl soln. (57), see indic. refs.]

CHEMICAL BEHAVIOR OF C

Pyrolysis of C. [C in s.t. at 360° for 10 hrs. is completely decomposed (64) into carbon + HCl.] (See also above under detn. of C.)

Oxidation of C. [C with O₂ in pres. of suitable cat. (e.g., Br₂ or H₂SO₄) gives (67)

chloroacetyl chloride (3:5235). — \ddot{C} with $O_2 + N_2$ in ultra-violet light evolves HCl but yields (68) only resinous (perhaps polymerization) products.]

[For study of rate of reactn. of C (in AcOH) with O3 see (69).]

[Note that C with NH₃ + air over Pt/Rh cat. at 820-850° gives (70) HCN.]

[C with air over (strongly chlorinated) CuO at 450° gives (76) much phosgene (3:5000).]

Stabilization of \bar{C} . [For stabilization of \bar{C} by addn. of small amts. of alc. NH₃ (71), with Et₃N (72), or with various phenols, amines, and aminophenols (73), see indic. refs.] (See also under corresp. subtopic of 1,1,2-trichloroethylene (3:5170).)

Polymerization of C. [C in the pres. of dibenzoyl peroxide (or other org. peroxides) on htg. under press. reacts with itself yielding mainly (74) a dimer, viz., 1,3,4,4-tetra-chlorobutene-1 (3:9058), accompanied by other prods.]

[For study of influence of radiation of 1980-1860 Å (from Al arc) and accompanying polymerization see (75).]

Reaction with halogens. Behavior of \bar{C} with Cl_2 . [\bar{C} adds 1 mole Cl_2 giving (69% yield (58)) 1,1,2,2-tetrachloroethane (3:5750); for study of this reactn. in light of 4360 \bar{A} see (77).] (See also under the individual cis- (3:5042) and trans- (3:5028) stereoisomers.)

Behavior with Br_2 . [\bar{C} adds 1 mole Br_2 giving (60) (57) 1,2-dibromo-1,2-dichloroethane [Beil. I-93, I_{1} -(29), I_{2} -(64)], b.p. 195° at 760 mm. (78) (59), b.p. 79.0-79.5° at 15 mm. (79); for study of photochem. addn. of Br_2 in gas phase (80) (81) and in CCl_4 soln. (81) (82) in sunlight (83) (84) see indic. refs.]

Behavior with 1Cl. [\bar{C} in CHCl₃ adds ICl in sunlight yielding (60) 2-iodo-1,1,2-trichloro-ethane, b.p. 77° at 9 mm., $D_1^{15} = 2.2760$ (60).]

Reaction with halogen hydrides. Reaction with HCl. [C in the absence of cat. does not add dry HCl; C with dry HCl in the pres. of small amts. AlCl₃ at 30-40° gives (87% yield (86)) (85) (104) 1,1,2-trichloroethane (3:5330) accompanied (85) by 1,1,2,3,4-pentachlorobutane (3:0750); this latter prod. and doubtless various others appear to be formed in the pres. of the AlCl₃ by various condensations among the various organic materials (see below).]

Reaction with H_2SO_4 . [\bar{C} is only slightly attacked at 20° by either 85% or 96% H_2SO_4 and no polymerization occurs (87); on running the H_2SO_4 layer into 10 vols. of cold aqual. evidence of formn. of chloroacetaldehyde (3:7212) was obtd. (87). — \bar{C} with conc. H_2SO_4 is unchanged up to 120° but at higher temps. carbonizes without evidence of formn. of chloroacetaldehyde (88).]

[However, \bar{C} with fuming H₂SO₄ (50% SO₃) or \bar{C} with SO₃ followed by aq. gives (88) (89) chloroacetaldehydesulfonic acid from which htg. with 80% H₂SO₄ gives (88) (89) chloroacetaldehyde (3:7212).]

Behavior with alkali. [C with alc. KOH (90) (91) loses 1 HCl yielding chloroacetylene (3:7000); this prod. sometimes (92) (93) causes spontaneous ignition of the system especially when its alc. soln. comes in contact with air in cleaning the reaction flask (91).] (See also under the individual cis- (3:5042) and trans- (3:5028) stereoisomers.)

[Note that C with alc. NaSH does not react even after 6 hrs. reflux. (92).]

Behavior with NH₃. [Č with liq. NH₃ under high press. reacts only very slightly although a small amt. of chloroacetylene (3:7000) (from loss of HCl) is formed (94).]

Behavior with metals. [For study of corrosion of common metals by C see (5).]

Behavior with other inorganic reactants. [C with liq. nitryl chloride (ClNO₂) in s.t. at 100° for 3 hrs. gives by addn. to unsatd. linkage (67% yield (95)) 2-nitro-1,1,2-trichloroethane, pale yel. oil, b.p. 63° at 13 mm. — C cautiously added to 4 vols. of a mixt. of conc. + fumg. HNO₃ and warmed gives (96) a small amt. of nitro-trichloromethane (chloropicrin). — C with liq. N₂O₄ at ord. temp. for 24 hrs. in an unsealed tube (use of sealed tube leads to serious explosions) reacts (96) to give a little oxalic acid dihydrate (1:0445) together with an unidentified lachrymatory oil.]

BEHAVIOR WITH ORGANIC REACTANTS

With hydrocarbons. [\bar{C} (1 mole) with cyclopentadiene (1 mole) (1:8030) in s.t. at 180-190° for 15 hrs. yields (97) two Diels-Alder type adducts. — For reactn. of \bar{C} with C_6H_6+Al/Hg see under individual cis- (3:5042) and trans- (3:5028) stereoisomers.]

With other chlorinated hydrocarbons. (For reaction of C with itself see above under polymerization.)

With methylene (di)chloride (3:5020). [\bar{C} (1 wt. pt.) with CH₂Cl₂ (3 wt. pts.) + AlCl₃ (0.3 wt. pt.) at 40° for 8 hrs. gives (24% yield (98)) 1,1,2,3-tetrachloropropane (3:6035)].

With chloroform (3:5050). $[\bar{C}$ (1 wt. pt.) with CHCl₃ (3 wt. pts.) + AlCl₃ (0.25 wt. pt.) stirred with sand for 20 hrs. at 30° (99) cf. (100) (101) (102) gives (yields: 63% (99), 70-75% at 50° (100), 46% at 17° in 22 hrs. (100)) 1,1,2,3,3-pentachloropropane (3:6280).]

With carbon tetrachloride (3:5100). [C with CCl₄ + AlCl₃ gives (101) (102) cf. (103) 1,1,1,2,3,3-hexachloropropane (3:6460); for reactn. of this system yielding heptachloropentenes see (103).]

With 1,1,2-trichloroethane (3:5330). [C with 1,1,2-trichloroethane + AlCl₃ (1%) at 35-40° for 5 days gives (104) two diastereoisomeric 1,1,2,3,4-pentachlorobutanes, viz., liq. (3:9068) and solid (3:0750).]

With 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750). [C with acetylene tetrachloride + AlCl₃ gives a mixt. from which can be isolated only (104) solid 1,1,2,3,4-pentachlorobutane (3:0750).]

With 1,1,1,2-tetrachloroethane (3:5555). [C with unsym.-tetrachloroethane + AlCl₃ at 40° for 10 days gives (104) 1,1,1,4,4-pentachlorobutene-2 (3:9054).]

With pentachloroethane (3:5880). [Č with pentachloroethane + AlCl₃ at 40° for 12 days presumably first forms both 1,1,2,2,3,4,4-heptachlorobutane (3:9056) and 1,1,1,2,3,4,4-heptachlorobutane, but the latter loses HCl and by further reaction and/or resinification is lost in the accompanying resins (104); the HCl thus split out adds (in the pres. of AlCl₃) to Č yielding 1,1,2-trichloroethane which then condenses with more Č as stated above (104).]

With hexachloropropene (3:6370). [\bar{C} with hexachloropropene + AlCl₃ in CH₂Cl₂ soln. yields (105) a single 1,1,2,3,3,4,5,5-octachloropentene-1, b.p. 145-147° at 11 mm., 113-113.5° at 2 mm., $D_{21}^{21} = 1.749$, $n_{21}^{20} = 1.5607$ (105). This prod. with conc. H₂SO₄ gives (80% yield (105)) a mixt. of pentachlorobutenecarboxylic acids (105).]

Behavior with organic OH or SH derivs. [\bar{C} (1 mole) with C_2H_6SH (2 moles) in alc. KOH (2.6 moles) refluxed $\frac{1}{2}$ hr. gives (yield not stated (106)) 1,2-bis-(ethylthio)ethylene, b.p. 170° at 13 mm.]

[C (1 mole) with benzyl mercaptan (2 moles) in alc. KOH refluxed 7 hrs. gives (yield not stated (106)) 1,2-bis-(benzylthio)ethylene, white ndls. from alc. or AcOH, m.p. 61°; this prod. in CS₂ adds 1 Br₂ giving 1,2-dibromo-1,2-bis-(benzylthio)ethane, ndls. from ether, m.p. 73-74°.]

[Č (1 mole) with thiophenol (2 moles) in alc. NaOEt (2 moles) refluxed 24 hrs., poured into aq., gives (yield not stated (108)) 1,2-bis-(phenylthio)ethylene, b.p. 235-242° at 760 mm., pl. from lt. pet., m.p. 62°.]

Č (1 mole) with p-tolylmercaptan (2 moles) in 7% alc. KOH refluxed 3 hrs. gives (90% yield (107)) 1,2-bis-(p-tolylthio)ethylene, ndls. from alc., m.p. 93°; this prod. in CHCl₃ adds 1 mole Br₂ giving (100% yield) 1,2-dibromo-1,2-bis-(p-tolylthio)ethane, cryst. from pet. ether, m.p. 72° (107).

[For analogous reactn. with \bar{C} of o-nitrothiophenol or p-nitrothiophenol see (106).]

[C (1 mole) with an alk. salt of thiosalicylic acid (o-mercaptobenzoic acid) reacts similarly giving (109) (110) cf. (111) (112) 1,2-bis-(o-carboxyphenylthio)ethylene ("S,S-vinylene-

bis-thiosalicylic acid") [Beil. X-128, X_1 -(55)]; this prod. with KOH/NaOH at 220-230° gives (113) 3-hydroxythionaphthene (thioindoxyl) [Beil. XVII-119, XVII₁-(60)], or by actn. of acid condensing agents (e.g., fuming H_2SO_4 , $ClSO_3H$, etc.) yields (114) the important dyestuff thioindigo [Beil. XIX-177, XIX₁-(690).] — Note that the corresp. condens. of \bar{C} with salicylic acid (o-hydroxybenzoic acid) or with anthranilic acid (o-aminobenzoic acid) cannot be effected (112).]

Behavior with other misc. organic reactants. [\tilde{C} with paraformaldehyde (1:0080) + conc. H₂SO₄ gives (115) a resin (cf. behavior of 1,1,2-trichloroethylene (3:5170)).]

[\bar{C} (1 mole) with EtMgBr (2 moles) yields (116) C_2H_6 + BrMgC=C-MgBr + MgCl₂.] [\bar{C} does not (117) react with acetyl iodide even after 150 days at 25°.]

COLOR TESTS FOR C

- © Color test with α-naphthol/cyclohexanol. C

 (1 drop) with 2 ml. of a 2% soln. of α-naphthol (1:1500) in cyclohexanol (1:6415) + 2 pellets solid NaOH boiled 25 seconds, cooled, gives after acidification with AcOH or 85% H₂SO₄, stdg. 1 min., and shaking a violet or red-violet color (118). [Note that under these conditions the response given by methylene (di)chloride (3:5020) is green-blue; by both CHCl₃ (3:5050) and CCl₄ (3:5100) is intense blue; by 1,2-dichloroethane (ethylene dichloride) (3:5130) is colorless to pale green; by 1,1,2-tertachloroethane (acetylene tetrachloride) (3:5750) is intense green-blue; by pentachloroethane (3:5880) is gray-green; by 1,1,2-trichloroethylene (3:5170) is intense green-blue; and by tetrachloroethylene (3:5460) is green (118).]
- Mercury bis-(chloroacetylide) $Hg(-C \equiv C Cl)_2$. Shining white pl. from hot CHCl₃; although reported to melt at 185° (119) (120) (121) has also been found (122) to explode with great violence well below that temperature, i.e., 174–175° (122). [From \bar{C} with aq. $Hg(CN)_2 + KOH$ on shaking at room temp. (91) (123) for 48 hrs. (119), or from \bar{C} in alc. run into a stirred aq. soln. of $HgCl_2 + NaCN + KOH$ (120), or from \bar{C} shaken with an aq. soln. of HgO + NaCN + NaOH (122). Note, however, that in fact this prod. results only from the higher-boilg. (cis) stereoisomer of \bar{C} (3:5042) and that the lower-boilg. (trans) stereoisomer (3:5028) reacts much more slowly and quite differently to yield mercury bis-(α , β -dichloroethylenide), m.p. 50.3° (122). Note further that by the above treatment 1,1,2-trichloroethylene (3:5170) gives mercury bis-(trichloroethylenide), m.p. 83°, but this prod. is much more sol. in CHCl₃ than the analogous material from \bar{C} (for use in detect. of \bar{C} in pres. of 1,1,2-trichloroethylene see (123)).]
- 3:5030 (1) Salkowski, Brochem. Z. 107, 191-201 (1920); Cent. 1920, IV 515. (2) Margosches, Hinner, Friedmann, Z. anorg. allgem. Chem. 137, 81-90 (1924). (3) Margosches, Baru, J. prakt. Chem. (2) 103, 216-226 (1921/2). (4) Margosches, Hinner, Z. deut. Öl. u. Fett-Ind. 44, 97-100 (1924); Cent. 1924, I 2648; C.A. 18, 3731 (1924). (5) Gowing-Scopes, Analyst 39, 4-20 (1914). (6) Webster, Pharm. Weekblad 51, 1443-1446 (1914); Cent. 1915, I 248; not in C.A. (7) Jorissen, Chem. Weekblad 25, 228-230 (1928); Cent. 1928, I 2854. (8) Coward, Jones, Ind. Eng. Chem. 18, 970-974 (1926). (9) Jorrissen, Ind. Eng. Chem. 19, 430-431 (1927). (10) Jorissen, Meuwissen, Rec. trav. chim. 44, 132-140 (1925).
- (11) Jorissen, Velisek, Rec. trav. chim. 43, 85 (1924). (12) Langen van der Valk, Rec. trav. chim. 48, 206-207 (1929). (13) Jorissen, Langen van der Valk, Rec. trav. chim. 44, 810-813 (1925). (14) Michael, Hibbert, Ann. 396, 83 (1912). (15) Chem. Fabrik Griesheim-Elektron, Chem. Ztg. 32, 256 (1908). (16) Churchill, Chem. Markets, 25, 587-592 (1929). (17) Waterfill, Ind. Eng. Chem. 24, 616-619 (1932). (18) Davenport, (to Chicago Pneumatic Tool Co.), U.S. 1,818,117, Aug. 11, 1931; Cent. 1932, I 559; C.A. 25, 5481 (1931). U.S. 1,803,098, April 28, 1931; Cent. 1935, C.A. 25, 3746 (1931). (19) Klein, Ger. 406,029, Nov. 13, 1924; Cent. 1925, I 46; not in C.A.: cf. Ger. 404,960, Oct. 24, 1924; Cent. 1925, I 146; not in C.A. (20) Carrier (to Carrier Eng. Corpn.), Brit. 237,949, Aug. 28, 1925; [Cent. 1926, I 751]; C.A. 20, 1876 (1926):

French 580,060, Oct. 29, 1924; Cent. 1925, I 1780; not in C.A.: Can. 257,007, Jan. 5, 1926; Cent. 1926, II 1563; not in C.A.

(21) Carrier (to Carrier Eng. Corpn.), Brit. 283,263, April 9, 1924; C.A. 20, 2036 (1926); not in Cent. French 580,095, Oct. 29, 1924; Cent. 1925, I 1780; not in C.A. (22) Ramus, French 707,106, July 3, 1931; Cent. 1931, II 1779; not in C.A. (23) I.G., French 663,845, Aug. 26, 1929; Cent. 1929, II 2261; C.A. 24, 628 (1930). (24) Mann, Chem. Zig. 56, 452 (1932); Cent. 1932, II 2851; C.A. 26, 4392 (1932). (25) Standard Oil Development Co., French 790,852, Nov. 28, 1935; Cent. 1936, I 2672; C.A. 30, 3223 (1936). (26) Mellor, Bingham, Pool (to British Celanese, Ltd.), Brit. 470,333; Sept. 9, 1937; Cent. 1937, II 3957; C.A. 32, 806 (1938). (27) von Oettingen, J. Ind. Hyg. Toz. 19, 409-411 (1937). (28) Bonino, Mascherpa, Arch. idal. sci. farmacol. Vol. giubilare A. Benedicenti 15, 22 pp. (1937); Cent. 1938, I 4687; C.A. 32, 4662 (1938). (29) Barsoum, Saad, Quart. J. Pharm. Pharmakol. 7, 205-214 (1934); Cent. 1934, II 2550; C.A. 28, 6194 (1934). (30) Beck, Susstrunk, Arch. Gewerbepath. Gewerbehyg. 2, 81-91 (1931); Cent. 1931, I 468; C.A. 26, 1666-1667 (1932).

(31) Muller, Arch. exptl. Pathol. Pharmakol. 109, 276-294 (1925); Cent. 1926, I 1448; C.A. 20, 455 (1926). (32) Lehmann, Arch. Hyg. 74, 1-60 (1911); Cent. 1911, II 885; C.A. 6, 3125 (1912). (33) Albrecht, Wien. klin. Wochschr. 39, 65-68 (1926); 37, 685-687 (1924); Cent. 1926, I 1842; Cent. 1924, II 709; neither in C.A. (34) Meyer, Gottlieb-Billroth, Z. physiol. Chem. 112, 55-79 (1921). (35) Joachimoglu, Biochem. Z. 120, 203-211 (1921); Cent. 1921, III 1212; C.A. 16, 3686 (1921). (36) Wittgenstein, Arch. exptl. Path. Pharmakol. 83, 235-247 (1918); Cent. 1918, II 1054; C.A. 12, 2378 (1918). (37) Gabbano, Z. Hyg. Infektionskrankh. 109, 183-193, 194-200 (1928); Cent. 1928, II 2667-2668; not in C.A. (38) Joachimoglu, Biochem. Z. 124, 130-136 (1921); Cent. 1922, I 363; C.A. 16, 946 (1922). (39) Winteringham, J. Soc. Chem. Ind. 61, 190-192 (1942). (40) Smyth, Ind. Eng. Chem., Anal. Ed. 8, 379 (1936).

(41) Berl, Bitter, Ber. 57, 99 (1924). (42) Winteringham, J. Soc. Chem. Ind. 61, 187-190 (1942). (43) Rauscher, Ind. Eng. Chem., Anal. Ed. 9, 296-299 (1937). (44) Lucas, Pressman, Ind. Eng. Chem., Anal. Ed. 10, 140-142 (1938). (45) Mailhe, Compt. rend. 172, 1583 (1921); Bull. soc. chim. (4) 29, 535-539 (1921). (46) Consortium fur Elektrochem. Ind., Ger. 216,070, Nov. 11, 1909; Cent. 1909, II 2103; C.A. 4, 812 (1910). (47) Kaufler (to A. Wacker Soc. Elektrochem. Ind.), U.S. 1,419,969, June 20, 1922; [Cent. 1923, II 1152]; C.A. 16, 2695 (1922): Ger. 345,259, Dec. 8, 1921; [Cent. 1922, II 443]; not in C.A.: Brit. 156,080, Jan. 27, 1921; Cent. 1921, II 1061; C.A. 15, 1535 (1921). (48) Consortium fur Elektrochem. Ind., Ger. 217,554, Jan. 17, 1910; Cent. 1910, I 700; C.A. 4, 1651 (1911). (49) Wiegand (to Chem. Fabrik von Heyden), Ger. 566,034, Dec. 14, 1932; Cent. 1933, I 1350; C.A. 27, 1012 (1933). (50) Wiegand (to Chem. Fabrik von Heyden), Ger. 567,272, Dec. 31, 1932; Cent. 1933, I 1842; C.A. 27, 1365 (1933).

(51) Askenasy, Vogelsohn, Z. Elektrochem. 15, 773 (1909). (52) Aten, Chem. Weekblad 19, 352 (1922); Cent. 1922, III 984; (C.A. 16, 3593 (1922)]. (53) Nicodemus, J. prakt. Chem. (2) 83, 312-317 (1911). (54) I.G., French 805,563, Nov. 24, 1936; Cent. 1937, I 2258; C.A. 31, 4345 (1937). (55) Hermann, Baum (to Consortium fur Elektrochem. Ind.) U.S. 1,921,879, Aug. 8, 1933; C.A. 27, 5086 (1933): Brit. 348,346, April 20, 1929; C.A. 26, 5106; not in Cent.: Ger. 570,954, Feb. 22, 1933; C.A. 27, 4222 (1933); not in Cent.: French 694,054, Nov. 28, 1930; Cent. 1931, I 1514; C.A. 25, 1843 (1931). (56) Reilly (to Dow Chem. Co.), U.S. 2,140,548, Dec. 20, 1938; Cent. 1939, I 3625; C.A. 33, 2540 (1939). (57) Sabanajev, Ann. 216, 261-262 (1882). (58) Kharasch, Norton, Mayo, J. Org. Chem. 3, 53-54 (1938). (59) van der Walle, Bull. soc. chim. Belg. 28, 305-307 (1914). (60) van der Walle, Henne, Bull. sci. acad. roy. Belg. (5) 11, 781-793 (1925); Cent. 1926, I 3136; C.A. 20, 1787 (1926).

(61) Chem. Fabrik Griesheim Elektron, Ger. 254,069, Nov. 22, 1912; Cent. 1913, I 83; C.A. 7, 869 (1913): Ger. 264,006, Sept. 10, 1913; Cent. 1913, II 1178; C.A. 8, 211 (1914). (62) Klein (to Ruhr Chemie, A.G.), Ger. 613,607, May 23, 1935; Cent. 1935, II 1256; C.A. 29, 8007 (1935). (63) I.G., Swiss 213,747, June 3, 1941; Cent. 1942, I 2706; not in C.A. (64) Berthelot, Jungfleisch, Compt. rend. 69, 542 (1869); Ann. Suppl. 7, 253-254 (1870). (65) Langguth, Chimie & industrie 25, 22-25 (1931). (66) Tompkins, Ger. 196,324, March 19, 1908; C.A. 2, 2289 (1908). (67) Consortium für Elektrochem. Ind., Ger. 340,872, Sept. 19, 1921; Cent. 1921, IV 1101; C.A. 16, 2867 (1922). (68) Müller, Ehrmann, Ber. 69, 2209 (1936). (69) Noller, Carson, Martin, Hawkins, J. Am. Chem. Soc. 58, 25 (1936). (70) I.G., French 42,610, Aug. 23, 1933; Cent. 1933, II 2748; C.A. 28, 1144 (1934).

(71) Dietrich, Lohrengel (to Reichsmonopolverwaltung für Branntwein), Ger. 649,118, Sept. 13, 1937; Cent. 1937; II 4102; C.A. 32, 951 (1938). (72) Imperial Chem. Ind., Ltd., French 744,128, April 12, 1933; Cent. 1933, II 605; C.A. 27, 3941 (1933). (73) Roessler-Hasslacher Chem. Co., French 732,569, Sept. 22, 1932; Cent. 1932, II 3785; C.A. 27, 304 (1933); Ger. 573,105, March 3, 1932; [C.A. 27, 2961 (1933)]; not in Cent. (74) Bauer, U.S. 2,267,712, Dec. 30, 1941; C.A. 36, 2564 (1942): Rohm, Hass, Brit. 517,195, Jan. 23, 1940; [C.A. 35, 6699 (1941)]; not in

3:5035 1.1-DICHLOROETHANE

at 743 mm. (9)

56.7-56.9°

Cont.: French 840,867, May 5, 1939; Cent. 1939, II 4349; C.A. 34, 1781 (1940). (75) Mahncke, Noyes, J. Am. Chem. Soc. 58, 932-933 (1936). (76) Biesalski, Z. angew. Chem. 37, 317 (1924). (77) Müller, Schumacher, Z. Elektrochem. 43, 807-808 (1937). (78) Timmermans, Bull. soc. chim. Belg. 27, 334-343 (1913), Cent. 1914, I 618. (79) Chavanne, Bull. soc. chim. Belg. 26, 280-294 (1912); 28, 234-240 (1914); Cent. 1912, I1 1006; 1914, II 1144. (80) Ghosh, Bhattacheryys, Murthi, J. Indian Chem. Soc. 14, 425-434 (1937).

(81) Ghosh, S. K. Bhattacharyya, S. C. Bhattacharyya, Z. physik. Chem. B-32, 145-157 (1936).
(82) Hofmann, Kirmreuther, Ber. 42, 4483 (1909).
(83) Herz, Rathmann, Ber. 46, 2589 (1913).
(84) Bruner, Fischler, Z. Elektrochem. 26, 84 (1884).
(85) Müller, Honn, J. prakt. Chem. (2)
133, 290 (1932).
(86) Prins, Rec. trav. chim. 45, 80-81 (1926).
(87) Brooks, Humphrey, J. Am. Chem. Soc. 40, 843-844.
(88) Lepouse, Bull. soc. chim. Belg. 34, 133-142 (1925).
(89) Ott (to Chem. Fabrik vorm. Weiler-ter-Meer, Ger. 362,744, Oct. 31, 1922; Cent. 1923, II 1246; C.A. 18, 1129 (1924).
(90) Klimont, Chem. Zig. 46, 521-522 (1922).

(91) Hofmann, Kirmreuther, Ber. 42, 4233-4234 (1909).
(92) Thron, Chem. Ztg. 48, 142 (1924).
(93) Fromm, Landmann, Ber. 56, 2292 (1923).
(94) Stahler, Ber. 47, 912 (1914).
(95) Steinkopf, Huhner, Ber. 75, 1326-1327 (1942).
(96) Burrows, Hunter, J. Chem. Soc. 1932, 1358-1359.
(97) Alder, Rickert, Ann. 543, 10-11, 26-27 (1940).
(98) Lehmann (to I.G.), Ger. 715,069, Dec. 16, 1941; Cent. 1942, I 2534; C.A. 38, 2051 (1944).
(99) Heilbron, Heslop, Irving, J. Chem. Soc. 1936, 782-783.
(100) Prins, Engelhard, Rec. trav. chim. 54, 307-312 (1935).

(101) Prins, J. prakt. Chem. (2) 89, 415, 417, 421 (1914). (102) Prins, Ger. 261,689, July 2, 1913; Cent. 1913, II 394, [C.A. 7, 3641 (1913)]. (103) Kirkbride (to Imperial Chem. Ind., Ltd.), U.S. 2,297,564, Sopt. 29, 1942; C.A. 37, 1450 (1943). (104) Prins, Rec. trav. chim. 56, 119-125 (1937). (105) Prins, Rec. trav. chim. 56, 779-784 (1937). (106) Fromm, Benzinger, Schafer, Ann. 394, 325-334 (1912). (107) Fromm, Siebert, Ber. 55, 1021 (1922). (108) Cusa, McCombie, J. Chem. Soc. 1937, 769. (109) Munch, Chem. Zlg. 32, 811 (1908); Z. angew Chem. 21, 2059 (1908). (110) B.A.S.F., Ger. 237,773, Sept. 18, 1911; Cent. 1911, 1079; C.A. 6, 1659 (1912).

(111) Bohn, Ber. 43, 994-995 (1910). (112) Ioffe, Mazel, J. Russ. Phys.-Chem. Soc. 62, 2001-2012 (1930); Cent. 1931, I 2879; C.A. 25, 4129 (1931). (113) B.A.S.F., Ger. 221,465, April 23, 1910; Cent. 1916, I 1767; C.A. 4, 2740 (1910). (114) B.A.S.F., Ger. 205,324, Dec. 24, 1908; Cent. 1909, I 605; C.A. 3, 1694 (1909). (115) Prins, Rec. trav. chim. 51, 471 (1932). (116) Binaghi, Gazz. chim. ital. 57, 672-673 (1927). (117) Stevens, J. Am. Chem. Soc. 56, 450-452 (1934). (118) Weber, Chem. Zig. 57, 836 (1933); Cent. 1933, II 3889; C.A. 28, 727 (1934). (119) Bashford, Emeleus, Briscoe, J. Chem. Soc. 1938, 1358. (120) Ingold, J. Chem. Soc. 125, 1535 (1924).

(121) Hofmann, Kirmreuther, Ber. 41, 316 (1908). (122) FitzGibbon, J. Chem. Soc. 1938, 1218-1222. (123) Schmalfuss, Werner, Z. anal. Chem. 97, 314-317 (1934).

CH₂.CHCl₂

C₂H₄Cl₂

Beil, I - 83

0.000	(Ethylidene (di)ch		022310		02114012	I ₁ -(23)
	unsymdichloroeth	,				I_{2} -(52)
B.P.			F.P.			
57.30°	at 760 mm.	(1)(2)	- 96.6°	(1)	$D_4^{25} = 1.16790$	(1)
57.28	-57.34° cor.	(3)	-96.7°	(2)	$D_4^{20} = 1.17570$	(1)
57.25°	at 760 mm.	(4)	97.4°	(8)		(8)
57.0-5	57.1°	(5) (6) (7)	-99°	(9)	$D_4^{15} = 1.18350$	(1)
57.1°	at 760 mm.	(8)			$n_{\rm D}^{20} =$	= 1.41638 (8)

Liquid. — [For b.p. at various press. from 70-277 mm. see (11).] — Alm. insol. aq. [for precise data see (5) (6) (7) (11).] — [For f.p./compn. data of mixts. with 2,2-dichloropropane (3:7140) see (10).] — [For use as dry cleaning fluid see (12); for use as corrosion inhibitor for alk. on tinned metal see (13).]

Č forms with EtOH (1:6130), b.p. 78.3°, a const.-boilg. mixt., b.p. 54.6°, contg. 88.5 wt. % Č (4); Č forms with isopropyl alc. (1:6135), b.p. 82.45°, a const.-boilg. mixt., b.p. 56.6°, contg. 82 wt. % Č (4); Č forms with ter-butyl alc. (1:6140), b.p. 82.5°, a const.-boilg. mixt., b.p. 57.1°, contg. 94 wt. % Č (14); Č forms with acetone (1:5400), b.p. 56°, a const.-boilg. mixt., b.p. 57.55°, contg. 70 wt. % Č (14); Č forms with CS₂, b.p. 46.3°,

const.-boilg. mixt., b.p. 44.75°, contg. about 28 wt. % \bar{C} (14). [For study of b.p., D, and vapor-liq. equil. of binary mixts. of \bar{C} with CHCl₃ (3:5050), CCl₄ (3:5100), or with 1,2-dichloroethane (3:5130) see (27).]

[For soly. of aq. in \bar{C} see (29); for adsorption of \bar{C} by activated carbon at various temps. see (30).)

[For prepn. of \tilde{C} from acetaldehyde (1:0100) with PCl₅ see (15) (16) (17); from vinyl chloride (3:7010) by catalyzed addn. of HCl see (18) (19) (20) (note that in absence of catalyst addn. of HCl to vinyl chloride is very slow (21)); for formn. of \tilde{C} (22.6%) together with other products from ethane with Cl₂ above 290° in pres. of ethylene see (28).

Č on passing over pumice at dark red heat yields (22) (23) vinyl chloride (3:7010) + HCl.

[For reactn. of \tilde{C} + AlCl₃ with 1,2-dichloroethylene (3:5030) or with trichloroethylene (3:5170) yielding polychlorobutanes see (24); for reactn. of \tilde{C} with amylidene disodium see (25).]

 \bar{C} on htg. in s.t. at 120° with aq. alc. soln. of 2 moles Na (or K) α -naphtholate yields (26) acetaldehyde di- α -naphthylacetal, ndls., m.p. 117° (26).

3:5035 (1) Timmermans, Martin, J. chim. phys. 23, 770-771 (1926). (2) Timmermans, Bull. soc. chim. Belg. 25, 300-327 (1911); Cent. 1911, II 1015. (3) Maryott, Hobbs, Gross, J. Am. Chem. Soc. 63, 660 (1941). (4) Lecat, Rec. trav. chim. 46, 242 (1927). (5) Gross, Physik. Z. 32, 589 (1931). (6) Gross, Z. physik. Chem. B-6, 215-220 (1929). (7) Gross, J. Am. Chem. Soc. 51, 2362-2365 (1929). (8) Henne, Hubbard, J. Am. Chem. Soc. 58, 404 (1936). (9) Schiff, Ann. 220, 96 (1883). (10) van de Vloed, Bull. soc. chim. Belg. 48, 260 (1939).

(11) Rex, Z. physik. Chem. 55, 358 (1906). (12) Parkhurst (to Stand. Oil of Cal.), U.S. 1,948,045, Feb. 20, 1934; Cent. 1934, II 863; C.A. 28, 2924 (1934). (13) Nitti (to E. R. Squibb and Sons), U.S. 2,152,658, Apr. 4, 1939; Cent 1939, II 2473; C.A. 33, 4956 (1939). (14) Lecat, Ann. soc. sci. Bruxelles, 49, 110 (1929). (15) Geuther, Ann. 105, 323-324 (1858). (16) Wurts, Frapoli, Ann. 108, 223-224 (1858). (17) Beilstein, Ann. 113, 110-112 (1860). (18) Nutting, Petrie, Huscher (to Dow Chem Co.), U.S. 2,007,144, July 2, 1935, Cent. 1935, II 3829, C.A. 29, 5460 (1935). (19) Wilbaut, van Dalfsen (to Dow Chem. Co.), U.S. 1,990,968, Feb. 12, 1935; Cent. 1935, II 2580; C.A. 29, 2178 (1935). (20) Coleman (to Dow Chem. Co.), U.S. 1,900,276, March 7, 1933; Cent. 1933, I 3364; C.A. 27, 2965 (1933).

(21) Kharasch, Hannum, J. Am. Chem. Soc. 56, 712-714 (1934). (22) Biltz, Ber. 35, 3524-3525 (1902). (23) Biltz, Küppers, Ber. 37, 2398-2423 (1904). (24) Consortium für Elektrochemische Ind., Brit. 453,414, Oct. 8, 1936; Cent. 1937, I 1012. (25) Morton, Massengale, J. Am. Chem. Soc. 62, 120-123 (1940). (26) Fosse, Bull. soc. chim. (3) 23, 516 (1900). (27) Kaplan, Monakhova, J. Gen. Chem. (U.S.S.R.) 7, 2499-2512 (1937); Cent. 1938, II 1572; C.A. 32, 2404 (1938). (28) Vaughan, Rust, J. Org. Chem. 5, 466-467 (1940). (29) Staverman, Rec. trav. chim. 69, 836-841 (1941); Cent. 1942, I 1352; C.A. 37, 2638 (1943). (30) Pearce, Eversole, J. Phys. Chem. 38, 383-393 (1934).

See also both trans-1,2-dichloroethylene (3:5028) and ordinary (mixt. of cis and trans) 1,2-dichloroethylene (3:5030); the following text is restricted to studies on substantially pure cis-stereoisomer.

Note carefully that 1,2-dichloroethylene is *not* the same as ethylene (di)chloride (3:5130) (there are an almost incredible number of errors in the literature involving this point); neither is it the same as the now very important 1,1-dichloroethylene (vinylidene (di)chloride) (3:5005).

GENERAL DATA ON C

Note that substantially pure \bar{C} is commercial solvent in U.S.A. under designation "Di-60" (referring to the two chlorine atoms and the b.p.) [for study of thermal conductivity and for tabulation of constants of comml. \bar{C} see (18). — For toxicity of \bar{C} see (40) (23). — For use of \bar{C} in extraction of caffeine from coffee see (24)].

[For data on vap. press. of \bar{C} over temp. range 27-59.8° see (12). — For data on flammability of \bar{C} see (19). — For ebullioscopic constant of \bar{C} , viz., 34.4° (for 1 mole solute in 100 g. \bar{C}), see (20).]

Binary systems contg. $\bar{\mathbf{C}}$. (See also below under azeotropes.) — $[\bar{\mathbf{C}} + trans-1,2-dichloroethylene (3:5028):$ for use of n_D^{25} in detn. of composition of mixt. see (11); for f.p./compn. data (cutectic, f.p. -91° , contg. about 71% $\bar{\mathbf{C}}$) see (17). — For f.p./compn. data on binary systems $\bar{\mathbf{C}} + ethylene$ (di)chloride (3:5130), $\bar{\mathbf{C}} + 1,1,2,2$ -tetrachloroethane (acetylene tetrachloride) (3:5750), or $\bar{\mathbf{C}} + ethylene$ (di)bromide see (17). — For study of soly. of various other cis/trans isomers in $\bar{\mathbf{C}}$ see (5).]

Quaternary systems contg. \bar{C} . [For study of system contg. \bar{C} + CHCl₃ (3:5050) + trichloroethylene (3:5170) + EtBr (eutectic, f.p. -139.1°, contg. 13.8 wt. % \bar{C} + 19.7 wt. % CHCl₃ + 21.6 wt. % trichloroethylene + 44.9 wt. % EtBr recommended as a non-inflammable mixt. for low-temp. cryostats) see (22); for mixt. of the above four compds. + methylene dichloride (3:5020) (similarly recommended) see (22).]

Azeotropes contg. $\bar{\mathbf{C}}$. Binary azeotropes — $\bar{\mathbf{C}}$ with aq. forms a const.-boilg. mixt., b.p. 55.3°, contg. 96.65% $\bar{\mathbf{C}}$ (41) (42). — $\bar{\mathbf{C}}$ with EtOH (1:6130) forms a const.-boilg. mixt., b.p. 57.7° at 760 mm. (21) (41) (42), contg. 90.20% $\bar{\mathbf{C}}$ (41) (42) = 81.4 mole % $\bar{\mathbf{C}}$ (21).

Ternary azeotropes. \bar{C} with EtOH (1:6130) + aq. forms a const.-boilg. mixt., b.p. 53.8°, contg. 90.50% \bar{C} + 6.65% EtOH + 2.85% aq. (41) (42).

PREPARATION OF C

Pure \tilde{C} is usually obtd. by careful fractional distillation at ord. press. of the mixt. of cis and trans stereoisomers comprising ord. 1,2-dichloroethylene (3:5030) [for brief comments on this mode of sepn. see (1) (2) (6) (7) (8) (9) (10) (11) (13) (15) (27); note that some workers (13) recommend distn. in atmosphere of CO_2 . — For detn. of the % compn. of mixts. of \tilde{C} with its stereoisomer by means of n_D^{25} see (11); by means of dielectric const. see (13) (27)].

[For study of possibility of sepn. of \tilde{C} from its stereoisomer by differential adsorption on silica gel see (25).]

[For prepn. of \bar{C} from pure trans stereoisomer (3:5028) by isomerization with 6 wt. % Br₂ in dark for 24 hrs. followed by subsequent fractionation of the resultant mixt. see (11).]

ISOMERIZATION OF C

 \bar{C} under the influence of heat, light, or various catalysts in part isomerizes to trans-1,2-dichloroethylene (3:5028). — [For study of thermal isomerization of \bar{C} in vapor phase at 185–275° (26), up to 350° (27), up to 975° (28), in liquid phase or in various solutions (13) see indic. refs.; note that the equilibrium mixt. at 300° conts. $60.8 \pm 0.7\%$ \bar{C} , at 350° conts. $59.4 \pm 0.3\%$ \bar{C} (27), at 975° conts. 52.3% \bar{C} (28). — For study of kinetics of thermal isomerization see (29).]

[For patent on isomerization of pure \tilde{C} to a mixt. contg. 18% trans stereoisomer by means of a small amt. Br₂ at 30° or above in pres. of cat. or in vapor phase at not over 300° see (30).]

CHEMICAL BEHAVIOR OF C

Reactions with inorganic compds. \tilde{C} (in vapor phase at 95° in light of 4360 Å (31)) with Cl₂ (in absence of O₂), or \tilde{C} as liquid with SO₂Cl₂ (1½ moles) in pres. of trace of dibenzoyl peroxide refluxed 3 hrs. in dark (8), adds 1 mole halogen giving (85% yield (8)) 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750).

 \tilde{C} with Br₂ in sunlight adds 1 mole halogen yielding (2) (32) 1,2-dibromo-1,2-dichloro-ethane [Beil. I-93, I₁-(29), I₂-(64)], b.p. 195° at 760 mm. (3) (33), b.p. 79.0-79.5° at 15 mm. (2). — [For extensive study of influence of O₂ and other factors see (32); for study of kinetics in CCl₄ soln. see (2) (34) (35); note that rate of addn. of Br₂ either directly or in CCl₄ is half as great as for the stereoisomeric trans form (3:5028) but that it is increased in pres. of SbBr₃ (35).]

 \tilde{C} in the absence of AlCl₃ or other cat. does not add dry HCl; satn. of \tilde{C} with dry HCl changes n_D^{25} by an amount corresp. to only 2% change in compn. (11).

[Č with alc. KOH splits out 1 HCl yielding chloroacetylene (3:7000); note that this reactn. is about 20 times as fast for Č as for its trans stereoisomer (2).]

Č with aq. NaOH/Hg(CN)₂behaves quite differently from its trans stereoisomer (3:5028): on shaking at room temp. with specified conens. (16) Č begins to react within 30 min., losing 1 HCl and pptg. mercuric bis-(chloroacetylide), Hg(—C≡C—Cl)₂; this prod. cryst. from CHCl₃ (36) (37) (38) in white shining pl. with characteristic acetylene-like odor and although alleged to melt at 185° (36) (37) has also been found to explode with great violence well below that temp., i.e., 174–175° (16).

Reactions with organic compds. [\bar{C} with C_6H_6+Al/Hg at 0° gives same prods. as does the ordinary (mixture) 1,2-dichloroethylene (3:5030) (presumably indicating partial isomerization of \bar{C}); these prods. include dibenzyl, triphenylethane, tetraphenylethane, etc. (15).]

3:5042 (1) Maryott, Hobbs, Gross, J. Am. Chem. Soc. 63, 660 (1941). (2) Chavanne, Compt. rend. 154, 776-777 (1912); Cent. 1912, I 1539; Bull. soc. chim. Belg. 26, 289-294 (1912); Cent. 1913, II 1006; Bull. soc. chim. Belg. 28, 234-240 (1914); Cent. 1914, II 1144. (3) Timmermans, Bull. soc. chim. Belg. 27, 334-343 (1913); Cent. 1914, I 618. (4) Bonino, Brühl, Gazz. chim. idl. 59, 648-649 (1929); Z. Physik 58, 195 (1929). (5) Lebrun, Bull. soc. chim. Belg. 39, 423-433 (1930). (6) Ebert, Bull. Z. physik. Chem. A-152, 451-452 (1931). (7) Mahncke, Noyes, J. Chem. Phys. 3, 536 (1935). (8) Kharasch, Brown, J. Am. Chem. Soc. 61, 3433 (1939). (9) Sachsse, Physik. Z. 36, 365 Note (1935). (10) Walker, Trans. Faraday Soc. 31, 1434 (1935).

(11) Jones, Taylor, J. Am. Chem. Soc. 62, 3480-3485 (1940). (12) Herz, Rathmann, Chem. Ztg. 37, 622 (1913). (13) Wood, Dickinson, J. Am. Chem. Soc. 61, 3259-3263 (1939). (14) Bonino, Gazz. chim. ital. 55, 342 (1925). (15) Bäeseken, Bastet, Rec. trav. chim. 32, 197-203 (1913). (16) FitzGibbon, J. Chem. Soc. 1938, 1218-1222. (17) Timmermans, Bull. soc. chim. Belg. 36, 184-187 (1927). (18) Bates, Hazzard, Palmer, Ind. Eng. Chem. 33, 375-376 (1941). (19) Huff, U.S. Bur. Mines, Repts. Investigations 3490, 36 pp. (1940); C.A. 34, 5661 (1940). (20) Walden, Zastrow, Roudolf, Ann. Acad. Sci. Fennicae, A-29, No. 23 (Komppa Festschrift), 26 pp. (1927); Cent. 1928, I 166; C.A. 22, 1515 (1928).

26 pp. (1927); Cent. 1928, I 166; C.A. 22, 1515 (1928).

(21) Lecat, "L'Azeotropisme," Brussels 1918, Lecat No. 345. (22) Kanolt, Natl. Bur. Standards (U.S.) Sci. Papers S-520, Vol. 20, 619-633 (1926). (23) Ferguson, Nature 137, 361-362 (1936). (24) Brunner, Swiss 167,162, April 16, 1934; Cent. 1934, II 2617; C.A. 28, 5552 (1934). (25) Hesse, Tschachotin, Naturwissenschaften 30, 387-392 (1942), Cent. 1942, II 1325; C.A. 37, 6211 (1943). (26) Wood, Stevenson, J. Am. Chem. Soc. 63, 1650-1653 (1941). (27) Olson, Maroney, J. Am. Chem. Soc. 56, 1320-1322 (1934). (28) Maroney, J. Am. Chem. Soc. 57, 2397-2398 (1935). (29) Tamamusi, Akiyama, Isii, Z. Elektrochem. 47, 340-345 (1941); C.A. 35, 6859 (1941). (30) Mugdan, Rost (to Consortium fur Elektrochem. Ind.), Ger. 595,464, April 11, 1934; Cent. 1935, I 2599.

(31) Müller, Schumacher, Z. physik. Chem. B-35, 455-457 (1937). (32) Verhoogen, Bull. soc. chim. Belg. 34, 434-456 (1925). (33) van de Walle, Bull. soc. chim. Belg. 28, 307 (1914). (34) Herz, Rathmann, Ber. 46, 2589 (1913). (35) Bruner, Fischler, Z. Elektrochem. 20, 84 (1914). (36) Bashford, Emeléus, Briscoe, J. Chem. Soc. 1938, 1358. (37) Ingold, J. Chem. Soc. 125, 1535 (1924). (38) Hofmann, Kirmreuther, Ber. 42, 4233-4234 (1909). (39) Awberry, Griffiths, Proc. Phys. Soc. (London) 48, 378 (1936). (40) Lehman, Schmidt-Kehl, Arch. Hyg. Bakt. 116, 131-268 (1936); C.A. 31, 477 (1937); not in Cent.

(41) Chavanne, Bull. soc. chim. Belg. 27, 205-209 (1913); Cent. 1913, II 1376; C.A. 8, 1105 (1914). (42) Gowing-Scopes, Analyst 39, 6 (1914).

```
3:5050 CHLOROFORM
                                                                 CHCl<sub>3</sub>
                                                                                 Beil. I - 61
           (Trichloromethane)
                                                                                      I_{1}-(9)
                                                                                      I_{2}-(14)
  B.P.
                                       F.P.
                                                          D_4^{30} = 1.47060 (12)
 [62.0°
                  at 760
                                  (2)1
                                        -63.0^{\circ}
                                                    (27)
                           mm.
                                                                       n_{\rm D}^{254} = 1.44295 (49)
                                               (28) (61)
                                                          D_4^{25} = 1.47988 \ (12)
 [61.97°
                  at 760
                                  (3)]
                                       -63.2^{\circ}
                                                    (29)
                           mm.
                                                    (26)
                                                                  1.47972 (20)
 [61.64°
                  at 760
                                  (4)
                                        -63.3°
                                                    (30)
                                                                  1.47955 (45)
                           mm.
                                  (1)]
                                        -63.41°
                                                    (31)
                                                                  1.4794
                                                                             (43)
 [61.40°
                  at 758
                           mm.
                                  (5)
                                       -63.495^{\circ}
                                                    (32)
                                                                  1.4793
                                                                             (44)
61.36-61.38° at 763.9 mm.
                                 (6)
                                       -63.5^{\circ}
                                                    (33)
                                                                  1.4791
                                                                             (21)
                                          (34) (35) (36)
                                                                  1.4789
                                                                             (19)
                                          (37) (12) (38)
                                                                  1.4702
                                                                             (46)
 61.33-61.38° at 760
                           mm.
                                 (7)
                                       -63.57^{\circ}
                                                   (17)
                                                                        n_{\rm D}^{25} = 1.44460 (50)
 61.3° u.c.
                  at 759
                                       -63.6°
                                 (8)
                                                    (39)
                           mm.
                                                                               1.4433 (51)
 61.28°
                  at 761
                           mm.
                                 (9)
                                       -63.7°
                                                    (40)
                                                                               1.4431
                                                                                         (19)
 61.20-61.25° at 760
                                       -64.19°
                           mm. (10)
                                                   (41)
                                                                               1.44309 (52)
 61.21°
                 at 760
                           mm. (11)
                                       -66.5° .
                                                   (42)
                                                                               1.4424
                                                                                         (44)
 61.20°
                 at 760
                           mm. (12)
                                                                              = 1.4437
                       (1) (15) (16)
                                      See Note 2.
                                                                             = 1.44500 (53)
```

1.4458

(7)

 $\{17\}$

```
B.P. (contd.)
61.152°
                at 760
                                                       D_4^{20} = 1.48921 (13)
                         mm. (13)
61.15°
                at 760
                         mm. (14)
                                                               1.48917 (12)
61.09°
                at 760
                         mm. (17)
                                                              1.48913 (13)
61.07-61.09° at 760
                         mm. (18)
                                                              1.48901 (13)
61.05-61.10° at 760
                         mm. (50)
                                                              1.4890
                                                                         (47)
61.05-61.10° at 758
                        mm. (19)
                                                              1.4889
                                                                         (10)
61.0°
                              (20)
                                                                         (48)
61.0°
                at 755
                         mm. (21)
                                                              1.4817
                                                                         (62)
60.94-60.96° at 755
                        mm. (22)
                                                                     n_{\rm D}^{20} = 1.44637 (10)
60.93°
                at 744.2 mm. (4)
60.9°
                at 754.3 mm. (23)
                                                                            1.446
                                                       D_{4}^{18.85} = 1.4828 (54)
60.9°
                at 732 mm. (24)
                                                                  n_{\rm D}^{18.85} = 1.44572 (54)
60.7°
                at 743.8 mm. (25)
                                                       D_4^{15} = 1.49845 \quad (12)
60.39°
                at 735.6 mm. (4)
56.0°
                at 664
                        mm. (21)
                                                              1.4963 (21)
                                                                     n_{\rm D}^{15} = 1.44858 \,(12)
55.10°
                at 632.8 mm. (26)
53.8°
                at 616
                        mm. (21)
                                                                            1.4466 (55)
                                                                    n_{\rm D}^{12.5} = 1.4506 \quad (56)
50.5°
                at 550
                        mm. (21)
47.0°
                at 481
                        mm. (21)
                                                       See Note 3.
42.8°
                at 416
                        mm. (21)
                                         Note 1. For b.p. of C at various pressures
40.40°
                at 371.8 mm. (26)
38.0°
                                      from 355-2347 mm. see (13); for vap. press. of
                at 342
                        mm. (21)
                                      \bar{C} over range -62.1^{\circ} to 0^{\circ} (57) or -64.2^{\circ} to
33.0°
                at 287
                        mm. (21)
28.115°
                at 221.8 mm. (26)
                                       -10.7° (58) see indic. refs.
27.0°
                at 223 mm. (21)
```

See Note 1.

Note 2. For influence of high press. on m.p.

of C see (33); for study of rate of solidification see (35). Note 3. For D_t^t over range -61.3° to $+59.8^{\circ}$

see (59). [For extraordinarily comprehensive reviews of the history and general chemistry of C see

[See also methylene (di)chloride (3:5020) and carbon tetrachloride (3:5100).]

MISCELLANEOUS PHYSICAL PROPERTIES OF C

(1) (60).

VARIOUS SOLUBILITY RELATIONS

With water. C is only very slightly sol. aq. and is eas. volat. with steam; e.g., 100 g. aq. at 15° dissolves 0.852 g. C (18); water satd. with C conts. at 20° 0.8% C (63) cf. (64). For studies of soly. of aq. in C at 0° (65), 20° (63), 25° (65), and 30° (65) see indic. refs.; note that at 20° \bar{C} satd. with aq. conts. 99.8% \bar{C} and has $D_4^{20} = 1.486$ (63).

With various inorganic compounds. [For data on soly. in C of H₂ (66), O₂ (78), HCl (67) (68) (69) (79), HBr (68) (69), H₂S (67), NH₃ (67), CO₂ (70) (80) (81), N₂O (81), and NO₂ (70) see indic. refs. — For data on soly. of I₂ in $\bar{\mathbb{C}}$ see (71) (72) (73) (74); for study of nature of I₂ solns. in C see (75); for soly. of I₂ in vapor of C see (76).]

With organic materials. [For study of absorption of vapor of C by kerosene see (77).]

BINARY SYSTEMS CONTAINING C

(See also azeotropes containing C)

 \tilde{C} with various inorganic compounds. $\tilde{C} + aq.$: for soly. data and diag. see (64); note that a previously described (82) hydrate of \tilde{C} could not be confirmed (64). $-\tilde{C} + Cl_2$: for f.p./compn. data and diag. (note that 4 different compounds are formed) see (34). $-\tilde{C} + Br_2$: for f.p./compn. data and diag. see (34) (36) (note that no compds. are formed and that eutectic has m.p. -72° (34) with about 86 mole \tilde{C}).

 $\tilde{\mathbf{C}}$ with org. cpds. of Order 1. \tilde{C} + n-hexane (1:8530): for f.p./compn. data see (83); for densities over range -90° to $+60^{\circ}$ see (85). $-\tilde{C}$ + C_6H_6 (1:7400): for f.p./compn. data and diag. see (38); for D_{25}^{25} /compn. data over entire range see (19); for D_{25}^{25} /compn. data see (18); for liq. vapor equil. see (19) (117) (112) (124). $-\tilde{C}$ + toluene (1:7405): for f.p./compn. data see (83); for data on specific gravity of system from 15-25° see (86); for study of liq-vapor equil. see (123). $-\tilde{C}$ + cyclohexane (1:8405): for f.p./compn. data see (83); for D_{40}^{20} compn. see (47).

 $\bar{C} + MeOH$ (1:6120): for f.p./compn. data see (37) (84); for D_D^{25} /compn. and n_D^{25} /compn. see (44). $-\bar{C} + EtOH$ (1:6130): for D_4^{25} /compn. data see (45) (46). $-\bar{C} + benzyl$ alc. (1:6480): for density/compn. data over entire range see (87).

 \bar{C} + diethyl ether (1:6110): for f.p./compn data and diag. see (42) (88); for D_4^{20} /compn. see (47). — \bar{C} + disopropyl ether (1:6125): for D_4^{20} /compn. see (47). — \bar{C} + dioxane-1,4 (1:6400): for D_4^{20} /compn. see (47). — \bar{C} + ethylene glycol dimethyl ether (1:6141): for study of heat of mixing see (89). — \bar{C} + tetraethylene glycol dimethyl ether: for study of heat of mixing see (89).

 \ddot{C} + dimethyl carbonate (1:3046): for D_4^{25} /compn. data see (20). — \ddot{C} + diethyl carbonate (1:3150): for D_4^{25} /compn. data see (20).

 \bar{C} + acetone (1:5400): for f p./compn. data see (27); for D_2^{20} /compn. (47), D_2^{25} /compn. (19) (46), n_D^{25} /compn. (19), and n_D^{25} /compn. (49) data see indic. refs.; for refractive index/compn. for light of various wave lengths see (52).

With org. cpds. of Order 2. \ddot{C} + nutrobenzene: for f.p./compn. data and diag. (eutectic, f.p. -71.0° conts. 81.5 wt. % \ddot{C}) see (61). $-\ddot{C}$ + anulune: for f.p./compn. data and diag. see (27). $-\ddot{C}$ + N,N-dimethylandine: for D_{4}^{25} , D_{4}^{40} , n_{D}^{248} , and $n_{D}^{39.5}$ over entire range of composition see (43). $-\ddot{C}$ + quinoline: for D_{4}^{20} /compn. data see (47).

With org. cpds. of Order 3. $\bar{C}+CH_2Cl_2$ (3:5020): for f p./compn. data and diag. (eutectic, f.p. -108.4° conts. 29.5 wt. % \bar{C}) see (39); for data on b.p., D_4^{20} , and liq.-vapor equil. see (90). $-\bar{C}+CCl_4$ (3:5050): for f.p./compn. data and diag. (eutectic, f.p. -81.4° conts. 50.6 wt. % \bar{C} (39)) (36) (83) (91) see indic. refs.; for D_4^{20} /compn. (48) (90), D_{25}^{25} /compn. (8), b.p. and liq.-vapor equil. (90) see indic. refs. $-\bar{C}+1,1$ -dichloroethane (3:5035): for b.p., D_4^{20} , and liq.-vapor equil. see (90). $-\bar{C}+1,2$ -dichloroethane (3:5130): for data on vap. press. (92) and liq.-vap. equil. (93) see indic. refs. $-\bar{C}+1,1,1$ -trichloroethane (3:5058): for f.p./compn. data see (94). $-\bar{C}+1,1,2$ -trichloroethylene (3:5170): for f.p./compn. data and diag. (eutectic, f.p. -100.2° , conts. 31.2 wt. % \bar{C}) see (39). $-\bar{C}+\beta,\beta'$ -dichlorodiethyl ether (3:6025): for D_4^{20} /compn. data see (47).

With org. cpds. of higher orders. $\bar{C}+1,2$ -dibromoethane: for D_4^{20} /compn. data see (47). $-\bar{C}+CBr_4$: for f.p./compn. data and diag. see (91). $-\bar{C}+CHI_3$: for vap. press. data see (95). $-\bar{C}+CS_2$: for f.p./compn. data see (83); for D_{15}^{15} compn. (96) or D_{25}^{25} /compn. (8) see indic. refs.; for liq.-vapor equil. data see (97).

TERNARY SYSTEMS CONTAINING C (See also azeotropes containing C)

 \ddot{C} + acetone (1:5400) + H_2O : for studies of liq. equil. at 25° see (98) (99) (100) (101) (102). — \ddot{C} + acetone (1:5400) + MeOH (1:6120): for ternary b.p. diag. see (103). — \ddot{C} + acetone (1:5400) + diethyl ether (1:6110): for data on refraction see (104). — \ddot{C} + acetone (1:5400) + disopropyl ether (1:6125): for ternary b.p. diag. see (103).

 \bar{C} + acetone (1:5400) + \bar{C}_6H_6 (1:7400): for ternary b.p. diag. see (103) (19) (105); for refractive data see (104).

 \bar{C} + acetone (1:5400) + CH_2Cl_2 (3:5020): for ternary b.p. diag. see (103).

 \bar{C} + acetic acid (1:1010) + aq.: for studies of liq. equil. at 25° see (104) (106) cf. (99). — \bar{C} + acetic acid + lubricating oil: for studies of liq. equil. at 25° see (107).

 $\bar{C} + CH_2Cl_2$ (3:5020) + CCl_4 (3:5100): eutectic, f.p. -111.4°, conts. 27 wt. % \bar{C} + 60 wt. % CH_2Cl_2 + 13 wt. % CCl_4 (39).

QUATERNARY SYSTEMS CONTAINING C

 \bar{C} + acetone (1:5400) + AcOH (1:1010) + aq.: for study of liq. equil. at 25° see (100); for study of use of system in mixed solv. extraction of lubricating oils see (107) (108). — \bar{C} + trans-1,2-dichloroethylene (3:5028) + 1,1,2-truchloroethylene (3:5170) + C_2H_5Br : eutectic, f.p. -139.1°, conts. 17.7 wt. % \bar{C} + 13.8 wt. % trans-1,2-dichloroethylene + 21.6 wt. % trichloroethylene + 44.9 wt. % C_2H_5Br (39).

BINARY AZEOTROPES CONTAINING C

 $\overline{C} + H_2O$: \overline{C} forms with aq. a const.-boilg. mixt., b.p. 56.1°, contg. 97.5 wt. % \overline{C} (14). C + MeOH (1:6120): C forms with MeOH a const.-boilg. mixt., b.p. 53.5° (103) (109), contg. 87.5 wt. % (103) = 65 mole % (109) \ddot{C} , cf also (110) (111) (4) (112) (113). $-\ddot{C}$ + EtOH (1:6130): C forms with EtOH a const.-boilg. mixt., b.p. 59.3° at 760 mm. (111), 59.35° at 760 mm. (14), contg. 93.2 wt. % \bar{C} (111) cf. (14) = 84 mole % \bar{C} (111) (see also (4) (110)) of $D_{15}^{15} = 1.4112$ (14); for thermodynamic study of this system see (114); for study of liq.-vap. equil. see (45). — \ddot{C} + isopropyl alc. (1:6135): \ddot{C} forms with isopropyl alc. a const.-boilg. mixt., b.p. 60.8° at 760 mm. (111), contg. 95.5 wt. % \overline{C} (111) = 92 mole % \bar{C} (111). — \bar{C} + formic acid (1:1005): \bar{C} forms with formic acid a const.-boilg. mixt., b.p. 59.15° at 760 mm. (115), contg. 85 wt. % C (115). — C + ethyl formate (1:3000): C forms with ethyl formate a const.-boilg. mixt., b.p. 62.8° (116), 62.7° (111) at 760 mm., contg. 87 wt. % \bar{C} . — \bar{C} + methyl acetate (1:3005): \bar{C} forms with methyl acetate a const.boilg. mixt., b.p. 64.8° at 760 mm. (111), contg. 77 wt. % C (111); b p. 63.0° at 726.3 mm. contg. 50 wt. % C (117); b.p. 62.6° at 717.5 mm. contg. 56 wt. % C (117); for study of constant evapn. system see (125). — \bar{C} + disopropyl ether (1:6125): \bar{C} forms with diisopropyl ether a const.-boilg. mixt., b.p. 70.5°, contg. 36.5% wt. % \bar{C} (103). — \bar{C} + acetone (1:5400): Č forms with acetone a const.-boilg. mixt., b.p. 64.5° at 760 mm. (109) (103) (19) (105) (111), contg. 79.5 wt. % Č (111) (103), 78 wt. % Č (19) (105), 65.5 mole % Č (109); b.p. 62.4° at 732.0 mm. contg. 80 wt. % C (117); b.p. 62.25° at 719 mm. contg. 86 wt. % C (117) cf. also (112); b.p. 61.95° at 716.5 mm. contg. 85 wt. % C (117): for studies of liq.-vapor equil. of \bar{C} + acetone see (19) (105) (117) (112), for study of vap. press. see (26) (49) (118) (119) (120) (121); for study of distn. of \bar{C} + acetone in wetted wall column see (122).

TERNARY AZEOTROPES CONTAINING C

 \bar{C} + EtOH (1:6130) + aq.: \bar{C} forms with EtOH + aq. a ternary const.-boilg. mixt., b.p. 55.4-55.5° at 760 mm., contg. about 92.5 wt. % \bar{C} + 4.0 wt. % EtOH + 3.5 wt. % aq. (14).

OTHER SELECTED PHYSICAL CHARACTERISTICS OF C

[For study of thermal conductivity of \bar{C} (126) (127) see indic. refs.; for studies of heat capacity of \bar{C} (17) as calcd. from spectroscopic data (128) (129) see indic. refs.; for study of critical temp. of \bar{C} and its microdetn. see (130); for studies on value of ebullioscopic const., viz., 3.766° per mole solute in 100 g. \bar{C} (131), and review of prior work see (131).]

[For studies of adsorption of C on various carbons (132) (135) (155), animal charcoal (133) (134), wood or cocoanut charcoal (136) (137) (138) (139) (140) (141) (142), glass wood (143) (144), glass powder (145), alumina gel (146) (147), silica gel (148), vitreous silica (149), Fe(OH)₃ gel (150), Cr(OH)₃ gel (151) cf. (152), TiO₂ gel (153) (154), see indic. refs.]

PHYSIOLOGICAL ASPECTS OF C

 \tilde{C} was first prepared in 1831 by three independent workers, viz., Liebig, Souberain, and Guthrie (for amplification see (1)). \tilde{C} has long been used in medicine especially as an anesthetic but a detailed account of this aspect is beyond the scope of this book. [For history and clinical use of \tilde{C} see (156); for report of 3000 cases of anesthesia with \tilde{C} see (157). For examples of articles commemorative of the centenary of the discovery of \tilde{C} and its use in anesthesia see (158) (159) (160) (161).]

The vapor of \tilde{C} in conens. of 6.8-8.2% by volume in air will kill most animals in a short time; a conen. of 1.4% by volume is dangerous to life after 30-60 min exposure; the max. conen. tolerable for 60-min. exposure without serious disturbances is 0.5-0.6% by volume; the max. conen. tolerable for several hrs. or for prolonged exposure with but slight symptoms is 0.2% by volume (163).

[For impt. study of toxicity of C including its effect upon various organs see (164).]

USES OF C

 \ddot{C} is widely used as solvent and chemical reactant and any detailed survey of this aspect is beyond the scope of this book. [However, for use of \ddot{C} as solvent for ozonization reactions (24), as means of dehydration of EtOH (165), in mixt. with 100% HNO₃ + Ac₂O as nitrating or nitroesterifying reagent (166), in colorimetric detn. of I₂ (167), or in prepn. of AlCl₃ from Al + Br₂ + \ddot{C} (168) see indic. refs.]

DETECTION OR DETERMINATION OF C

Detection of C. [For study of isolation of C from very dil. solns. by distn. see (169).] Note that many of the tests for C may be given by other haloforms (e.g., CHBr₃, CHI₃, etc.) or by trichloroderivatives which under particular test conditions yield CHCl₃ by cleavage (e.g., chloral (3:5210), chloral hydrate (3:1270), 1,1,1-trichloro-2-methyl-propanol-2 = "chloretone" (3:2662), loss of CO₂ (trichloroacetic acid (3:1150)) or other decompns.

[For study of detectn. of \bar{C} by color reaction with pyridine + alk. (Fujiwara reaction) see (170); note also further references to this test under detn. of \bar{C} (below) and under trichloroethylene (3:5170).]

[For detectn. of C by reaction with aq. NaOH + NH₄OH to give NaCN and after acidification detectn. of resultant HCN by drop test methods see (171).]

[For color reactions of \bar{C} with phenols under various circumstances, e.g., \bar{C} with resorcinol (1:1530) + NaOH (172) (173), with α -naphthol (1:1500) + cyclohexanol (1:6415) (174), with 2,7-dihydroxynaphthalene (1:1594) + cyclohexanol (175), see indic. refs. For use of last two methods in distinction of \bar{C} from CH₂Cl₂ (3:5020) and from CCl₄ (3:5100) see (173) (174); also at end of text of this compound under \mathfrak{P} .]

[For distinction of Č from CCl₄ (3:5100) by its greater solvent power for papaverine hydrochloride (176) or quinine sulfate (177) see indic. refs.]

Note that C reduces Fehling's soln. on htg. whereas CCl₄ does not (177).

Note also that Č with aniline + alc. alk. on htg. gives characteristic odor of phenyl isocyanide (carbylamine test) (178).

Determination of C. Methods for the quant. detn. of C may be classified into two groups: (1) those depending upon total conversion of the chlorine to the ionized form followed by its determination by conventional methods; and (2) methods based upon color reactions.

[For studies of methods of the first type involving decomposition of \tilde{C} by combustion in air (179) (187) or H_2 flame (180), by combined combustion and hydrolysis in moist air at 1000–1100°C. (181) cf. (182), by alkaline hydrolysis (183) (185), by reduction using Na + triethanolamine (184) see indic. refs. For automatic apparatus for detn. of small conens. of \tilde{C} in air see (186); for detn. of \tilde{C} in mixtures contg. nonvolatile chlorides see (188) (189) (190) (191).]

[For studies on use of color reaction with pyridine and alkali (Fujiwara reaction) as means for quant. detn. of \bar{C} in air, soil, blood, tissue, etc., see (170) (192) (193) (194) (195) (196) (197) (198) (199). — For use of color reaction of \bar{C} with α -naphthol (1:1500) or β -naphthol (1:1540) in alc. KOH as colorimetric method for detn. of \bar{C} see (200).]

DETECTION OF OTHER COMPOUNDS IN C

[For studies on detn. of EtOH (1:6130) in \bar{C} see (201) (202) (203); on detection of acetone (1:5400) in \bar{C} see (204) (205); on detection of aldehydes in \bar{C} see (206); on detection of CCl₄ (3:5100) in \bar{C} see (175) (207) (208) (209); on detection of COCl₂ (3:5000) in \bar{C} see (210) (211) (212) (213) and also under phosgene (3:5000).]

PREPARATION OR FORMATION OF C

From methane. The formation of \bar{C} together with CH₃Cl (3:7005), CH₂Cl₂ (3:5020), CCl₄ (3:5100), and other products has been very extensively studied from many viewpoints. The literature of this reaction, however, is so extensive and diffuse that no complete survey can be detailed in this book. For concise reviews of the older literature see (1) (214); for additional references see text of methylene (di)chloride (3:5020) under its formation from methane.

From carbon tetrachloride. [For prepn. of \bar{C} from CCl₄ (3:5100) by reduction using Zn + H₂SO₄ (215) (216) cf. (1) (214), finely divided Fe + aq. (217) + cat. (218) (219), Fe(OH)₂ + aq. alk. (220), or electrolytic reduction (221) see indic. refs.]

From other halogenated hydrocarbons. [For formn. of \tilde{C} from mixts. of CH₂Cl (3:7005) + CH₂Cl₂ (3:5020) with Cl₂ + cat. at 400-650° (223), from CHCl₂F + AlCl₃ as directed (CHClF₂ is also formed) (224), from CCl₃Br with boilg. alk. Na₂AsO₃ (225), from 1.1,2,2-tetrachloroethane (3:5750) or its dehydrochlorination prod. trichloroethylene (3:5170) by pyrolysis at 700° (226), from 1,1,1,2,2,3,3-heptachloropropane (3:0200) over Cu₂Cl₂ below 250° (227) see indic. refs.]

From various carbonyl compounds. [For prepn. of \bar{C} from acetaldehyde (1:0100) with alkaline hypochlorite soln. at 70-80° (228) (229) cf. (1) (214) see indic. refs. For prepn. of \bar{C} from trichloroacetaldehyde (chloral) (3:5210) or from chloral hydrate (3:1270) by warming with alkalies or alkaline reagents see texts of these compounds.]

[For prepn. of C from acetone (1:5400) with alkaline hypochlorite solns. (228) (230) (231) cf. (1) (214) or by electrolysis of alkali chloride in aq. acetone (232) (233) (234) see

indic. refs. For formn. of C from various chlorinated ketones by action of alkali hypochlorites (haloform reaction) see (235) (236).]

From alcohols. [For concise reviews of prepn. of \bar{C} from EtOH (1:6130) by action of alkaline hypochlorite solns. see (1) (214); for formn. of \bar{C} from various other primary and secondary alcohols in similar fashion see (237).]

From miscellaneous sources. [For prepn. of \bar{C} from trichloroacetic acid (3:1150) by loss of CO_2 under a wide variety of conditions see text of that compound under decarboxylation; from dichloroacetyl chloride (3:5290) on warming with AlCl₃ see text of that compound; from mixtures of salts of fatty acids with inorganic chlorides by electrolysis see (238); from lignin with alkali hypochlorite see (239).]

[For prepn. of trichlorodeuteriomethane (deuteriochloroform) (CDCl₃) from chloral deuterate + NaOD (443) or from chloral (3:5210) + D₂O + CaO (444) see indic. refs.; for rate of isotopic exchange between \bar{C} and D₂O see (445).]

CHEMICAL BEHAVIOR OF C

Pyrolysis of Č. [C̄ passed at red heat over asbestos (240), over Pt wire at 1000° (241), with 1% I₂ over pumice at red heat (242) cf. (243), or in electric arc (249) undergoes decomposition, and various proportions of carbon, HCl, hexachloroethane (3:4835), hexachlorobenzene (3:4939), tetrachloroethylene (3:5460), pentachloroethane (3:5880), and other products are claimed to result. C̄ over htd. TiO₂ gives (245) HCl + CO + hexachlorobenzene (3:4939) + TiCl₄. For other studies of pyrolysis of C̄ at 368-400° (246), at 425° (247), and at 512° (248) see indic. refs.]

Oxidation of C. C is readily oxidized to carbonyl chloride (phosgene) (3:5000) by air, oxygen, ozone, or chemical oxidizing agents. In view of the extremely toxic character of phosgene, and of the extensive use of C in anesthesia, this aspect is of great importance and has been very extensively studied.

By air or oxygen. [For an extensive account of the earlier literature on the oxidation of $\bar{\mathbb{C}}$ in air and light see (250). Note that such oxidation is not effected by air in absence of light, nor by light in absence of air (251). $\bar{\mathbb{C}}$ with limited air in sunlight reacts according to the following equation: $\mathrm{CHCl_3} + \mathrm{O} \to \mathrm{COCl_2}$ (3:5000) + HCl (252) but with excess air in sunlight in sense $\mathrm{2CHCl_3} + \mathrm{5O} \to \mathrm{2CO_2} + \mathrm{3Cl_2} + \mathrm{H_2O}$ (252). Note that $\bar{\mathbb{C}}$ + air over dry KOH gives (253) some phosgene (3:5000). For later studies on the photochemical oxidation of $\bar{\mathbb{C}}$ (254) in tropical sunlight (255), including search for possible intermediate peroxides (256) (257), see indic. refs. For studies on chlorine-sensitized photochem. oxidn. of $\bar{\mathbb{C}}$ see (258) (259) (260). For oxidn. of $\bar{\mathbb{C}}$ by atomic oxygen see (261). The photochem. oxidn. of $\bar{\mathbb{C}}$ is repressed by various inhibitors of which EtOH has been most extensively studied (262).]

By ozone. [\bar{C} dissolves ozone yielding a blue soln. in which some \bar{C} is gradually oxidized (270) (271) to phospene; for study of \bar{C} as ozonization solvent see (24).]

By other chemical means. [\bar{C} with ClSO₃H at 120° (263), with K₂Cr₂O₇ + H₂SO₄ (264), or with air over CuO at 350-550° (265) gives phosgene (3:5000). Note, however, that \bar{C} with conc. H₂SO₄ above 200° gives (266) (267) CO + CO₂ + HCl + SO₂ while \bar{C} with an equimolal mixt. of H₂S₂O₇ + SO₃ at 55-60° as directed (268) cf. (269) reacts in sense CHCl₃ + H₂S₂O₇ + SO₃ \rightarrow CO + 3ClSO₃H with S₂O₅Cl₂ (pyrosulfuryl chloride) being formed using more SO₃, and H₂SO₄ using less SO₃.]

Inflammability of \tilde{C} . [For studies of inflammability of \tilde{C} in air, oxygen, or O_2/N_2O mixts. see (272) cf. (273).]

Reduction of \tilde{C} . [\tilde{C} with Zn + alc. HCl (274), Zn + AcOH (275), Zn dust + alc. NH₃ (276) (277) (278), Al/Hg + aq. (275), Fe + AcOH (275), or Si₃H₃ + AlCl₃ in abs. of air

(279) gives CH_2Cl_2 (3:5020) or further reduction products, e.g., CH_3Cl (3:7005) or CH_4 (280); \bar{C} with conc. HI on htg. gives (281) CH_2I_2 [Beil. I-71, I_1 -(18), I_2 -(37)]; \bar{C} with atomic hydrogen gives (282) CH_3Cl (3:7005) + HCl.]

Substitution of C. Note that the text of this section refers only to replacement of the single hydrogen atom of CHCl₃.

Fluorination. [The product of replacement of the H atom of \bar{C} by F (289), viz., trichlorofluoromethane, CCl₃F [Beil. I-64], is usually prepd. by indirect means from sources other than \bar{C} , e.g., from CCl₄ (3:5100) + F₂ in pres. of As + Br₂ (283). However, beyond noting a few leading articles on its physical consts., including b.p. = 23.66° (284), 23.77° (285) at 760 mm., m.p. = -110.48° (284), vapor press. (284) (285), liquid density (286), and P/V/T relationships (287), no complete review of CCl₃F and its relatives (cf. (288)) can be given here.]

Chlorination. \bar{C} on suitable chlorination yields CCl₄ (3:5100). [E.g., \bar{C} with Cl₂ in sunlight (290) or u.v. light (291) (292) (293) (294), at 260-320° (295), or in pres. of FeCl₃ (296) or of aq. (297), or \bar{C} with ICl at 165° (298), or \bar{C} with aq. NaOCl (reaction very slow and incomplete (299)) gives CCl₄ (3:5100). Note, however, that \bar{C} is not chlorinated with SO₂Cl₂ even in presence of organic peroxides (200).

Bromination. \bar{C} on suitable bromination gives bromotrichloromethane. [E.g., \bar{C} with Br₂ in s.t. (301) (298) at 225-275° for 14 hrs. as directed (302), or \bar{C} with Br₂ in light of 5460 Å (303) or 2650 Å in pres. of O₂ (304), or over carbon at 180-350° (305), or \bar{C} with aq. NaOBr (299), gives CCl₃Br [Beil. I-67, I₂-(31)], b.p. 105° (302), 104.2-104.35° at 758.5 mm. (308), m.p. -21° (302). For prepn. of CCl₃Br from trichloroacetyl bromide by pyrolysis at 400° at ord. press. see (306); for studies of behavior of CCl₃Br with Cl₂ in light (307) (308) or of its halogen-sensitized photochem. oxidn. (309) see indic. refs.]

Iodination. [C with aq. NaOI (299) gives iodotrichloromethane, CCl₃I [Beil. I-71], b.p. 142° (299) (310); for prepn. of this prod. from CCl₄ (3:5100) with AlI₃ in CS₂ (310) or from trichloroacetyl iodide by distn. at ord. press. (306) see indic. refs.]

Nitration. [\bar{C} with HNO₃ in s.t. at 90–100° for 120 hrs. (311) or in boilg. acetyl nitrate (312) gives nitrotrichloromethane (chloropicrin) [Beil. I-76, I₁-(20), I₂-(41)], b.p. 111–112°, but this product is usually prepd. by other means, e.g., from calcium picrate with Ca (OCl)₂ (313) (314).]

Nitrosation. [No record can be found of any reaction between chloroform and nitrous acid. However, nitrosotrichloromethane [Beil. I₂-(39)] has been obtd. indirectly from sodium trichloromethane sulfinate, CCl₃-SOONa, by the action of HNO₃ (315) (316). It is a dark blue liq., b.p. 5.0-5.5° at 70 mm. (315), but decomposing on distn. at ord. press. The compound is of considerable interest because on reduction with H₂S (315), Al/Hg (315), SnCl₂ (316), or SO₂ (316) it yields dichloroformaldoxime, Cl₂C—NOH, a chemical warfare agent with especially terrifying characteristics.]

Hydrolysis of \tilde{C} . \tilde{C} on hydrolysis gives formic acid (1:1005) in such a form that the reaction mixt. is able to reduce Fehling soln. or NH₄OH/AgNO₃ even at room temp. or more rapidly on warming (dif. from CCl₄ (3:5100), 1,2-dichloroethane (3:5130), 1,1,2,2-tetrachloroethane (3:5750) and hexachloroethane (3:4835)). Note that, although some CO has been detected, yet formaldehyde (1:0145) is not produced (317).

[\bar{C} with aq. on protracted htg. in s.t. at 225° gives (318) HCOOH (1:1005) + CO + HCl. — \bar{C} with aq. caustic alkali on htg. gives salts of HCOOH (1:1005) (319) accompanied by CO (320) (321) (322); for studies on kinetics of hydrolysis of \bar{C} in aq. alc. in light from Hg vapor lamp see (323).]

 $[\bar{C}]$ is also hydrolyzed in alc. alk. solns. even more readily than CCl₄ (3:5100) (324) (191); for use of this principle in estimation of \bar{C} see above under determination of \bar{C} . For study of kinetics of hydrolysis of \bar{C} with alc. KOH (325), with N/10 KOH in 95% alc. at 90°

(326) cf. (327), or with Ba(OH)₂ or TiOH in 50% alc. (328) (327) see indic. refs. Note that Č with alc. KOH is also claimed by one worker (253) to give ethylene.]

[For further details on ability of C to reduce Fehling soln. see (317) (329) (330).]

Behavior of \tilde{C} with inorganic salts. [\tilde{C} with AlCl₃ gives a gummy hygroscopic addn. prod. which with aq. regenerates \tilde{C} (331), but \tilde{C} with AlBr₃ is more or less (yields: 58–90% (332), 100% (333)) converted to bromoform [Beil. I-68, I₁-(16), I₂-(33)], b.p. 149.55° at 760 mm. (334), m.p. 8.05° (334), $D_4^{25} = 2.87757$ (334), $D_4^{20} = 2.89054$ (334), $D_4^{15} = 2.90350$ (334), $n_5^{15} = 1.60088$ (334).]

[\bar{C} with CaI₂ in s.t. at 100° is partially converted (335) to CHI₃, but \bar{C} with aq. KI even in pres. of Cu decomposes yielding (336) CH₄ + H₂ + CO + CO₂.]

[For leading reference on behavior of C with various metal fluorides see (337).]

Behavior of \tilde{C} with metals. [\tilde{C} with alkali or even alkaline-earth metals undergoes explosive decompn. on htg. or even at room temp. if subjected to sufficient mechanical shock. For studies of the explosion of \tilde{C} with alkali metals see (338) (339) (340); for further data on explosions of \tilde{C} with Li, Na, K, Ca, Sr, Ba, and Mg, especially with reference to sensitivity to mechanical shock, see (341). \tilde{C} with molten Na at 260-370° as directed (342) gives $\tilde{C} + H_2 + CH_4$ with smaller amts. of C_2H_6 , C_2H_4 , and C_2H_2 ; for study of \tilde{C} with Na vapor see (343).]

[For study of hazards of behavior of CHCl₃/CCl₄ mixts. with Al or Mg see (344); for extensive study of corrosion of metals by C see (345).]

[Note that C with Mg in boilg. ether does not react, even in pres. of various catalysts (346).]

Behavior of \bar{C} with various organic reactants. With carbon monoxide. $[\bar{C}$ with CO + water vapor above 200° in pres. of suitable cat. as directed is claimed (347) to give acetic acid (1:1010); \bar{C} with CO + AlCl₃ at 150° and 900 atm. for 6 hrs. gives (21% yield (348)) dichloroacetyl chloride (3:5290).]

With hydrocarbons. [Č (excess) with octene-1 (1:8375) in pres. of small amts. (0.02 mole) of dibenzoyl peroxide (or diacetyl peroxide) adds to unsatd. linkage giving (349) 1,1,1-trichlorononane; under similar conditions Č adds to one of the unsatd. linkages of diallyl (1:8045) giving 8,8,8-trichloroheptene-1. — (For other addns. of Č to unsatd. linkages see below).]

[C with C₆H₆ (excess) in pres. of AlCl₃ (350) (351) (352) (353), FeCl₃ (354), chromium powder (355), or Al powder (356) gives triphenylmethane (1:7220); other aromatic hydrocarbons presumably give analogous results but cannot be detailed here.]

With saturated halohydrocarbons. [\tilde{C} (1.2 moles) with EtBr (3.8 moles) + AlCl₃ (0.07 mole) on htg. as directed (357) gives EtCl (3:7015) + 90% yield CHBr₃ (for physical constants see above under behavior of \tilde{C} with inorganic salts (AlBr₃)). — \tilde{C} (1 mole) with MeI (3 moles) + AlCl₃ (0.04 mole) on similar treatment gives MeCl (3:7005) + (95% yield (357)) iodoform, m.p. 119°. — \tilde{C} with CHBr₃ + 5-10% KCl in pres. of moistened AlCl₃ under CO₂ in s.t. at 135° for 14 hrs. undergoes a redistribution reaction giving (358) 17% \tilde{C} + 43% CHCl₂Br + 31% CHClBr₂ + 9% CHBr₃.]

With unsaturated halohydrocarbons. [\bar{C} (3 wt. pts.) with ord. 1,2-dichloroethylene (3:5030) + AlCl₃ (0.25 wt. pt.) stirred with sand for 20 hrs. at 30° (359) cf. (360) (361) (362) gives (yields: 63% (359), 70-75% at 50° (360), 46% at 17° in 22 hrs. (360)) 1,1,2,3,3-pentachloropropane (3:6280).]

[\bar{C} with 1,1,2-trichloroethylene (3:5170) + AlCl₃ at 20° gives (361) (362) 1,1,1,2,3,3-hexachloropropane (3:6460); note that at higher temp., e.g., 50-60°, yield is greatly diminished and several other prods. (361) are formed.]

[\bar{C} (2 moles) with 1,1,2,2-tetrachloroethylene (3:5460) + AlCl₃ (0.2 mole) refluxed 15-20 hrs. gives (85-93% yield (363)) (364) (365) (366) (367) (368) (369) 1,1,1,2,2,3,3-

heptachloropropane (3:0200); for study of equil. of system $\tilde{\mathbf{C}}$ + tetrachloroethylene (3:5460) + unsym.-heptachloropropane (3:0200) see (370).]

With unsaturated nitriles. [\bar{C} with acrylonitrile (vinyl cyanide) in pres. of trimethylbenzyl-ammonium hydroxide at 0-5° for 24 hrs. or solid KOH at 0-5° for 4 hrs. adds to unsatd. linkage giving (11-12% yield (371)) (372) γ, γ, γ -trichloro-n-butyronitrile, m.p. 41°, b.p. 214-216° at 760 mm., 90-95° at 12 mm. (371) (372).]

With alcohols or alcoholates. [Č with MeOH over cat. at 200-350° gives (373) MeCl (3:7005); Č with EtOH under similar conditions gives (373) EtCl (3:7015).]

[C with Na alcoholates gives the corresp. trialkyl orthoformates. E.g., C with NaOCH₃ gives (374) (375) trimethyl orthoformate (1:3087); C with NaOC₂H₅ gives (27-31% yield (376), 36% (377)) (374) (375) triethyl orthoformate (1:3241); orthoformate esters of higher ales. are similarly prepd. cf. (374) (377). For study of behavior of C with mixts. of sodium alcoholates see (378); for treatise on chemistry of aliphatic orthoesters see (379).]

With mercaptans or mercaptides. [\bar{C} with NaSCH₃ should yield trimethyl trithioorthoformate [Beil. II₁-(39)], m.p. 16° (380), b.p. 220° dec. (380), 103-104° at 12 mm. (381), 96° at 9 mm. (380), n_D^{15} = 1.5696 (381), but this prod. has been reported only by other means, e.g., from CCl₄ (3:5100) with NaSCH₃ (381) and from anhydrous HCOOH (1:1005) with CH₃SH in s.t. at ord. temp. (380).]

[\bar{C} with NaSC₂H₅ gives (382) (383) (386) triethyl trithioorthoformate [Beil. II-95, II₁-(39)], b.p. 235° dec. (380), 174° at 760 mm. (384), 136.5° at 23 mm. (385), 133° at 21 mm. (386), 126.5-128° at 12 mm. (381), 127-128° cor. at 12 mm. (387), $D_4^{20} = 1.053$ (386), $n_D^{15} = 1.5410$ (381), but this product is usually prepd. by indirect means, e.g., from anhydrous HCOOH (1:1005) with C₂H₅SH in pres. of dry HCl (384) (385) or from CCl₄ (3:5100) with NaSC₂H₅ (381).]

With phenols or phenolates. \vec{C} with phenols (or with substituted phenols having at least one free ortho or para position) in presence of aq. alk. condenses with eventual introduction of the formyl radical and formn. of phenolic aldehydes (Reimer-Tiemann reaction (388)). The countless recorded examples of this reaction cannot be detailed here but the following leading references will be found useful. [For modern studies of the Reimer-Tiemann reaction see (389) (390); for studies of influence of substituents in the phenolic component see (391) (392) (393) (394) (395); for extension of the Reimer-Tiemann reaction to other classes such as substituted indoles (396), thiazoles (397) see indic. refs.; for application to β -naphthol (1:1540) giving (38-48% yield (398)) 2-hydroxy-1-naphthaldehyde, m.p. 79-80°, to β -tetralol (5,6,7,8-tetrahydronaphthol-2) (399) see indic. refs.; for studies on theory of Reimer-Tiemann reaction see (400) (401) (402).

[\bar{C} with dry KOC₆H₅ at 110° for 4 hrs. under N₂ gives (15% yield (403)) triphenyl orthoformate [Beil. VI-152, VI₂-(153)], ndls. from alc., m.p. 76-77° (404), 75° (403), 71.5° (405); note that this prod. is also formed (405) in the Reimer-Tiemann reaction of. (390).]

With aldehydes or ketones. \bar{C} with aromatic (but not aliphatic (406)) aldehydes in pres. of aq. KOH undergoes addition yielding trichloromethyl-aryl-carbinols. [E.g., \bar{C} with benzaldehyde (1:0195) + aq. KOH gives (16% yield (406)) (407) cf. (408) trichloromethylphenyl-carbinol [Beil. VI-476, VI₁-(237), VI₂-(447)], m.p. 37° (409), b.p. 145° at 15 mm. (409) cf. (406) (corresp. acetate, m.p. 87.5° (409); corresp. benzoate, m.p. 97.5° (409); corresp. p-nitrobenzoate, m.p. 109° (410)). For analogous behavior of \bar{C} + alkali with o-chlorobenzaldehyde (3:6410) (411), m-chlorobenzaldehyde (3:6475) (412), p-chlorobenzaldehyde (3:0765) (413), p-tolualdehyde (1:0215) (412), and furfural (1:0185) (406) see indic. refs. Note that trichloromethyl-aryl-carbinols are also obtd. by reaction of arom. hydrocarbons with chloral (3:5210) q.v.]

[\overline{C} with acetone (1:5400) in pres. of dry powdered KOH (0.5 mole) below 0° (414) or 2-3° (415), or KOH in alc. as directed (416), or even NaNH₂ (418) gives (yields: 25% (416),

23% (414)) (417) (415) 1,1,1-trichloro-2-methylpropanol-2 $(\beta,\beta,\beta$ -trichloro-ter-butyl alcohol = "Chloretone") (3:2662) q.v.; note that use of NaOH lowers the yield (414) and that Ca(OH)₂ (416), Zn(OH)₂ (414), or Al(OH)₃ (414) yields no such product; note also that the crude prod. contains some diacetone alcohol (1:6423) best removed by treatment with aq. (416) since otherwise it forms with the "Chloretone" a const.-boilg. mixt.]

[$\ddot{\mathbf{C}}$ (2 moles) with ethyl methyl ketone (1:5405) in pres. of dry powdered KOH (419) or of NaNH₂ (418) gives (13.5% yield (419)) by addition 1,1,1-trichloro-2-methylbutanol-2 [Beil. I₂-(424)], b.p. 162-165° (418), 110-113° dec. at 620 mm. (419), $D_4^{20} = 1.2128$ (419), $D_D^{20} = 1.4460$ (419). Note, however, that analogous addition of $\ddot{\mathbf{C}}$ does not occur with diethyl ketone (1:5420) (420), di-n-propyl ketone (1:5447) (420), ethyl n-propyl ketone (420), methyl isobutyl ketone (1:5430) (420), or methyl phenyl ketone (acetophenone) (1:5515) (419), but will occur to a very small extent with cyclopentanone (1:5446) (421) or cyclohexanone (1:5465) (421) cf. (418).]

With amines. C with primary amines in pres. of alc. caustic alkali condenses with loss of 3 HCl giving the corresp. isocyanides whose extremely characteristic odor has caused this general procedure to be used as a test (422) for primary amines. The reaction has, however, been very little studied in the aliphatic series.

[\bar{C} with CH₃NH₂ + alc. NaOH should give methyl isocyanide (methyl carbylamine) [Beil. IV-56, IV₁-(328), IV₂-(561)], b.p. 59.6° at 760 mm. (423), 59-60° (424), $D_4^{20} = 0.734$ (424), $D_4^{20} = 0.7464$ (425), $n_{He}^{20} = 1.343$ (424), but this highly explosive (425) (426) (427) substance has been reported only by other means, e.g., from MeI with dry AgCN (425) (423), CuCN (428), or CH₃HgI (429). — \bar{C} with C₂H₅NH₂ + alc. NaOH gives (430) ethyl isocyanide (ethyl carbylamine) [Beil. IV-107, IV₁-(351), IV₂-(600)], b.p. 78.1° at 760 mm. (431), 78° (424), $D_4^{20} = 0.747$ (424), $D_4^{20} = 0.7405$ (425), $n_{He}^{20} = 1.362$ (424), but this less explosive prod. (427) is usually obtd. by other means, e.g., from EtI with AgCN (425) (431), etc. — \bar{C} with n-BuNH₂ + aq. NaOH gives (only 5% yield (432)) n-butyl isocyanide (n-butyl carbylamine) which is better obtd. (40% yield (432)) from n-BuI + AgCN.]

[Č with aniline in alc. KOH (433) (435) cf. (438) or in C_6H_6 + NaNH₂ (436), or better in MeOH/NaOH (50% yield (434)) or powdered KOH without solvent (35–40% yield (437)) cf. (438), gives phenyl isocyanide (phenyl carbylamine) [Beil. XII-191, XII₁-(168)], b.p. 165–166° at ord. press. with partial polymerization (435), 78° at 40 mm. (435), 64° at 20 mm. (435), $D_4^{18.1} = 0.9823$ (424), $n_{\rm He}^{13.1} = 1.52828$ (424). — For analogous reactions of Č with ρ -toluidine giving ρ -tolyl isocyanide [Beil. XII-788], b.p. 183–184° cor. at 753 mm. (439), with ρ -toluidine giving (440) (441) ρ -tolyl isocyanide [Beil. XII-903], b.p. 99° at 32 mm. (441), 94° at 25 mm. (434), m.p. 21° (441), 19.5° (434), with ρ -methoxyaniline (ρ -anisidine) giving ρ -methoxyphenyl isocyanide, b.p. 112° at 16 mm. (438), with ρ -phenylenediamine to give (442) either ρ -aminophenyl isocyanide, m.p. 74°, or ρ -phenylenediisocyanide see indic. refs. — Many other isocyanides are known but cannot be detailed here.]

Color reaction with α-naphthol/cyclohexanol. A. C (1'drop) with 2 ml. of a 2% soln. of α-naphthol (1:1500) in cyclohexanol (1:6415) + 1 pellet of solid NaOH, boiled 25 seconds and cooled, gives (174) blue color; one portion of this blue soln. underlaid with equal vol. of 85% H₂SO₄, stood 1 minute and shaken turns intensely blue; a second portion of the alkaline blue soln. acidified with equal vol. of AcOH (1:1010) stood 1 minute and shaken becomes orange-yellow. [Note that the alkaline boiling also gives a blue color with CH₂Cl₂ (3:5020) and with CCl₄ (3:5100) while other chlorinated solvents (174) give yellow-brown, gray, or brown; in the H₂SO₄ treatment CH₂Cl₂ (3:5020) gives greenish-blue and CCl₄ (3:5100) a red, color.]

- B. C (1 drop) with 2 ml. cyclohexanol (1:6415) + a few mgms. α -naphthol (1:1500) + 2 ml. 20% aq. KOH boiled 15 seconds with vigorous shaking gives (175) blue color in upper layer. [Neither CH2Cl2 (3:5020) nor CCl4 (3:5100) gives any color, and this form of the test may be used to detect as little as $1\%\ \bar{\mathrm{C}}$ in either of the other two.]
- P Color test with 2,7-dihydroxynaphthalene/cyclohexanol. C (1 drop) with 2 ml. pure cyclohexanol (1:6415) + 1 pellet NaOH + a few mgms. 2,7-dihydroxynaphthalene htd. at 197° (b.p. of ethylene glycol) for 45 seconds, decanted from undissolved NaOH, cooled, and shaken with 2 ml. AcOH + 4 ml. 96% EtOH, gives deep red color (175). [Note that under these conditions CH₂Cl₂ (3:5020) gives a steel-blue color while CCl₄ (3:5100) gives pale yellow-brown color (175).]
- **P** Color test with cyclopentanol. \tilde{C} (1 drop) in 1 ml. cyclopentanol (1:6412) + 1 pellet NaOH boiled for 25 seconds, then shaken vigorously for 35 seconds, then treated with 4 ml. 96% EtOH and shaken, gives with C only a pale citron-yellow color (175). [Note that in this test CH₂Cl₂ (3:5020) gives a deep red color which intensifies or turns reddish-brown upon addition of EtOH; CCl4 (3:5100) gives an intense brown color.l
- 3:5050 (1) Baskerville, Hamor, J. Ind. Eng. Chem. 4, 212-220, 278-288, 362-372, 422-429, 499-506, 571-578 (1912). (2) Perkin, J. Chem. Soc. 45, 530 (1884). (3) Pettit, J. Phys. Chem. 3, 351 (1899). (4) Thayer, J. Phys. Chem. 3, 36-40 (1899). (5) Tyrer, J. Chem. Soc. 99, 1643 (1911). (6) Turner, J. Chem. Soc. 97, 1188 (1910). (7) Maryott, Hobbs, Gross, J. Am. Chem. Soc. 63, 660 (1941). (8) Linebarger, Am. Chem. J. 18, 439, 442, 447 (1896). (9) Biltz, Sapper, Z. anorg. allgem. Chem. 203, 283 (1932). (10) Mathews, J. Am. Chem. Soc. 48, 570 (1926).
- (11) Tyrer, J. Chem. Soc. 105, 2538 (1914). (12) Timmermans, Martin, J. chim. phys. 23. 763-765 (1926). (13) Zmaczynski, J. chm. phys. 27, 503-517 (1930). (14) Wade, Finnemore, J. Chem. Soc. 85, 938-947 (1904). (15) Beckmann, Liesche, Z. physik. Chem. 88, 29 (1914). (16) Thorpe, J. Chem. Soc 37, 196 (1880). (17) Stull, J. Am. Chem. Soc. 59, 2729 (1927). (18) Gross, Saylor, J. Am. Chem. Soc. 53, 1744-1751 (1931). (19) Reinders, de Minjer, Rec. trav. chim. 59, 371-391 (1940). (20) Bowden, Butler, J. Chem. Soc. 1939, 79-83.
- (21) Herz, Rathmann, Chem. Ztg. 36, 1417 (1912). (22) Cauwood, Turner, J. Chem. Soc. 167, 280 (1915). (23) Schiff, Ann. 220, 95 (1883). (24) Greenwood, J. Org. Chem. 10, 414-418 (1945). (25) Arbusow, Z. physik. Chem. 131, 58 (1928). (26) Beckmann, Faust, Z. physik. Chem. 89, 235-246 (1915). (27) Tsakalatos, Guye, J. chim. phys. 8, 348-350 (1910). (28) Eucken, Lindenberg, Ber. 75, 1961-1962 (1942). (29) Archibald, McIntosh, J. Am. Chem. Soc. 26. 305-306 (1904). (30) Timmermans, Bull. soc. chim. Belg. 25, 300-327 (1911); Cent. 1911, II 1015.
- (31) Skau, J. Phys. Chem. 37, 609-614 (1933). (32) Timmermans, van der Horst, Kamerlingh-Onnes, Cent. 1923, IV 377. (33) Bridgman, J. Chem. Phys. 9, 795 (1941); Proc. Am. Acad. Arts Sci. 74, 399-424 (1942). (34) Wheat, Browne, J. Am. Chem. Soc. 58, 2410-2413 (1936). (35) Michel, Bull. soc. chim. Belg. 48, 138 (1939). (36) Sameshima, Hiramatsu, Bull. Chem. Soc. Japan 9, 260-262 (1934). (37) Sapgir, Bull. soc. chim. Belg. 38, 401-402 (1929). (38) Wroczynski, Guye, J. chim. phys. 8, 201-203 (1910). (39) Kanolt, Sci. Papers U.S. Bur. Standards 20, 619-633 (1926). (40) Henning, Ann. Physik (4) 43, 292-294 (1914).
- (41) Keyes, Townshend, Young, J. Math. Phys. 1, 306, 310 (1922). (42) Smits, Berckmans. Proc. Acad. Sci. Amsterdam 21, 401-404 (1919); C.A. 13, 1175 (1919). (43) Davies, Evans, Whitehead, J. Chem. Soc. 1939, 645. (44) Conrad, Hall, J. Am. Chem. Soc. 57, 863-866 (1935). (45) Scatchard, Raymond, J. Am. Chem. Soc. 60, 1279 (1938). (46) Graffinder, Heymann, Z. Physik 72, 756 (1931). (47) Earp, Glasstone, J. Chem. Soc. 1935, 1709-1723. (48) Goss, J. Chem. Soc. 1940, 758. (49) Zawidski, Z. physik. Chem. 35, 147 (1900). (50) Williams, Daniels, J. Am. Chem. Soc. 46, 907 (1924).
- (51) Harris, J. Chem. Soc. 127, 1063-1064 (1925). (52) Hubbard, Z. physik. Chem. 74, 221-224 (1910). (53) Kanonnikoff, J. prakt. Chem. (2) 31, 352-353 (1885). (54) Brühl, Schröder, 224 (1910). (53) Kanonnkon, J. prakt. Chem. (2) 31, 352-353 (1885). (54) Brull, Schröder, Z. physik. Chem. 51, 520 (1905). (55) Beythien, Hennicke, Pharm. Zentralhalle 48, 1006 (1907). (56) Gladstone, J. Chem. Soc. 59, 293 (1891). (57) Stock, Stiebler, Ber. 56, 1089 (1923). (58) Drucker, Jiméno, Kangro, Z. physik. Chem. 90, 529 (1915). (59) Smyth, Morgan, J. Am. Chem. Soc. 50, 1554 (1928). (60) Gillo, Ann. chim. (11) 12, 303-326 (1939). (61) Hrynakowski, Szmyt, Z. physik. Chem. A-182, 405-412 (1938). (62) Grünert, Z. anorg. allgem. Chem. 164, 257 (1927). (63) Evans, Ind. Eng. Chem., Anal. Ed. 8, 206-208 (1936). (64) Gibby, Hall, J. Chem. Soc. 1931, 691-693. (65) Staverman, Rec. trav. chim. 60, 836-841 (1941).
- (66) Maxted, Moon, Trans. Faraday Soc. 32, 769-775 (1936). (67) Bell, J. Chem. Soc. 1931,

1376-1377. (68) Hamai, Science Repts. Tohoku Imp. Univ. (1) 25, 357-363 (1936); Cent. 1936, II 3784. (69) Howland, Miller, Willard, J. Am. Chem. Soc. 63, 2807-2811 (1941). (70) Hamai, Science Repts. Tohoku Imp. Univ. (1) 25, 344-356 (1936); Cent. 1936, II 3783.

(71) Grimbert, Malmy, Poirot, J. pharm. chim. (7) 29, 5-9 (1924); C.A. 18, 1413 (1924). (72) Malmy, J. pharm. chim. (8) 4, 111-114 (1926); C.A. 20, 3599 (1926). (73) Arctowski, Z. anorg. Chem. 11, 276 (1896). (74) Margosches, Hinner, Friedmann, Z. anorg. allgem. Chem. 137, 81-90 (1924). (75) Eugen Chirnoaga, Eugenia Chirnoaga, Z. anorg. allgem. Chem. 218, 273-300 (1934). (76) Brull, Ellerbrock, Z. anorg. allgem. Chem. 217, 353-366 (1933). (77) Gross, Simmons, Trans. Am. Inst. Chem. Engrs. 40, 121-141 (1944); C.A. 38, 3166 (1944). (78) Fischer, Pfleiderer, Z. anorg. allgem. Chem. 124, 61-69 (1922); Ges. Abhandl. Kenntnis Kohle, 5, 569-575 (1920). (79) Williams, Chem. News 122, 62 (1921); C.A. 15, 1113 (1921). (80) Just, Z. physik. Chem. 37, 354 (1901).

(81) Kunerth, Phys. Rev. (2) 19, 517 (1922).
(82) Chancel, Parmentier, Compt. rend. 100, 25 (1885).
(83) Timmermans, Bull. soc. chim. Belg. 37, 413-420 (1928).
(84) Wyatt, Trans. Faraday Soc. 25, 43-48 (1929).
(85) Smyth, Morgan, J. Am. Chem. Soc. 50, 1555 (1928).
(86) Leslie, Geniesse, Ind. Eng. Chem. 18, 590-596 (1926).
(87) Gordon, J. Am. Pharm. Assoc. 20, 15-17 (1930); C.A. 25, 4358 (1931).
(88) Wyatt, Trans. Faraday Soc. 25, 48-53 (1929).
(89) Zellhoefer, Copley, Marvel, J. Am. Chem. Soc. 60, 1343-1345 (1938).
(90) Kaplan, Monakhova, J. Gen. Chem. (U.S.S.R.), 7, 2499-2512 (1937); Cent. 1938, II 1572; C.A. 32, 2404 (1938).

(91) Verstraete, Bull. soc. chim. Belg. 43, 520-527 (1934).
(92) Kireev, Skvortsova, J. Phys. Chem. (U.S.S.R.) 7, 63-70 (1936); Cent. 1937, II 755; C.A. 31, 25 (1937).
(93) Kireev, Monakhova, J. Phys. Chem. (U.S.S.R.) 7, 71-76 (1936); Cent. 1937, II 755; C.A. 31, 25 (1937).
(94) van de Vloed, Bull. soc. chim. Belg. 48, 259 (1939).
(95) Litvinov, J. Phys. Chem. (U.S.S.R.)
14, 782-788 (1940); C.A. 36, 3998 (1942).
(96) van Klooster, J. Am. Chem. Soc. 35, 147 (1913).
(97) Hirshberg, Bull. soc. chim. Belg. 41, 182-184 (1932).
(98) Hand, J. Phys. Chem. 34, 1961-2000 (1931).
(99) Tarasenkov, Paulsen, Acta Physicochim. (U.R.S.S.) 11, 75-86 (1939).
(100) Brancker, Hunter, Nash, J. Phys. Chem. 44, 683-698 (1940).

(101) Bancroft, Hubard, J. Am. Chem. Soc. 64, 347-353 (1942). (102) Treybal, Ind. Eng. Chem. 36, 875-881 (1944). (103) Ewell, Welch, Ind. Eng. Chem. 37, 1224-1231 (1945). (104) Litvinov, Kozakevich, Zavodskaya Lab. 10, 43-46 (1941); C.A. 35, 5009-5010 (1941). (105) Reinders, de Minjer, Rec. trav. chrm. 59, 392-406 (1940). (106) Wright, Thompson, Leon Proc. Roy. Soc. (London) 49, 183-190 (1891). (107) Brancker, Hunter, Nash, Ind. Eng. Chem. 33, 880-884 (1941). (108) Hunter, Ind. Eng. Chem. 34, 963-970 (1942). (109) Ewell, Harrison, Berg, Ind. Eng. Chem. 36, 871-875 (1944). (110) Ryland, Am. Chem. J. 22, 390 (1899).

(111) Lecat, "L'Azeotropisme" (1918).
(112) Tyrer, J. Chem. Soc. 101, 1104-1113 (1912).
(113) Kireev, Sitnikov, J. Phys. Chem. (U.S.S.R.) 15, 492-499 (1941); C.A. 36, 6404 (1942).
(114) Redlich, Schutz, J. Am. Chem. Soc. 66, 1007-1011 (1944).
(115) Lecat, Ann. soc. sci. Bruzelles 48-B, I 54 (1928); Cent. 1928, II 854.
(116) de Kolossowsky, Alimow, Bull. soc. chim.
(5) 2, 688 (1935).
(117) Soday, Bennett, J. Chem. Education 7, 1336-1340 (1930).
(118) Lewis, Murphree, J. Am. Chem. Soc. 46, 7 (1924).
(119) de Landsberg, Bull. soc. chim. Belg. 49, 72-76 (1940); C.A. 35, 1283 (1941).
(120) Litvinov, J. Phys. Chem. (U.S.S.R.) 14, 562-570 (1940); C.A. 35, 2046 (1941).

(121) Levy, Ind. Eng. Chem. 33, 931 (1941). (122) Johnston, Pigford, Trans. Am. Inst. Chem. Engrs. 38, 25-51 (1942); C.A. 36, 1809 (1942). (123) Rosanoff, Bacon, White, J. Am. Chem. Soc. 36, 1814, 1822 (1914). (124) Miller, Bull. soc. chim. Belg. 53, 97-106 (1944); C.A. 40, 4565 (1946). (125) Robinson, Wright, Bennett, J. Phys. Chem. 36, 658-663 (1932). (126) Bates, Hazzard, Palmer, Ind. Eng. Chem. 33, 374-375 (1941). (127) Hutchinson, Trans. Faraday Soc. 41, 87-90 (1945). (128) Spencer, Flannagan, J. Am. Chem. Soc. 64, 2511-2513 (1942). (129) Vold, J. Am. Chem. Soc. 57, 1192-1195 (1935). (130) Harand, Monatsh. 65, 153-184 (1935).

(131) Centnerszwer, Lazniewski, Z. physik. Chem. A-169, 263-265 (1932). (132) Driver, Firth, J. Chem. Soc. 121, 2409-2414 (1922). (133) Alekseevskii, Zhur. Prikladnoi Khun. 1, 182-184 (1928); Cent. 1929, II 708; C.A. 23, 4390 (1929). (134) Alekseevskii, J. Russ. Phys. Chem. Soc. 55, 403-432 (1924); Cent. 1925, II 642; C.A. 20, 2609 (1926). (135) Alekseevskii, Musin, J. Applied Chem. (U.S.S.R.) 12, 704-719 (1939); C.A. 34, 2652 (1940). (136) Pearce, Reed, J. Phys. Chem. 35, 905-914 (1931). (137) Pearce, Johnstone, J. Phys. Chem. 34, 1260-1279 (1930). (138) Pearce, McKinley, J. Phys. Chem. 32, 360-379 (1938). (139) Tryhorn, Wyatt, Trans. Faraday Soc. 22, 134-138 (1926); Cent. 1926, II 1518; C.A. 20, 1545 (1926). (140) Coolidge, J. Am. Chem. Soc. 48, 596-627 (1924).

(141) Lamb, Coolidge, J. Am. Chem. Soc. 42, 1146-1170 (1920). (142) Migal, J. Gen. Chem. (U.S.S.R.) 5, 197-210 (1935); Cent. 1936, I 1590; C.A. 29, 5006 (1935). (143) Drucker, Ullmann, Z. physik. Chem. 74, 593-594 (1910). (144) Drucker, Z. Elektrochem. 16, 697 (1910). (145) Isselstein, Physik. Z. 29, 877 (1928). (146) Perry, J. Phys. Chem. 29, 1462-1468 (1925). (147)

Munro, Johnson, Ind. Eng. Chem. 17, 88-92 (1925). (148) Grimm, Raudenbusch, Wolff. Z. angew. Chem. 41, 106 (1928). (149) Palmer, Clark, Proc. Roy. Soc. (London) A-149, 375 (1935). (150) Perry, Ind. Eng. Chem. 19, 746-748 (1927).

(151) Chambers, King, J. Chem. Soc. 1940, 162. (152) Harbard, King, J. Chem. Soc. 1940, 19-29. (153) Higuti, Bull. Inst. Phys. Chem. Research (Tokyo) 18, 675-684 (1939); C.A. 34, 4959 (1940). (154) Nikitin, Yur'ev, J. Russ. Phys.-Chem. Soc. 61, 1029-1034 (1929); Cent. 1936, I 347; C.A. 24, 539 (1930). (155) Engel, Coull, Trans. Am. Inst. Chem. Engrs. 38, 947-965 (1942); C.A. 37, 16 (1943). (156) Stewart, Anesthesiology 2, 635-640 (1941); C.A. 36, 865 (1942). (157) Thelander, Med. J. Australia 27, 683-688 (1940). (158) Kunnemann, Deut. tierdrztl. Wochschr. 39, 621-622 (1931); Cent. 1931, II 3074. (159) Speter, Schmerz, Narkose-Anaesthesie 4, 261-264 (1931); Cent. 1932, I 2922. (160) Speter, Chem. Ztg. 55, 781-782 (1931); 56, 742-743 (1932): Pharm. Zentralhalle 72, 628-630 (1931).

(161) Cohen, Pharm. Weekblad 69, 363-368 (1932). (162) Liberalli, Rev. soc. brasil. chim. 2 379-384 (1931). (163) Sayers, Dalla Valle, Yant, Ind. Eng. Chem. 26, 1251-1255 (1934). (164) von Oettingen, J. Ind. Hyg. Toxicol. 19, 360-371 (1937). (165) Pestemer, Gubitz, Naturwissenschaften 22, 504-509 (1934). (166) Darzens, Mém. poudres 25, 437-439 (1932/33); Cent. 1934, II 2925; C.A. 28, 5671 (1934). (167) Malyaroff, Matskiewitsch, Mikrochemie 13, 85-90 (1933). (168) L. Givaudan and Cie, French 801,532, Aug. 6, 1936; Cent. 1936, II 3455; C.A. 31, 511 (1937). (169) Benedetti-Pichler, Schneider, Z. anal. Chem. 86, 69-80 (1931). (170) Webb, Kay, Nichol, J. Ind. Hyg. Toxicol. 27, 249-255 (1945).

(171) Frehden, Fürst, Mikrochim. Acta 3, 133-135 (1938). (172) Ware, Chemist and Druggist 123, 282 (1935); C.A. 30, 983 (1936). (173) Schwarz, Z. anal. Chem. 27, 668-669 (1888). (174) Weber, Chem. Zig. 57, 836 (1933); Cent. 1933, II 3889; C.A. 28, 727 (1934). (175) Weber, Chem. Ztg. 61, 807-808 (1937); Cent. 1938, I 950; C.A. 32, 74 (1938). (176) Rozeboom, Pharm. Weekblad 72, 689 (1935); Cent. 1935, II 2096; C.A. 29, 5386 (1935). (177) Schoorl, Pharm. Weekblad 72, 751 (1935); Cent. 1935, II 3954; [C.A. 29, 5986 (1935)]. (178) Hofmann, Ber. 3, 767 (1870). (179) Beyer, Biochem. Z. 302, 287-293 (1939), C.A. 34, 3203 (1940). (180) Treadwell, Zurcher, Helv. Chim. Acta 22, 1371-1380 (1939).

(181) Smyth, Ind. Eng. Chem., Anal. Ed. 8, 379 (1936). (182) Olsen, Smyth, Ferguson, Scheflan, Ind. Eng. Chem., Anal. Ed. 8, 260-263 (1936). (183) 'Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," 6th Ed., 710-711 (1945). (184) Winteringham, J. Soc. Chem. Ind. 61, 186-187 (1942); C.A. 37, 1951 (1943). (185) Fabre, Ann. pharm. franc. 2, 108-115 (1944); C.A. 40, 5087 (1946). (186) Thomas, Ivie, Abersold, Hendricks, Ind. Eng. Chem., Anal. Ed. 15, 287-290 (1943). (187) Winteringham, J. Soc. Chem. Ind. 61, 190-192 (1942); C.A. 37, 1951 (1943). (188) Matchett, J. Assoc. Official Agr. Chem. 22, 761-764 (1939). (189) Roberts, Murray, Am. J. Pharm. 101, 654-657 (1929); C.A. 24, 916-917 (1930). (190) Matchett, J. Assoc. Official Agr. Chem. 14, 360-367 (1931).

(191) Kunke, J. Assoc. Official Agr. Chem. 12, 264-276 (1929). (192) Kulkarni, Indian J. Med. Research 32, 189-195 (1944); C.A. 40, 4101 (1946). (193) Kulkarni, Current Sci. 12, 324-325 (1943); C.A. 38, 5244 (1944). (194) Habgood, Powell, Brit. J. Ind. Med. 2, 39-40 (1945): C.A. 39, 5273 (1945). (195) Ussing, Acta Physiol. Scand. 9, 214-220 (1945); C.A. 39, 5272 (1945). (196) Adams, J. Pharmacol. 74, 11-17 (1942); C.A. 36, 1343 (1942). (197) Daroga, Pollard, J. Soc. Chem. Ind. 60, 218-222 (1941); C.A. 35, 7882 (1941). (198) Gettler, Blume, Arch. Path. 11, 554-560 (1931); Cent. 1931, II 2189; C.A. 25, 4935 (1931). (199) Cole, J. Biol. Chem. 71,

173-180 (1927). (200) Moffitt, Analyst 58, 2-4 (1933).

(201) Thouvenin, Ann. chim. anal. 26, 72 (1944); C.A. 40, 1117 (1946). (202) Fabre, Brard, J. pharm. chim. (8) 19, 5-14 (1934); Cent. 1934, I 3627; C.A. 28, 3841 (1934). (203) Francois, J. pharm. chim. (8) 19, 383-385 (1934); Cent. 1934, II 1502; C.A. 28, 4537 (1934). (204) Caron, Raquet, Flouquet, Produits pharm. 1, 224-226 (1946); C.A. 40, 5877 (1946). (205) Beal, Szalkowski, J. Am. Pharm. Assoc. 22, 223-227 (1933); Cent. 1933, I 3753; C.A. 27, 3897 (1933). (206) de Carvalho, Rev. quim. farm. 1, 136-137 (1936); Cent. 1937, II 1617; not in C.A. (207) Höst-Madsen, J. pharm. chim. (8) 21, 246-247 (1935); Cent. 1935, II 1216; C.A. 29, 4899 (1935). (208) Ciogolea, J. pharm. chim. (8) 19, 377-383 (1934); Cent. 1934, II 1502; C.A. 28, 4537 (1934). (209) Sivadjian, J. pharm. chim. (8) 9, 434-437 (1929); Cent. 1929, II 1830; C.A. 23, 5544 (1929). (210) Anger, Wang, Mikrochim. Acta 3, 24-26 (1938).

(211) Rosenthaler, Pharm. Acta Helv. 12, 6-7 (1937); Cent. 1937, I 3828; C.A. 31, 2358 (1927). (212) Allport, Analyst 56, 706-710 (1931). (213) Olsen, Ferguson, Sabetta, Scheffan, Ind. Eng. Chem., Anal. Ed. 3, 189-191 (1931). (214) Ullmann, "Enzyklopädie der technischen Chemie," 2nd revised ed. 3, 361-370 (1929). (215) Geuther, Ann. 107, 214-217 (1858). (216) Coupin, J. pharm. chim. (6) 3, 314-315 (1896); Cent. 1896, II 15; cf. Cent. 1896, I 362. (217) Smith, U.S. 753,325, March 1, 1904; not in either Cent. or C.A. (218) Coleman, Hadler (to Dow Chem. Co.), U.S. 2,095,240, Oct. 12, 1937; Cent. 1938, I 1218; C.A. 31, 8549 (1937). (219) Coleman, Hadler, Zuckermandel (to Dow Chem. Co.), U.S. 2,104,703, Jan. 4, 1938; Cent. 1938, I 3387; C.A. 32, 1718 (1938). (220) Soc. Chim. des Usines du Rhône, Ger. 416,014, July 7, 1925: French 586,006, Mar. 13, 1925; Cent. 1925, II 1795; not in C.A.

(221) Byers, van Ardsel, U.S. 1,534,027, April 21, 1925; Cent. 1925, II 91; [C.A. 19, 1667 (1925)]. (222) Richter, van Ardsel (to Brown Co.), U.S. 1,535,378, April 28, 1925; Cent. 1925, II 1223-1224; [C.A. 19, 1825 (1925)]. (223) Levine (to du Pont Co.), U.S. 1,975,727, Oct. 2, 1934; Cent. 1935, I 1934; [C.A. 28, 7268 (1934)]. (224) Croco (to Kinetic Chemicals, Inc.), U.S. 1,994,035, March 12, 1935; Cent. 1935, II 2580, [C.A. 29, 2974 (1935)]. (225) Griffith, Hunter, J. Chem. Soc. 125, 463 (1924). (226) Nicodemus, J. prakt. Chem. (2) 83, 312-322 (1911). (227) Böesseken, van der Scheer, de Voogt, Rec. trav. chim. 34, 78-95 (1915). (228) Carlisle (to du Pont Co.), U.S. 1,915,354, June 27, 1933; Cent. 1933, II 2503; C.A. 27, 4252 (1933). (229) Consortium für Elektrochemische Industrie, Ger. 339,914, Aug. 19, 1921; Cent. 1921, IV 910; not in C.A.: Ger. 347,460, Jan. 18, 1922; Cent. 1922, II 1110; not in C.A. (230) Orndorff, Jessel, Am. Chem. J. 10, 363-367 (1888).

(231) Baril, J. Chem. Education 17, 565-566 (1940). (232) Teeple, J. Am. Chem. Soc. 26, 536-543 (1904). (233) Tscherbakow, Russ. 7181, Dec. 31, 1928; Cent. 1930, II 132; not in C.A. (234) Feyer, Z. Elektrochem. 25, 115 (1919). (235) Fuson, Bull, Chem. Revs. 15, 275-309 (1934). (236) Aston, Newkirk, Dorsky, Jenkins, J. Am. Chem. Soc. 64, 1413-1416 (1942). (237) Ssuknewitsch, Tschilingarjan, Ber. 68, 1210-1216 (1935); 69, 1537-1542 (1936). (238) Fichter, Ruegg, Helv. Chim. Acta 20, 1578-1590 (1937). (239) Harris, Sherrard, Mitchell, J. Am. Chem. Soc. 56, 892 (1934). (240) Ramsay, Young, Jahresber. 1886, 620.

(241) Löb, Z. Elektrochem. 7, 903-921 (1901). (242) Joist, Lob, Z. Elektrochem. 11, 938-944 (1905). (243) Besson, Compt. rend. 116, 102-103 (1893). (244) Conduché, Compt. rend. 158, 1182 (1914). (245) Renz, Ber. 39, 249-250 (1906). (246) Lessig, J. Phys. Chem. 36, 2325-2337 (1932). (247) Herndon, Reid, J. Am. Chem. Soc. 50, 3070, 3073 (1928). (248) Verhoek, Trans. Faraday Soc. 31, 1525-1526 (1935). (249) Tarczynski, Z. Elektrochem. 22, 252-254 (1916). (250) Ref. 1, pp. 281-288, 362-364.

(251) Schoorl, van den Berg, Pharm. Weekblad 43, 8-10 (1906); Cent. 1906, I 442. (252) Schoorl, van den Berg, Pharm. Weekblad 42, 877-888 (1905); Cent. 1905, II 1623. (253) Moosler, Monatsh. 29, 573-581 (1908). (254) Hill, J. Am. Chem. Soc. 54, 32-40 (1932). (255) Chatterji, Dhar, Z. anorg. allgem. Chem. 191, 155-160 (1930). (256) Clover, J. Am. Chem. Soc. 45, 3133-3138 (1923). (257) Chapman, J. Am. Chem. Soc. 57, 419-422 (1935). (258) Chapman, J. Am. Chem. Soc. 57, 416-419 (1935). (259) Schumacher, Sundhoff, Z. physik. Chem. B-34, 300-308, (1936). (260) Schumacher, Wolff, Z. physik. Chem. B-26, 453-462 (1934).

(261) Harteck, Kopsch, Z. physik. Chem. B-12, 345-346 (1931). (262) Ref. 1, pp. 364-370. (263) Dewar, Cranston, Zeit. fur Chemie 1869, 734. (264) Emmerling, Lengyel, Ann. Suppl. 7, 101-103 (1870). (265) Biesalski, Z. angew. Chem. 37, 314-317 (1924). (266) Senderons, Aboulenc, Compt. rend. 202, 1548-1550 (1936). (267) Milbauer, Chem. Obzor 12, 57-62 (1937), Cent. 1937, II 1507; C.A. 31, 6093 (1937). (268) Mazurs, Z. anorg. allgem. Chem. 249, 278-280 (1942). (269) Armstrong, Ber. 2, 712-713 (1869); 3, 731 (1870); J. prakt. Chem. (2) 1, 249-250 (1870). (270) Harries, Ann. 343, 340 (1905).

(271) Erdmann, Ann. 362, 147-148 (1908). (272) Huff, U.S. Bur. Mines, Rept. Investigations 3794 (1945); C.A. 39, 1293 (1945). (273) Jorissen, Ongkiehong, Rec. trav. chim. 45, 636-637 (1926). (274) Greene, Jahresber. 1879, 490. (275) Bachrach, Oel-u. Fett- Ind. 10, No. 4, 42 (1934); Cent. 1935, II 1872; not in C.A. (276) Perkin, Zent. für Chemie 1868, 714. (277) Perkin, Chem. News 18, 106 (1868). (278) Thorpe, J. Chem. Soc. 37, 194 (1880). (279) Stock, Stiebler, Ber. 56, 1091 (1923). (280) Sabanejew, Ber. 9, 1810 (1876).

(281) Lieben, Zeit. für Chemie 1868, 712. (282) Fromherz, Schneller, Z. physik. Chem. B-26, 158-160 (1933). (283) Simons, Bond, McArthur, J. Am. Chem. Soc. 62, 3478-3479 (1940). (284) Osborne, Garner, Doescher, Yost, J. Am. Chem. Soc. 63, 3486-3499 (1941). (285) Benning, McHarness, Ind. Eng. Chem. 32, 497-499 (1940). (286) Benning, McHarness, Ind. Eng. Chem. 32, 814-816, 980 (1932). (287) Benning, McHarness, Ind. Eng. Chem. 32, 698-701 (1932). (288) Seger, Die Chemie 1942, 58-59. (289) Miller, J. Am. Chem. Soc. 62, 341-344 (1940). (290) Regnault, Ann. 33, 332-334 (1840).

(291) Gault, Truffault, Compl. rend. 179, 467 (1924). (292) Schumacher, Wolff, Z. physik. Chem. B-25, 161-176 (1934). (293) Schwab, Heyde, Z. physik. Chem. B-8, 147-158 (1930). (294) Schwab, Heyde, J. Phys. Chem. (U.S.S.R.) 2, 460-467 (1931); Cent. 1933, 1 20; not in C.A. (295) Taylor, Hanson, J. Chem. Phys. 7, 418-425 (1939). (296) S. S. Bhatnagar, N. A. Yajnik, P. L. Kapur, A. S. Bhatnagar, J. Indian Chem. Soc. 18, 350-358 (1941). (297) Aschan, Cent. 1919, I 220; C.A. 13, 2868 (1919). (298) Friedel, Silva, Bull. soc. chim. (2) 17, 537-539 (1872). (299) Dehn, J. Am. Chem. Soc. 31, 1225-1226 (1909). (300) Kharasch, Brown, J. Am. Chem. Soc. 51, 2144-2145 (1939).

(301) Paterno, Bull. soc. chim. (2) 17, 212 (1872). (302) LeCompte, Volkringer, Tchakirian, Compt. rend. 204, 1927-1928 (1937). (303) Braunwarth, Schumacher, Kolloid-Z. 89, 184-194 (1939); C.A. 34, 942 (1940). (304) Willard, Daniels, J. Am. Chem. Soc. 57, 2240-2245 (1935). (305) Schwab, Lober, Z. physik. Chem. A-186, 321-331 (1940). (306) Simons, Sloat, Meunier, J. Am. Chem. Soc. 61, 435-436 (1939). (307) Schumacher, Z. physik. Chem. B-42, 324-326 (1939). (308) Vesper, Rollefson, J. Am. Chem. Soc. 56, 1455-1461 (1934). (309) Franke, Schumacher, Z. physik. Chem. B-42, 297-323 (1939). (310) Besson, Bull. soc. chim. (3) 9, 174-175 (1880).

(311) Mills, J. Chem. Soc. 9, 641-642 (1871); Ann. 160, 117-120 (1871). (312) Pictet, Khotinsky, Ber. 40, 1165 (1907). (313) Trumbull, Sohl, Burt, Seaton, J. Ind. Eng. Chem. 12, 1068 (1920). (314) Trumbull, Seaton, Durham, J. Ind. Eng. Chem. 12, 1068-1069 (1920). (315) Prandtl, Sennewald, Ber. 62, 1754-1768 (1929). (316) Prandtl, Dollfus, Ber. 65, 754-759 (1932). (317) Vorlander, Guthke, Ber. 62, 549-554 (1929). (318) André, Jahresber. 1886, 627. (319)

Dumas, Ann. chim. (2) 56, 120 (1834). (320) Geuther, Ann. 123, 121-122 (1862).

(321) Desgrez, Compt. rend. 125, 780 (1897). (322) Thiele, Dent. Ann. 302, 273-274 (1898). (323) Benrath, Ann. 382, 232-233 (1911). (324) Matuszak, Ind. Eng. Chem., Anal. Ed. 6, 374-375 (1934). (325) Saunders, J. Phys Chem. 4, 660-674 (1900). (326) P. Petrenko-Kritschenko, D. Talmud, B. Talmud, W. Butmy-de-Katzman, A. Gandleman, Z. physik. Chem. 116, 313-318 (1925). (327) Petrenko-Kritschenko, Opotzky, Ber. 59, 2132 (1926). (328) Petrenko-Kritschenko, Ber. 61, 847, Note 3 (1928). (329) Raikov, Z. angew. Chem. 30, 278-280 (1917). (330)

Kippenberger, Arch. Pharm. 238, 85-87 (1900).

(331) Böeseken, Rec. trav. chim. 22, 306-307 (1903). (332) Pouret, Compt. rend. 130, 1191 (1900); Bull. soc. chim. (3) 25, 191-193 (1901). (333) Harlow, Ross (to Dow Chem. Co.), U.S. 1,891,415, Dec 20, 1932; Cent. 1933, I 1683; [C.A. 27, 1890 (1933)]. (334) Timmermans, Martin, J. chim. phys. 25, 416-417 (1928). (335) Spindler, Ann. 231, 263-264 (1885) (336) Berthelot. Ann. chm. (3) 51, 57 (1857). (337) Ruff, Ber. 69, 301-303 (1936). (338) Davis, McLean J. Am. Chem. Soc. 60, 720-722 (1938). (339) Staudinger, Z. Elektrochem. 31, 549-552 (1925). (340) Staudinger, Z. angew. Chem. 35, 658-659 (1922).

(341) Lenze, Metz, Z. ges. Schiess- u. Sprengstoffw. 27, 255-258, 293-296, 337-340, 373-376 (1932). (342) Saffer, Davis, J. Am. Chem. Soc. 67, 641-645 (1945) (343) von Hartel, Meer, Polanyi, Z. physik. Chem. B-19, 139-163 (1932). (344) Clogston, Underwriter's Lab., Bull. Research No. 34, 5-15 (1945), C.A. 40, 210 (1946). (345) Staub, Ann. chim. (12) 1, 105-156 (1946). (346) Tseng, Natl. Cent. Univ. (Nanking) Sci. Repts. A-1, No. 2, 1-4 (1931); Cent. 1938, 1 53; C.A. 26, 2166 (1932). Trans. Sci. Soc. China 7, 233-237 (1932). (347) Dieterle, Eschenbach, Ger. 537,610, Nov. 6, 1931; Cent. 1932, I 1155-1156; [C.A. 26, 1300 (1932)]. (348) Theobald (to du Pont Co.), U.S. 2,378,048, June 12, 1945; C.A. 39, 4085 (1945). (349) Kharasch, Jensen. Urry, Science 102, 128 (1945). (350) Schwarz, Ber. 14, 1516-1520 (1881).

(351) Friedel, Crafts, Ann. chim. (6) 1, 489-497 (1884); Bull. soc. chim. (2) 37, 6-11 (1882). (352) Allen, Kölliker, Ann. 227, 107-109 (1885). (353) Biltz, Ber. 26, 1960-1962 (1893). (354) Meissel, Bcr. 32, 2422-2423 (1899). (355) Chakrabarty, Dutt, J. Indian Chem. Soc. 5, 516 (1928).

(356) Ray, Dutt, J. Indian Chem. Soc. 5, 108 (1928). (357) Soroos, Hinkamp, J. Am. Chem. Soc. 67, 1642 (1945). (358) Forbes, Anderson, J. Am. Chem. Soc. 67, 1911-1914 (1945). (359) Heilbron, Hislop, Irving, J. Chem. Soc. 1936, 782-783. (360) Prins, Engelhaid, Rec. trav. chim.

54, 307-312 (1935).

(361) Prins, J. prakt. Chem. (2) 89, 415, 417, 421 (1914). (362) Prins, Ger. 261,689, July 2, 1913; Cent. 1913, II 394, [C.A. 7, 3641 (1913)]. (363) Farlow, Org. Syntheses Coll. Vol. 2 (1st ed.), 312-313 (1943); 17, 58-59 (1937). (364) Prins, Rec. trav. chim. 54, 249-252 (1935). (365) Ref. 361, pp. 414-415, 424 (1914). (366) Henne, Ladd, J. Am. Chem. Soc. 60, 2494 (1938). (367) Prins, Rec. trav. chim. 57, 659, 662, Note (1938). (368) Boeseken, Prins, Cent. 1911, I 466. (369) Prins, Rec. trav. chim. 51, 1065-1080 (1932). (370) Böeseken, van der Scheer, de Voogt, Rec. trav. chim. 34, 78-95 (1915).

(371) Bruson, Niederhauser, Riener, Hester, J. Am. Chem. Soc. 67, 601 (1945). (372) Niederhauser, Bruson (to Resinous Products and Chem. Co.), U.S. 2,379,097, June 26, 1945, C.A. 39. 4618 (1945). (373) I.G., French 793,731, Jan. 30, 1936; Cent. 1936, I 4074; [C.A. 30, 4514 (1936)]. (374) Sah, Ma, J. Am. Chem. Soc. 54, 2964-2966 (1932). (375) Deutsch, Ber. 12, 115-119 (1879). (376) Kaufmann, Dreger, Org. Syntheses Coll. Vol. 1 (2nd ed.), 258-261 (1941); (1st ed.), 253-256 (1932); 5, 55-58 (1925). (377) Chu, Shen, J. Chinese Chem. Soc. 10, 124-125 (1943); C.A. 38, 2930 (1944). (378) Post, Erickson, J. Am. Chem. Soc. 55, 3851-3854 (1933). (379) Post, "The Chemistry of Aliphatic Orthoesters," A.C.S. Monograph Series, No. 92 (1943). (380) Houben, Schultze, Ber. 44, 3235-3241 (1911).

(381) Backer, Stedehouder, Rec. trav. chim. 52, 440 (1933). (382) Gabriel, Ber. 10, 185-187 (1877). (383) Claesson, J. prakt. Chem. (2) 15, 176 (1877). (384) Post, J. Org. Chem. 5, 247 (1940). (385) Holmberg, Ber. 45, 364-365 (1912). (386) Holmberg, Ber. 40, 1740-1743 (1907).
(387) Houben, Ber. 45, 2942-2946 (1912). (388) Reimer, Tiemann, Ber. 9, 824-828, 1268-1278 (1876). (389) Sen, Ray, J. Indian Chem. Soc. 9, 173-179 (1932). (390) Armstrong, Richardson, J. Chem. Soc. 1933, 496-500.

(391) Hodgson, Jenkinson, J. Chem. Soc. 1927, 1740-1742. (392) Hodgson, Jenkinson, J. Chem. Soc. 1927, 3041-3044. (393) Hodgson, Jenkinson, J. Chem. Soc. 1929, 469-471. (394) Hodgson, Nixon, J. Chem. Soc. 1929, 1632-1639. (395) Hodgson, Jenkinson, J. Chem. Soc. 1929, 1639-1642. (396) Blume, Lindwall, J. Org. Chem. 10, 255-258 (1945). (397) Ochiai, Nagasawa, Ber. 72, 1470-1476 (1939). (398) Russell, Lockhart, Org. Syntheses 22, 63-64 (1942) (399) Arnold, Zaugg, Sprung, J. Am. Chem. Soc. 63, 1314-1316 (1941). (400) Auwers, Keil, Ber. 36, 1861-1867 (1903).

(401) Hodgson, J. Soc. Dyers Colourists 46, 39-44 (1930). (402) Gilman, Arntzen, J. Org. Chem. 10, 374-379 (1945). (403) Baines, Driver, J. Chem. Soc. 125, 907-908 (1924). (404) Auwers, Ber. 18, 2656-2657 (1885). (405) Tiemann, Ber. 15, 2685-2687 (1882). (406) Howard, J. Am. Chem. Soc. 47, 455-456 (1925). (407) Iozitsch, J. Russ. Phys.-Chem. Soc. 29, 97-103 (1897); Cent. 1897, I 1013-1014. (408) Rapson, Saunders, Stewart, J. Chem. Soc. 1944, 74-75. (409) Chattaway, Muir, J. Chem. Soc. 1934, 701-703. (410) Florence, Bull. soc. chm. (4) 49, 926-927 (1931).

(411) Howard, Castles, J. Am. Chem. Soc. 57, 376-377 (1935). (412) Howard, Stephens, J. Am. Chem. Soc. 60, 228-229 (1938). (413) Howard, J. Am. Chem. Soc. 57, 2317-2318 (1935). (414) Sah, Lei, Ma, Sci. Repts. Natl. Tsing Hua Univ. A-1, 209-214 (1932); Cent. 1932, II 3543-3544; C.A. 26, 5907 (1932). (415) Taffe, Roczniki Farm. 2, 99-107 (1923); Cent. 1924, II 304; C.A. 18, 2328 (1924). (416) Fisburn, Watson, J. Am. Pharm. Assoc. 28, 491-493 (1939); Cent. 1939, II 4464; C.A. 33, 9283 (1939). (417) Willgerodt, Ber. 14, 2451-2458 (1881). (418) Heilner (to Chem. Fabrik Dr. J. Wiernik and Co.), Ger. 515,539, Jan. 13, 1931; Cent. 1931, I 2394; C.A. 25, 2436 (1931). (419) Ekeley, Klemme, J. Am. Chem. Soc. 46, 1252-1254 (1924). (420) Howard, J. Am. Chem. Soc. 48, 774 (1926).

(421) Garland, Welch, J. Am. Chem. Soc. 53, 2414-2415 (1931). (422) Hofmann, Ber. 3, 767-768 (1870). (423) Gautier, Ann. chm. (4) 17, 215-233 (1869). (424) von Auwers, Ber. 66, 2125, 2138 (1927). (425) Lowry, Henderson, Proc. Roy. Soc. (London) A-136, 485-486 (1932). (426) Wöhler, Roth, Chem. Ztg. 50, 761-763, 781-782 (1926); Cent. 1926, Il 2704; [C.A. 21, 496-497 (1927)]. (427) Lemoult, Compt. rend. 143, 902 (1906), 148, 1603 (1909). (428) Hartley, J. Chem. Soc. 1928, 780-781. (425) Coates, Hinkel, Angel, J. Chem. Soc. 1928, 543. (430) Hofmann, Ann. 106, 109 (1868).

(431) Gauthier, Ann. chim. (4) 17, 233-248 (1869). (432) Davis, Yelland, J. Am. Chem. Soc. 59, 1998 (1937). (433) Hofmann, Ann. 144, 117-120 (1867). (434) Hammick, New, Sidgwick, Sutton, J. Chem. Soc. 1930, 1876-1878. (435) Nef, Ann. 270, 274-277 (1892). (436) Meunier, Desparmet, Compt. rend. 144, 274 (1907); Bull. soc. chim. (4) 1, 343 (1907). (437) Biddle, Goldberg, Ann. 310, 7 (1900). (438) Lindemann, Wiegrebe, Ber. 63, 1656-1657 (1930). (439) Nef, Ann. 270, 309-320 (1892). (440) Nef, Ann. 270, 320-322 (1892).

(441) Smith, Am. Chem. J. 16, 373-375 (1894). (442) New, Sutton, J. Chem. Soc. 1932, 1416-1419. (443) Breuer, J. Am. Chem. Soc. 57, 2236-2237 (1935). (444) Truchet, Compt. rend. 202, 1997-1998 (1936). (445) Horiuti, Sakamoto, Bull. Chem. Soc. Japan 11, 627-628 (1936); Cent. 1937, I 562; C.A. 31, 4189 (1937).

3:5060 OXALYL (DI)CHLORIDE
$$O=C-C1$$
 $C_2O_2Cl_2$ Beil. II - 542 II_1 -(234) II_2 -(508)

B.P. M.P.
$$-10.0^{\circ}$$
 (3) $D_4^{20} = 1.4785$ (3) $n_D^{20} = 1.4316$ (3) $62.1-62.3^{\circ}$ (2) -12.0° (1) 1.480 (4) 1.4301 (4) 61.1° at 743 mm. (3) $D_4^{13.4} = 1.4484$ (4) $D_4^{12.9} = 1.4888$ (4) $n_D^{12.9} = 1.43445$ (4) 1.43395 (4) 1.43395 (4)

[See also ethoxalyl chloride (3:5625).]

Colorless liq. whose vapors strongly attack respiratory passages. — Solns. of \bar{C} in ether, CHCl₃, or alkanes are colorless, but those in phenol, anisole, thioethers, piperonal, and dipentene are yellow (5). — Note that the presence in samples of \bar{C} of phosphorous compds.

(such as might remain from the reagts, used in its prepn.) increases the refractive index (4); such contaminants may be removed by treatment with Cl_2 and subsequent fractionation (4) (7). — \bar{C} is stable to fumg. H_2SO_4 .

 \bar{C} is an important reagent in organic synthesis; its reactions may conveniently be classified under four main types, viz.: (A) those in which it reacts as an acid chloride (either one or both groups being involved); (B) those in which it acts like a mixture of $COCl_2$ (3:5000) + CO; (C) those in which it acts as a chlorinating agent; and (D) those in which it acts as a dehydrating agent. Examples of all these types will be found in the subsequent text, but naturally combinations of the distinctive types may occur simultaneously.

 $\bar{\mathbf{C}}$ is also employed in the preparation of various dyestuffs although these cannot be discussed here. [For toxicity of $\bar{\mathbf{C}}$ see (6); for protection of stopcocks from action of $\bar{\mathbf{C}}$ see (16).]

Preparation. [For prepn. of \bar{C} from anhydrous oxalic acid (1:0535) with PCl₅ (2 moles) (yields: 70% (8), 45–50% (1)) in pres. of an inert solid or liq. diluent (9) and even in units as much as 5 times the original (10), or with PCl₃ in POCl₃ in stream of Cl₂ (11), or with COCl₂ (3:5000) in pres. of tertiary amines (14) see indic. refs.; from dicthyl oxalate (1:1055) with PCl₅ (poor yields) see (12) (1) (13).]

[For prepn. of \bar{C} from COCl₂ (3:5000) + CO, or from CO + Cl₂ over suitable cat. at 200-400° and 200 atm. press., see (15).]

[For form. of \tilde{C} (19% yield (1)) from ethoxalyl chloride (3:5625) with PCl₅ in s.t. at 170° see (1).]

Pyrolysis or decomposition of \bar{C} . $[\bar{C}$ on passing through tube at 600° (1) or on htg. at 340° for 70 hrs. in an evacuated s.t. (7) dec. quant. into COCl₂ (3:5000) and CO; note, however, that at 200° \bar{C} shows no trace of phospene even after 18 hrs. (7) and at ordinary temp. (when protected from light and moisture) can be preserved indefinitely.]

 \overline{C} (1 mole) on slight warming with AlCl₃ (2 moles) in CS₂ dec. quant. (1) into phosgene (3:5000) + CO and may thus serve as a source of COCl₂ in Friedel-Crafts reactns. (see below).

C when exposed to light of any wave length below 3800 Å slowly dec., the final prods. being COCl₂ (3:5000) + CO although the initial prods. appear to include Cl₂ and CO (16); this photochemical decn. plays an important part in its use as a reagent for introduction of the —CO.Cl group (chloroformylation) (see below).

Behavior of \tilde{C} with inorganic reactants. \tilde{C} with liq. aq. or dil. aq. alk. yields quant. (1) CO + CO₂ + HCl, no trace of oxalic acid (1:0445) or of its semi-acid chloride being formed; however, \tilde{C} as vapor on treatment with steam does yield also some oxalic acid crystals (1).

 $[\bar{C}]$ in ether on treatment with dry H₂S for several hrs. is unchanged, but if quinoline (2 moles) is added, vigorous reactn, occurs (1) with evolution of gaseous CO + COS.]

[\bar{C} on treatment with HBr gas for 12 hrs. gives (85% yield (7)) (17) (18) oxalyl (di)bromide [Beil. II₁-(236), II₂-(509)], b.p. 106° (18), 102-103° at 720 mm., 16-17° at 10 mm., f.p. -19.5° (7) (for study of thermal and photochemical decn. of this prod. see (18)). — \bar{C} with HI is reduced (7) yielding CO + I₂ (cf. phosgene (3:5000)).]

 \bar{C} with 2 NaI in dry acetone yields quant. (41) CO + I₂ + 2NACl but \bar{C} with aq. NaI does not set free iodine giving instead the usual aqueous hydrolysis with formn. of CO + CO₂ + 2HCl (41).

[\overline{C} (2 moles) with As₂O₃ (1 mole) gives (95% yield {19}) AsCl₃, b.p. 130°; similarly \overline{C} with dry CrO₃ refluxed 5 hrs. gives (80% yield {19}) chromyl chloride, CrO₂Cl₂, b.p. 114–116° at 748 mm.]

 $[\tilde{C} \text{ in } C_6H_6 \text{ with } H_2 \text{ in pres. of Pd/BaSO}_4 \text{ cat. gives only gaseous products, no trace of glyoxal or glyoxylic acid being formed (20).]}$

 $\ddot{\mathbf{C}}$ in $\mathbf{C_6H_6}$ with NH₃ gas in cold reacts vigorously yielding (21) oxalic acid diamide (oxamide) [Beil. II-545, II₁-(237), II₂-(509)], m.p. above 400° (and therefore useless as derivative for identification), + NH₄Cl. — $\ddot{\mathbf{C}}$ with hydrazine hydrate (excess) presumably yields oxalic acid dihydrazide ("oxalhydrazide") [Beil. II-559, II₁-(243), II₂-(514)], m.p. 244° dec., although this method of prepn. seems to be unreported.

 $[\bar{C} \text{ with K/Na alloy is (like many halogen compds.) sensitive to detonation by mechanical shock (GREAT DANGER) cf. (22). — For behavior of <math>\bar{C}$ with other metals see (7).]

Behavior of \bar{C} with organic reactants. Reaction of \bar{C} with alkanes and cycloalkanes. [C with satd. aliphatic hydrocarbons and with cycloparaffins in pres. of light and peroxides reacts to replace 1 H atom by the —CO.Cl group (22) (10); since this group represents the radical corresponding to the unisolatable acid chloride of formic acid, the process might well be designated as "chloroformylation"; however, since the resultant prods. may readily be hydrolyzed to the corresp. carboxylic acids, the process has also (unfortunately) been designated as "carboxylation." - E.g., C (1 mole) with cyclohexane (1:8405) (2 moles) + dibenzoyl peroxide (0.005 mole) refluxed for 24 hrs. in light from low-press. Hg vapor lamp (10) or 300-watt tungsten lamp (23) gives (yields: 85% (23), 65% (10)) cyclohexanecarboxylic acid chloride (hexahydrobenzoyl chloride) (3:8580). — Note that neither simple olefins such as 2-methylbutene-2 (1:8220), octene-1 (1:8375), hexadecene-1 (cetene) (1:7000), nor cycloalkenes such as cyclohexene (1:8070) undergo this type of reactn. (24), although phenylethylene (styrene) (1:7435) gives cinnamoyl chloride (3:0330) (9% yield of cinnamic ac. after hydrolysis (24)) and phenylacetylene (1:7425) gives β -chlorocinnamoyl chloride (16% yield of β -chlorocinnamic acid after hydrolysis (24)). — Note also that C under similar conditions with aralkyl hydrocarbons chloroformylates the side chain but yields are very low (5-10%) (25)

Reactions of \tilde{C} with aromatic hydrocarbons. [\tilde{C} with aromatic hydrocarbons (R.H.) in pres. of AlCl₃ shows both (A) and (B) types of reactn. mentioned above in 2nd paragraph; on one hand (A) \tilde{C} reacts like phosgene yielding R.CO.Cl (which during the usual subsequent treatment is hydrolyzed to the corresp. acid) and ketones of the type R₂CO; on the other (B) \tilde{C} reacts with 2 PH as a bifunctional acid chloride yielding the corresp. 1,2-diketones, which with some of the polycyclic hydrocarbons comprise new cyclic systems of the quinone type. Examples of these various combinations are listed below.]

[\bar{C} with $C_6H_6+AlCl_3$ in CS_2 gives according to mode of procedure either (1) 100% yield benzoyl chloride (3:6240) or 89% yield diphenyl ketone (benzophenone) (1:5150); note that no benzil (dibenzoyl) (1:9015) is formed here although it has been obtd. (in small proportion) together with benzophenone from oxalyl (di)bromide with $C_6H_6+AlBr_3$ in CS_2 (17). — \bar{C} with toluene + AlCl₃ in CS_2 gives (65% yield (26)) p-toluic acid (1:0795). — \bar{C} with o-xylene (1:7430) + AlCl₃ in CS_2 gives (75–80% yield (27)) (26) 3,4-dimethylbenzoic acid [Beil. IX-535, IX₁-(210)], m.p. 166°, accompanied by some 3,4,3',4'-tetramethylbenzil (4,4'-o-xylil), m.p. 128.5° cor. (27); \bar{C} with m-xylene (1:7420) similarly gives (40–50% yield (26)) 2,4-dimethylbenzoic acid [Beil. IX-531, IX₁-(290)], m.p. 126°; \bar{C} similarly with p-xylene (1:7415) gives (100% yield (26)) 2,5-dimethylbenzoic acid [Beil. IX-534, IX₁-(210)], m.p. 132°. — \bar{C} with ethylbenzone (1:7410) gives (29) p-ethylbenzoic acid [Beil. IX-529], m.p. 112°.]

[\bar{C} with arom. hydrocarbons contg. two uncondensed benzene nuclei shows a distinct tendency to yield dicarboxylic acids despite the fact that the first member is exceptional. E.g., \bar{C} with biphenyl (1:7175) + AlCl₃ in CS₂ gives (30) 40% yield di-p-xenyl ketone, m.p. 236°, + 25% p-xenil, m.p. 140-141°, although the formation in 75% yield of p-phenyl-benzoic acid (p-xenoic acid) [Beil. IX-671, IX₁-(280)], m.p. 224°, has also been reported (31); for examples of dicarboxylic acid formn. from \bar{C} + AlCl₃ with 2,2'-dimethylbiphenyl (26), diphenylmethane (32), phenyl p-tolylmethane (26), di-p-tolylmethane (26), α,β -

diphenylethane (bibenzyl) (32), α,β -diphenylethylene (stilbene) (32), triphenylmethane (32), see indic. refs.]

[$\bar{\mathbf{C}}$ with polycyclic arom. hydrocarbons frequently, but not always, also gives polycyclic quinones; e.g., $\bar{\mathbf{C}}$ with naphthalene (1:7200) + AlCl₃ in CS₂ gives (35) a mixt. of α -naphthoic acid (1:0785) + β -naphthoic acid (1:0800); $\bar{\mathbf{C}}$ with 2-methylnaphthalene (1:7605) + AlCl₃ in CS₂ gives (33) a mixt. of acids + 2,2'-dimethylnaphthil + 3-methylacenaphthene-quinone-1,2; for analogous results with 1,6-, 2,6-, and 2,7-dimethylnaphthalenes see (33) (34); $\bar{\mathbf{C}}$ with anthracene + AlCl₃ in CS₂ gives (70% yield (35)) aceanthrenequinone (1,9-oxalylanthracene) [Beil. VII₁-(436)], red pr. from C₆H₆, m.p. 270°, accompanied by some anthracene-9-carboxylic acid (meso-anthroic acid).]

[For behavior of \bar{C} + AlCl₃ with 2-methylanthracene (36) (38), 1,2-dibenzanthracene (37), retene or dihydroretene (39), or fluoranthene (40) see indic. refs.; many analogous cases are known but cannot be included here.]

Reaction of \bar{C} with alcohols and thiols. [\bar{C} with 2 moles primary alcs. especially in pressof pyridine yields corresp. neutral esters: e.g., \bar{C} with MeOH (1:6120) (2 moles) gives dimethyl oxalate (1:0415), m.p. 54°; \bar{C} with EtOH (1:6130) (2 moles) gives diethyl oxalate (1:1055), b.p. 185°; for analogous behavior of \bar{C} with n-propyl alc. (1:6150) yielding di-n-propyl oxalate (1:3726), with isobutyl alc. (1:6165) yielding di-isobutyl oxalate (1:3897), with isoamyl alc. (1:6200) yielding disoamyl oxalate (1:4181) all in 100% yield see (42). — \bar{C} with secondary alcs. (2 moles) also yields (42) (50) the corresp. neutral esters, but yields are less satisfactory and the ability of \bar{C} to act as a dehydrating agent begins to become evident (42); c.g., \bar{C} with methyl-phenyl-carbinol (1:6475) yields no ester, but only phenylethylene (styrene) (1:7435). — \bar{C} with tertiary alcs. replaces OH by Cl; e.g., \bar{C} with ter-butyl alc. (1:6140) gives ter-butyl chloride (3:7045); \bar{C} with triphenylcarbinol (1:5985) gives chlorotriphenylmethane (3:3410) (42).]

[Note that \bar{C} with only 1 mole of primary alcs. yields the corresponding half esterification prods.; e.g., \bar{C} (1 mole) with EtOH (1:6130) (1 mole) gives (60% yield (43)) ethoxalyl chloride (3.5625); for other examples together with use of such oxalic ester chlorides in prepn. of cellulose esters see (43).]

[C with ethylene glycol (1:6465) (1 mole) directly (42) or in pyridine (44) or in dry ether (45) gives (57% yield (45)) monomeric ethylene glycol oxalate (2,3-dioxodioxane-1,4) [Beil. XIX-153, XIX₁-(679)], m.p. 143° (45), 149° (44), 153° (42); for relationships of this monomer to the polymeric forms see (46).]

[\bar{C} with CH₃SH (2 moles) (13) in dry ether (47) gives dimethyl dithioloxalate [Beil. II-565, II₂-(514)], yel. cryst. from ether or lgr., m.p. 82.5-83.5° (13), 80° (47), b.p. 218° at 760 mm. (47). — \bar{C} with EtSH (2 moles) (13) (48) in dry ether (1) gives diethyldithioloxalate [Beil. II-565, II₁-(244)], m.p. 27-27.5° (13), 24-25° (1), b.p. 238-240° at 757 mm. (1), 235° (13).]

Behavior of \bar{C} with phenols and thiophenols. [\bar{C} (1 mole) with phenol (2 moles) in dry ether with metallic Na (2 moles) gives (21% yield (49)) diphenyl oxalate [Beil. VI-155, VI₁-(87)], m.p. 134° u.c. (49). — \bar{C} (1 mole) with σ -cresol (1:1400) (2 moles) + Na similarly gives (49) di- σ -otolyl oxalate [Beil. VI-355], ndls. from alc., m.p. 90-91° u.c. (49); \bar{C} with σ -cresol (1:1730) similarly gives (49) di- σ -tolyl oxalate [Beil. VI-379, VI₁-(187)], ndls. from alc., m.p. 105° u.c. (49); \bar{C} with σ -cresol (1:1410) similarly (49) or in pyridine (51) gives di- σ -tolyl oxalate [Beil. VI-398, VI₁-(201)], pl. from alc. + ether, m.p. 148° (49), 147° (51); for similar behavior of still other phenols see (51).]

[Note, however, that \tilde{C} (1 mole) with phenols (1 mole) in pres. of AlCl₃ leads to monoesterification followed by elimination of HCl and ring closure; e.g., \tilde{C} (1 mole) with β -naphthol (1:1540) + AlCl₃ in CS₂ gives (85% yield (52) (53)) 4,5-benzocumarandione-2,3 [Beil. XVII₁-(267)], orange ndls. from AcOH, m.p. 180-181° (52).]

[For behavior of \bar{C} with resorcinol (1:1530) + Na or K in moist ether see (54).]

[\bar{C} with β -thionaphthol (2-mercaptonaphthalene) + AlCl₃ in CS₂ esterifies and ringcloses with loss of HCl yielding (55) 4,5-benzothiocumarandione-2,3 (4,5-benzothionaphthenequinone-2,3), red pdr., m.p. 153°. — For extension of this type of reactn. to prepn. of halogenated thionaphthisatins from \bar{C} with halogenated 1- or 2-mercaptonaphthalenes + AlCl₃ see (56+.]

[For behavior of C with dithiopyrocatechol (o-dimercaptobenzene) see (57).]

[For study of a series of molecular cpds. of C with various hydroxy-azo compds. see (58). Behavior of C with phenol ethers. [C with mononuclear phenol ethers + AlCl3 reacts in general according to types A and B of paragraph 2 (above) so that after aqueous treatment involved in destroying the AlCl₃ there results either a diketone or a carboxylic acid; which of these is formed or their proportion varies with nature of components and with conditions. E.g., C (1 mole) with ansole (methyl phenyl ether) (1:7445) (2 moles) + AlCl₃ (2 moles) in CS₂ gives (yields: 90% (59), 80% (60), 76% (17)) anisil (4,4'-dimethoxybenzil) [Beil. VIII-428, VIII₁-(705)], golden-yel. ndls. from alc., m.p. 133° (60), 132° (59); C (1 mole) with phenetole (ethyl phenyl ether) (1:7485) (2 moles) + AlCl₃ in CS₂ gives (80% yield (29)) phenetil (4,4'-diethoxybenzil), pr. from ether + alc., m.p. 149°; \overline{C} similarly with o-cresol methyl ether (1:7480) + AlCl₃ in CS₂ gives (76% yield (61)) (59) 4,4'-dimethoxy-3,3'-dimethylbenzil, pale yel. ndls. from AcOH, toluene, or pyridine, m.p. 177° (61), 174° (59). — Note, however, that \bar{C} with m-cresol methyl ether (1:7510) + AlCl₃ in CS₂ yields no diketone, but only (59) 2-hydroxy-6-methylbenzoic acid (6-methylsalicylic acid) [Beil. X-217, X₁-(95)], m.p. 168°; C with p-cresol methyl ether (1:7495) gives no diketone but only (12% yield (59)) 2-hydroxy-5-methylbenzoic acid (5-methylsalicylic acid) [Beil. X-227, X₁-(98)], m.p. 149° (59). — Many analogous cases of each type are known but cannot be included here.]

[\bar{C} with pyrocatechol dimethyl ether (veratrole) (1:7560) + AlCl₃ gives (60) 2,3,2',3'-tetramethoxybenzophenone; \bar{C} with resorcinol dimethyl ether (1:7570) gives (60) 2,4,2',4'-tetramethoxybenzophenone; \bar{C} with hydroquinone dimethyl ether (1:7160) gives (60) 2,5,2',5'-tetramethoxybenzophenone, but \bar{C} with orcinol dimethyl ether (3,5-dimethoxytoluene) + AlCl₃ gives (29) by ring closure 6-methoxy-4-methylcoumarandione-2,3, m.p. 165° (29).]

Behavior of \bar{C} with organic acids or their derivatives. [\bar{C} with silver oxalate in dry ether does not yield the unknown oxalic anhydride but instead immediately evolves CO + CO₂ until all the salt has disappeared (1).]

[C with organic acids, their salts, or their anhydrides, gives the corresp. acid chlorides in good yield (19); furthermore under appropriate conditions C with aromatic acids gives good yields (50) of the corresp. arom. anhydrides; for numerous examples see indic. refs.]

Behavior of C with amines or their derivatives. C with primary or secondary amines (2 moles) reacts normally as a bifunctional acid chloride yielding corresp. N-substituted oxamides (see also below under D's).

[Note, however, that with amine salts reaction takes a different course. — E.g., \bar{C} with aniline hydrochloride at 15° evolves HCl and gives (100% yield (62)) oxanilyl chloride, $C_6H_5.NH.CO.CO.Cl$ [Beil. XII-283, XII₁-(206)], pr. from pet. ether, m.p. 82.5°; \bar{C} with α -naphthylamine.HCl in chlorobenzene at 15° similarly yields (12) N-(α -naphthyl)oxamidyl chloride, $C_{10}H_7.NH.CO.CO.Cl$, m.p. 86° (62); \bar{C} with β -naphthylamine.HCl similarly yields (62) N-(β -naphthyl)oxamidyl chloride, ndls. from C_6H_6 , m.p. 114–115° dec. (62). — Note that these prods. with condensing agents such as AlCl₃.FeCl₃ or H_2SO_4 ring-close with loss of HCl to yield homologs of isatin: e.g., N-(α -naphthyl)oxamidyl chloride + AlCl₃ at 80–85° for 8 hrs. gives (63) 6,7-benzoisatin [Beil. XXI-524, XXI₁-(414)] ("1,2-naphthisatin"), red ndls., m.p. 255°; N-(β -naphthyl)oxamidyl chloride with AlCl₃ in

nitrobenzene at 80° gives (75-80% yield (63)) 4,5-benzoisatin ("2,1-naphthisatin") [Beil. XXI-525, XXI₁-(415)], m.p. 252-253°.]

[Note, furthermore, that the above general synthesis of isatin homologs can be carried out starting with N-acylated arom. amines: e.g., \bar{C} with Na salt of N-(p-toluenesulfonyl)-p-toluidide in CS₂ splits out NaCl giving (64) N-(p-toluenesulfonyl)-N-(p-tolyl)oxamidyl chloride, cryst. from C₆H₆, m.p. 91–93° (64); this prod. on htg. with AlCl₃ loses HCl and ring-closes to N-(p-toluenesulfonyl)-5-methylisatin, cryst. from AcOH or C₆H₆, m.p. 202–205°, hydrolysis of which by stdg. 1 day with conc. H₂SO₄ yields (64) 5-methylisatin [Beil. XXI-509, XXI₁-(401)], red ndls. from aq. or alc., m.p. 187°.]

[For analogous reactn. of \tilde{C} with secondary arom, amines and ring closure to N-substituted isatins see (65).]

·[C with N,N-dimethylaniline gives various prods. according to conditions: C (1 mole) with dimethylaniline (2 moles) in dry ether in cold gives (100% yield (66)) (p-dimethylaminobenzoyl) formyl chloride, (CH₃)₂N.C₆H₄.CO.CO.Cl, stable only in soln. and on treatment with aq. giving (80% yield (66)) (p-dimethylaminobenzoyl) formic acid, golden-yel. Ifts. from AcOH or MeOH, m.p. 186–187° dec.; C (1 mole) with dimethylaniline (4 moles) in C₆H₆, stood 15 hrs. in cold, then heated gives tetramethyldiaminobenzil + the carbinol base of "Crystal Violet" (for many further details see (66)); for use of C in prepn. of "Crystal Violet" see (67).]

[C with o-aminothiophenol (80) or with its Zn salt (68) at 60-80° until reactn. begins, then htd. at 100° for 1 hr., gives (60% yield (68)) bis-2,2'-benzothiazolyl [Beil. XXVII-744, XXVII₁-(626)], m.p. 300.5° u.c. (68), 304° (80); similarly C with Zn salt of o-amino-selenophenol gives (69) bis-2,2'-benzoselenazolyl, m.p. 314° u.c. (69).]

Behavior of \bar{C} with certain amides. [\bar{C} with urea directly or in ether gives (8) (21) parabanic acid (N,N')-oxalylurea) [Beil. XXIV-449, XXIV₁-(401)], cryst. from alc., m.p. 244°, accompanied by more or less oxaldiureide, insol.. m.p. 270-275° dec. (8). — \bar{C} with N,N'-dimethylurea gives (70% yield (8)) N,N'-dimethylparabanic acid [Beil. XXIV-453, XXIV₁-(404)], m.p. 154° (8). — \bar{C} with N-phenylurea in ether refluxed 3 hrs. gives (88% yield (8)) N-phenylparabanic acid [Beil. XXIV-454, XXIV₁-(405)], lfts. from alc., m.p. 213-214° cor., after sintering at 208° (8). — \bar{C} with N,N'-diphenylurea in ether gives (100% yield (8)) N,N'-diphenylparabanic acid [Beil. XXIV-455, XXIV₁-(405)], ndls. from alc., m.p. 202° cor., after prelim. sintering (8).]

[For examples of condensation of \bar{C} with various other amides see (21) (70) (71) (73); with various amino acids see (72).]

Behavior of \bar{C} with carbonyl compounds. [\bar{C} with ketones often acts like PCl₅ by replacing the oxygen with 2 chlorine atoms with evolution of CO + CO₂: for many specific examples see (74); also note that \bar{C} with xanthone (1:7275) gives (75) (76) xanthone dichloride; \bar{C} with N-methyl- or N-phenylacridone gives (77) dichlorides.]

Behavior of \bar{C} with organometallic compounds. .[\bar{C} with nickel carbonyl reacts according to equation Ni(CO)₄ + (CO.Cl)₂ \rightarrow NiCl₂ + 6CO (13). — \bar{C} with Et₂Cd (from C₂H₅MgBr + CdCl₂) gives (27% yield (77)) 3-ethylhexanol-3-one-4 (diethyl-propionyl-carbinol) [Beil. I-841, I₂-(881)], b.p. ·178-179° (78). — For interference of \bar{C} with the Michler's ketone test for RMgX cpds. see (79).]

② Oxalyl (di)chloride/1,4-dioxane mol. cpd.: ndls. or pr. from pet. ether, m.p. 67-68° (81). [From C with 5 wt. pts. dioxane-1,4 (1:6400) in 25 vols. pet. ether at −5° in stream of dry air or N₂; the 1:1 mol. cpd. ppts. in 71-78% yield (81). — Note that this prod. may with aniline be converted to oxanilide (see below) or may be dislyd. in excess stand. alk. and titrated back with stand. acid; furthermore, on stdg. in moist air, it is quant. converted to oxalic acid dihydrate (1:0445). — Note also that

- under same conditions no ppt. results with acetyl chloride (3:7065), benzoyl chloride (3:6240), malonyl (di)chloride (3:9030), succinyl (di)chloride (3:6200), fumaryl (di)chloride (3:5875), sym.-phthaloyl (di)chloride (3:6900), unsym.-phthaloyl (di)chloride (3:2395) or terephthaloyl (di)chloride (3:2205) (81).]
- Oxanilide (oxalic acid dianilide): pl. from C₆H₆ or nitrobenzene m.p. 254° (21) 252-253° (71). [From C̄ + aniline in cold ether or from C̄ + aniline hydrochloride in boilg. C₆H₆ (21); note that by virtue of the relative insolubility of oxanilide and its easy quantitative formn. it is often employed as means for quant. detn. of C̄ cf. (1). Note also that the half reactn. prod. oxanilyl chloride m.p. 82.5° has been mentioned above in main text.]
- —— Oxal-bis-(p-toluidide): m.p. 268° (cf. 1:0445).
- —— Oxal-bis-(α -naphthalide): m.p. 234°.
- Oxal-bis-(β -naphthalide): m.p. 275°.
- **© Oxal-bis-(phenylhydrazide):** cryst. from alc. or AcOH m.p. 278° (82). [From \bar{C} (1 mole) in C_6H_6 with phenylhydrazine (4 moles) in dry ether (82).]
- --- Oxal-bis-(p-nitrophenylhydrazide): unreported.
- —— Oxal-bis-(2,4-dinitrophenylhydrazide); yel. cryst. from alc. m.p. 292° after darkening at about 270°. [Prepd. indirectly.]
- 3:5060 (1) Staudinger, Ber. 41, 3558-3566 (1908). (2) Kohlrausch, Pongratz, Ber. 67, 986 (1934). (3) Martin, Partington, J. Chem. Soc. 1936, 1181 (4) von Auwers, Schmidt, Ber. 46, 476-477 (1913). (5) Purvis, Jones, Tasker, J. Chem. Soc. 97, 2296 (1910). (6) Gerbis, Zentr. Gewerbehyg. Unfallverhut, 16, 293-294 (1929); Cent. 1930, I 1016; not in C.A. (7) Staudinger, Anthes, Ber. 46, 1431-1436 (1913). (8) Biltz, Topp, Ber. 46, 1392-1404 (1913). (9) Staudinger, Ger. 216,918, 216,919, Dec. 11, 1909; Cent. 1910, I 307. (10) Kharasch, Brown, J. Am. Chem. Soc. 64, 329-333 (1942).
- (11) Shtokman, Russ. 52,894, March 31, 1938; Cent. 1939, I 797; C.A. 34, 5468 (1940). (12) Fauconnier, Compt. rend. 114, 122 (1892). (13) Jones, Tasker, J. Chem. Soc. 95, 1904–1909 (1909). (14) Soc. Chem. Ind. Busel, Brit. 401,643, Dec. 14, 1933; Cent. 1934, II 2134; French 732,078, Sept. 12, 1932; Cent. 1934, I 287. (15) Wiezevich (to Standard Oil Development Co.), U.S. 2,055,617, Sept. 29, 1936; Cent. 1937, I 429; C.A. 30, 7586 (1936). (16) Krauskopf, Rollefson, J. Am. Chem. Soc. 58, 443–448 (1936). (17) Staudinger, Ber. 45, 1594–1596 (1912). (18) Tuttle, Rollefson, J. Am. Chem. Soc. 63, 1525–1530 (1941). (19) Adams, Ulich, J. Am. Chem. Soc. 42, 599–611 (1920). (20) Froschl, Maier, Monatsh. 59, 260–261, 268–269 (1932).
- (21) Bornwater, Rec. trav. chim. 31, 105-141 (1912). (22) Staudinger, Z. angew. Chem. 35, 658 (1922). (23) Kharasch, Brown, J. Am. Chem. Soc. 62, 454 (1940). (24) Kharasch, Kane, Brown, J. Am. Chem. Soc. 64, 333-334 (1942). (25) Kharasch, Kane, Brown, J. Am. Chem. Soc. 64, 1621-1624 (1942). (26) Liebermann, Rahts, Ber. 45, 1204-1207 (1912). (27) Coffey, Rec. trav. chim. 42, 426-428 (1923). (28) Scholl, Meyer, Keller, Ann. 513, 298 (1934). (29) Schonberg, Kraemer, Ber. 55, 1186, 1189-1193 (1922). (30) Silver, Lowy, J. Am. Chem. Soc. 56, 2429-2430 (1934).
- (31) Liebermann, Zsuffa, Ber. 44, 857 (1911). (32) Liebermann, Mitter, Ber. 45, 1207-1213 (1912). (33) Lesser, Gad, Ber. 60, 242-245 (1927). (34) Lesser, Gad (to I.G.), Ger. 470,277, Jan. 14, 1929; Cent. 1929, I 3037. (35) Liebermann, Zsuffa, Ber. 44, 202-210 (1911). (36) Dansi, Semproni, Gazz. chim. utal. 66, 182-186 (1936); Cent. 1937, II 1158; C.A. 31, 1022 (1937). (37) Dansi, Gazz. chim. utal. 67, 85-88 (1937); Cent. 1937, II 1368; C A. 31, 6227 (1937). (38) Butescu, Bull. soc. chim. (4) 43, 1269-1272 (1928). (39) Nyman, Ann. Acad. Sci. Fennicae A-41, No. 5, 80 pp. (1934); Cent. 1937, I 2348; C.A. 30, 2958 (1936). (40) von Braun, Manz, Ann. 496, 178-179 (1932).
- (41) Perret, Perrot, Bull. soc. chim. (5) 1, 1543 (1934). (42) Adams, Weeks, J. Am. Chem. Soc. 38, 2514-2519 (1916). (43) von Frank, Caro, Ber. 63, 1532-1543 (1930). (44) Ghosh, J. Chem. Soc. 167, 1593 (1915). (45) Bergmann, Wolff, J. prakt. Chem. (2) 128, 232 (1930). (46) Carothers, Arvin, Dorough, J. Am. Chem. Soc. 52, 322-3300 (1930). (47) Arndt, Milde, Eckert, Ber. 56, 1982 (1923). (48) Fairhall, J. Ind. Hyg. 8, 528-533 (1926); Cent. 1927, I 774-775; C.A. 21, 874 (1927). (49) Miksic, Pinterovic, J. prakt. Chem. (2) 119, 231-234 (1928). (50) Adams, Wirth, French, J. Am. Chem. Soc. 40, 424-431 (1918).
- (51) Adams, Gilman, J. Am. Chem. Soc. 37, 2716-2720 (1915). (52) Giua, Franciscis, Gazz. chim. ital. 54, 509-516 (1924); C.A. 19, 64 (1925). (53) Giua, Atti. congr. naz. chim. ind. 1924,

266; Cent. 1925, I 2309. (54) Miksic, J. prakt. Chem. (2) 119, 218-230 (1928). (55) Soc. Chem. Ind. Basel, Brit. 186,859, Nov. 2, 1922; Cent. 1923, II 998; Ger. 402,994, Sept. 19, 1924; Cent. 1925, I 303; Staudinger, Swiss 92,688, Jan. 16, 1922, 93,486, Mar. 16, 1922, 93,487, 93,488, 93,489, March 1, 1922; Cent. 1923, II 573. (56) Soc. Chem. Ind. Basel, Swiss 102,033, Jan. 16, 1924, + Swiss 104,921-104,928, May 16, 1924, + Swiss 106,135, Nov. 1, 1924; all in Cent. 1925, II 774-775. (57) Hurtley, Smiles, J. Chem. Soc. 1926, 2268-2270. (58) Fischer, Taurinisch, Ber. 64, 236-239 (1931). (59) Mitter, Mukherjee, J. Indian Chem. Soc. 16, 393-395 (1939). (60) Staudinger, Schlenker, Goldstein, Helv. Chim. Acta 4, 334-342 (1921).

(61) Schapiro, Ber. 66, 1370-1372 (1933). (62) Haller (to I.G.), Ger. 463,140, July 23, 1928; Brit. 282,891, Jan. 26, 1928; Cent. 19 8, II 1615-1616. (63) Haller (to I.G.), Ger. 448,946, Sept. 1, 1927; Cent. 1927, II 2228-2229. (64) I.G., Brit. 265,224, March 30, 1927; French 627,939, Oct. 15, 1927; Swiss, 125,475, April 16, 1928; 126,719, 126,720, 126,721, July 2, 1928; Cent. 1929, II 2104-2105. (65) Stollé, Ber. 46, 3915-3916 (1913); J. prakt. Chem. (2) 105, 142-148 (1923). (66) Staudinger, Stockmann, Ber. 42, 3485-3496 (1909). (67) Postowski, Cent. 1927, II 2183. (68) Bogert, Stull, J. Am. Chem. Soc. 48, 250 (1926). (69) Bogert, Stull, J. Am. Chem. Soc. 49, 2014 (1927). (70) Bornwater, Rec. trav. chim. 32, 334-339 (1913); 35, 124-129 (1915); 36, 250-257 (1916).

(71) Figee, Rec. trav. chim. 34, 289-325 (1915). (72) Meijeringh, Rec. trav. chim. 32, 140-157 (1913). (73) Stollé, Luther, Ber. 53, 314-317 (1920). (74) Staudinger, Ber. 42, 3966-3985 (1909). (75) Schonberg, Schütz, Ann. 454, 51 (1927). (76) Schönberg, Schütz, Bruckner, Peter, Ber. 62, 2560 (1929). (77) Gleu, Nitsche, Schubert, Ber. 72, 1094-1095, 1099 (1939). (78) Gilman, Nelson, Rec. trav. chim. 55, 527 (1936). (79) Gilman, Heck, J. Am. Chem. Soc. 52, 4952-4953 (1930). (80) Walter, Hubsch, Pollak, Monatsh. 63, 187, 196-197 (1933).

(81) Varvoglis, Ber. 71, 32-34 (1938). (82) Folymers, Rec. trav. chim. 34, 46-47 (1915).

```
3:5075 METHYL CHLOROFORMATE Cl.COOCH<sub>3</sub> C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>Cl Beil. III - 9
(" Methyl chlorocarbonate") III<sub>1</sub>-(5)
III<sub>2</sub>-(9)
```

B.P.
$$72-73^{\circ}$$
 at 767 mm. (1) $D_4^{20} = 1.2231$ (1) $n_D^{20} = 1.38675$ (1) $71.4-72.4^{\circ}$ (2) $71.2-71.5^{\circ}$ at 733 mm. (3) $D_4^{16 \ 9} = 1.2240$ (6) 71.4° cor. (4) $71.0-71.5^{\circ}$ at 750 mm. (7) $71-71.5^{\circ}$ (20) 69° at 720 mm. (5)

[See also ethyl chlorocarbonate (3:7295).]

C is colorless liquid with penetrating odor and strong lachrymatory properties.

[For prepn. of \tilde{C} from carbonyl chloride (phosgene)(3:5000) with MeOH see (8) (9) (7) (4) (10) (20) (21); from methyl formate (1:1000) with Cl₂ see (11) (12) (chloromethyl chloroformate (3:5275) is also formed); from pentachloroethyl chloroformate [Beil. III-13, III₁-(6)] (13) or from bis-(trichloromethyl) oxalate [Beil. III-17] (14) or from methyl trichloromethyl carbonate [Beil. III-17] III₁-(8) III₂-(15)] (15) with MeOH see indic. refs.]

Pyrolysis of \tilde{C} . Unlike the case of ethyl chloroformate (3:7295) the pyrolysis of \tilde{C} appears to have been little studied: in quinoline the decomposition temp. is given (16) (17) as 36°; presumably the decomposition yields MeCl (3:7005) + CO₂.

Reactions of the —COOMe group of \bar{C} . \bar{C} is not readily decomposed by cold aq. (4) (11) (18) and can even be washed to remove alc.; \bar{C} on boilg, with aq. or dil. acid or dil. alk., however, is readily hydrolyzed yielding MeOH (1:6120) + CO_2 + HCl.

[Č with Cl₂ under various conditions (19) (20) (21) (22) (23) yields successively chloromethyl chloroformate (3:5275) dichloromethyl chloroformate (3:5315) and ultimately trichloromethyl chloroformate ("diphosgene") (3:5515).]

[C (10% excess) with MeHSO₄ at 100° under reflux for 6-8 hrs. gives (100% yield (24))

 $Me_2SO_4 + HCl + CO_2$; \bar{C} (10% excess) with ClSO₃H carefully mixed finally refluxed gives (80% yield (25) (26)) methyl chlorosulfonate.]

Reactions of the chlorine atom of C. [C with thallous fluoride 6 hrs. in ice bath followed by reflux at 50° gives (24% yield (27)) methyl fluoroformate b.p. 40° (27).]

 \bar{C} with solid dry NaI gives (100% yield (20)) MeI + CO₂ + NaCl; note that \bar{C} with KI in acetone does not (28) liberate free iodine (dif. from carbonyl chloride (phosgene) (3:5000), chloromethyl chloroformate (3:5275), dichloromethyl chloroformate (3:5315), trichloromethyl chloroformate (diphosgene) (3:5515), or bis-(trichloromethyl) carbonate (triphosgene) (3:1915)).

[Č with solid NaCN (contg. 0.2-7.0% moisture) at not above 90° gives (29) methyl cyanoformate [Beil. II-547, II₁-(238), II₂-(510)], b.p. 97°.]

Č as carbomethoxylating agent. Č is widely employed as a means of introducing the —COOMe group into other organic molecules by reactn. of the chlorine atom with the H of alcoholic, phenolic, or enolic OH group (or their metallic alcoholates, phenolates, enolates, etc.); cf. ethyl chloroformate (3:7295), but this topic cannot be expanded here.

[\bar{C} with dimethyl malonate (1:3457) + Na in xylene (30) or \bar{C} with dimethyl sodio-malonate in C_6H_6 (31) or toluene (32) gives (yields: 59% (32), 40-42% (30) 30-35% (31)) trimethyl methanetricarboxylate (tri(carbomethoxy)methane) [Beil. II₁-(320), II₂-(680)], pr. from MeOH, m.p. 46°. — \bar{C} with dimethyl phenylmalonate + Na in ether gives (40% yield (33)) trimethyl phenylmethanetricarboxylate (phenyl-tri(carbomethoxy)methane), cryst. from least possible hot CHCl₃ by addn. of hot lgr., m.p. 84.5° (33).]

Č also reacts readily with NH₃, with primary and secondary amines, with amino acids, etc., to replace one of the H's attached to N by the —COOMe group (see also below and under **①**).

[\tilde{C} in C_6H_6 with dry NH₃ gives methyl carbamate (urethylan) [Beil. III-21, III₁-(9), III₂-(18)], extremely sol. in aq. (217 g. in 100 g. aq. at 11°), m.p. 54°, b.p. 177°. — \tilde{C} with 33% aq. MeNH₂ (34) or \tilde{C} with equiv. conc. aq. CH₃NH₂.HCl followed by addn. of strong aq. KOH (35) gives methyl N-methylcarbamate [Beil. III-64, III₁-(330), III₂-(567)], oil, sol. aq. but very sol. ether, b.p. 158° at 766 mm. — Countless analogous reactns. cannot be listed here.]

Č in MeOH with hydrazine hydrate in alc. + ether ppts. hydrazine HCl and on evapn. of filtrate gives (98% yield (36)) dimethyl sym.-hydrazinedicarboxylate (sym.-di-(carbomethoxy)hydrazine) [Beil. III₁-(46), III₂-(78)], cryst. from ether/alc., m.p. 132° (36) (note that the half-reactn. prod. viz., methyl hydrazine-monocarboxylate (methyl hydrazinoformate) (methyl carbazinate), m.p. 73°, is also known (37)). — Č (1 mole) with urea (2 moles) refluxed for 2-3 hrs. gives (75% yield (38)) methyl allophanate (N-carbomethoxy) urea [Beil. III-69, III₁-(31), III₂-(55)], spar. sol. hot aq., cryst. from dil. alc. or acetone, m.p. 216°.

 \bar{C} (1 mole) with phenylhydrazine (2 moles) in ether gives (39) methyl ω-phenylcarbazinate (β-carbomethoxyphenylhydrazine) [Beil. XV-286], pr. from aq., m.p. 115–117° (39). — \bar{C} with p-nitrophenylhydrazine in pyridine gives (40) β-carbomethoxy-p-nitrophenylhydrazine, m.p. 180° (40). — \bar{C} with 2,4-dinitrophenylhydrazine in pyridine gives (40) β-carbomethoxy-2,4-dinitrophenylhydrazine, pr. from aq. alc., m.p. 138° (40)

- Methyl N-phenylcarbamate (methyl carbanilate): lfts. from alc., m.p. 47° (41), 46° (42). [From C with aq. aniline (slight excess) (41) (18); also indirectly (42).]
 Methyl N-(p-tolyl)carbamate: unreported.
- N,N'-bis-(Benzyl)urea: ndls. from alc., m.p. 167.5-169° cor. (43). [From Č (1 ml.) with benzylamine (3 ml.) + trace NH₄Cl refluxed 1 hr. (43); note that in this react. the reagent amine not only reacts with the chlorine atom of Č but also ammonolyzes

the carbomethoxy group; the prod. is therefore a disubstituted urea rather than methyl N-benzylcarbamate, ndls. from pet. ether, m.p. 64-65° (44), which has been reported indirectly (44).]

- —— N-(Carbomethoxy)phthalimide: unreported.
- ---- N-(Carbomethoxy)-3-nitrophthalimide: unreported.
- ---- N-(Carbomethoxyl)-tetrachlorophthalimide: unreported. [Note that C with K tetrachlorophthalimide fails to react under reflux and explodes on htg. in s.t. (45).]
- with thiourea (1 mole) in conc. aq. soln. on treatment with NaHCO₃ in slight excess evolves CO₂ and ppts. S-(carbomethoxy)isothiourea bicarbonate, bulky white ppt., m.p. 62.5-63.5°; this ppt. dissolves readily in cold dil. HCl and upon addn. of PkOH ppts. the corresponding picrate; note, however, that the above bicarbonate on stdg. with aq. for 2 days changes spontaneously to N,N-dicarbomethoxythiourea, insol. aq., m.p. 117-118°, and thiourea (extractable with aq.) (46). Note, however, that Č (1 g.) with thiourea (1 g.) in EtOH (10 ml.) refluxed for 30 min., then treated with PkOH (1 g.), does not yield the above prod. but instead (47) S-methylisothiourea picrate, m.p. 224° (47).]
- 3:5075 (1) Karvonen, Ann. Acad. Sci. Fennicae A-10, No. 4, p. 18; Cent. 1919, III 808. (2) Mizushima, Kubo, Bull. Chem. Soc. Japan 13, 178 (1938). (3) Mohler, Helv. Chim. Acta 21, 787 (1938). (4) Rose, Ann. 205, 227-229 (1880). (5) Mohler, Polya, Helv. Chim. Acta 19, 1238 (1936). (6) von Auwers, Ber. 60, 2140 (1927). (7) Klepl, J. prakt. Chem. (2) 26, 447-448 (1882). (8) Cappelli, Gazz. chim. ıtal. 50, II 8-12 (1920); C.A. 15, 524 (1921). (9) Hentschel, Ber. 18, 1177 (1885). (10) Dumas, Peligot, Ann. chim. (2) 58, 52-54 (1835); Ann. 15, 39-40 (1835).
- (11) Hentschel, J. prakt. Chem. (2) 36, 210-213 (1887). (12) Bayer & Co., Ger. 297,933, Feb. 7, 1921; Cent. 1921, II 803. (13) Cloez, Ann. chim. (3) 17, 302-304 (1846); Ann. 60, 260-261 (1846). (14) Cahours, Ann. chim. (3) 19, 349-351 (1847); Ann. 64, 314-315 (1848). (15) Kling, Florentin, Jacob, Ann. chim. (9) 14, 203 (1920). (16) Carré, Bull. soc. chim. (5) 3, 1069 (1936). (17) Carré, Passedouet, Compt. rend. 200, 1767-1769 (1935). (18) Vles, Rec. trav. chim. 53, 964-966 (1934). (19) Hentschel, J. prakt. Chem. (2) 36, 99-113, 305-309 (1887). (20) Kling, Florentin, Lassieur, Schmutz, Ann. chim. (9) 13, 46-53 (1920).
- (21) Grignard, Rivat, Urbain, Ann. chm. (9) 13, 230-244 (1920). (22) Hood, Murdock, J. Phys. Chem. 23, 509 (1919). (23) Pomilio, Salvatore, Italian 338,820, Jan. 16, 1936; Cent. 1937, I 4689; not in C.A. (24) Kraft, Lyutina, J. Gen. Chem. (U.S.S.R.) 1, 190-192 (1931); Cent. 1931, II 3197; C.A. 26, 2167 (1932). (25) Kraft, Alekseev, J. Gen. Chem. (U.S.S.R.) 2, 726-729 (1932); Cent. 1933, II 1666; C.A. 27, 2426 (1933). (26) Kraft, Alekseev, Obsh. Chim. (U.S.S.R.) 2, 726-729 (1942); Chem. Prods. 6, 69-71 (1943); C.A. 38, 720 (1944). (27) Goswami, Sarkar, J. Indian Chem. Soc. 10, 537-539 (1933). (28) Perret, Biechler, Bull. soc. chim. (5) 3, 957-958 (1936). (29) Gluud, Nüssler, Keller (to Gesellschaft für Kohlentechnik), Ger. 592,539, Feb. 17, 1934; Cent. 1934, II 3437; C.A. 28, 3417 (1934). (30) Corson, Sayre, Org. Syntheses, Coll. Yol. 2 (1st ed.), 596-597 (1943); 13, 100-101 (1933).
- (31) Scholl, Egerer, Ann. 397, 355-357 (1913). (32) Backer, Lolkema, Rec. trav. chim. 57, 1237-1238 (1938). (33) Adickes, J. prakt. Chem. (2) 145, 240-241 (1936). (34) Franchimont, Klobbie, Rec. trav. chim. 7, 353 (1888). (35) Biltz, Jeltsch, Ber. 56, 1916 (1923). (36) Diels, Paquin, Ber. 46, 2007 (1913). (37) Diels, Fritsche, Ber. 44, 3022-3023 (1911). (38) Dains, Wertheim, J. Am. Chem. Soc. 42, 2307 (1920). (38) Heller, Ann. 263, 281 (1891). (40) Longo, Gazz. chim. ital. 63, 466-468 (1933); Cent. 1933, II 3415; C.A. 28, 122 (1934).
- (41) Heller, Ber. 18, 978 (1885). (42) Nekrassow, Melnikow, J. prakt. Chem. (2) 126, 91 (1930). (43) Dermer, King, J. Org. Chem. 8, 168-173 (1943). (44) Weerman, Jongkees, Rectrav. chim. 25, 243 (1906). (45) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409 (1934). (46) Dixon, Kennedy, J. Chem. Soc. 117, 84-85 (1920). (47) Levy, Campbell, J. Chem. Soc. 1339, 1443.

Liquid. — [For f.p./compn. data on mixts. of \bar{C} with 2,2-dichloropropane (3:7140) or with pentachloroethane (3:5880) see (8); for extensive study of vap. press., heat capacity, and other thermodynamic props. see (21); for soly. of aq. in \bar{C} see (22).] [For use of \bar{C} as dry cleaning fluid see (10); for use of \bar{C} in dewaxing of oils see (11).] [For detn. of \bar{C} in air by thermal decompn. method see (23).]

[For prepn. of \bar{C} from 1,1-dichloroethane (ethylidene dichloride) (3:5035) by actn. of Cl_2 see (12) (13) (7); for manufacture of \bar{C} from 1,1-dichloroethylene (vinylidene dichloride) (3:5005) by cat. addn. of HCl see (14) (15).]

C with Ca(OH)₂ at ord. temp. loses HCl yielding (16) 1,1-dichloroethylene (3:5005).

Č with aq. under specified conditions and catalyst hydrolyzes to yield (17) (18) AcOH, AcCl, or Ac₂O.

[For study of actn. of fluorine on C sec (19).]

 $\ddot{\mathbf{C}}$ with phenol + aq. NaOH gives (20) small yield of a mixt. of o-hydroxyacetophenone (1:1746) and p-hydroxyacetophenone (1:1527). [For impt. clarification of previous misapprehension of this reactn. see (20).]

- 3:5085 (1) Wiswall, Smyth, J. Chem. Phys. 9, 357 (1941). (2) Pierre, Ann. 80, 127 (1851).
 (3) Staedel, Ber. 15, 2563 (1882). (4) Henne, Hubbard, J. Am. Chem. Soc. 58, 404-406 (1936).
 (5) Maryott, Hobbs, Gross, J. Am. Chem. Soc. 63, 660 (1941). (6) Kohlrausch, Köppl, Monatsh.
 (6) Kohlrausch, Köppl, Monatsh.
 (7) Sutton, Proc. Roy. Soc. A-133, 673-674 (1931). (8) van de Vloed, Bull. soc. chim. Belg. 48, 259, 262 (1939). (9) Turkevich, Smyth, J. Am. Chem. Soc. 62, 2469 (1940). (10) Parkhurst (to Stand. Oil of Cal.), U.S. 1,948,045, Feb. 20, 1934; Cent. 1934, II 863; C.A. 28, 2924 (1934).
- (11) Sharples Specialty Co., French 801,583, Aug. 7, 1936; Cent. 1937, I 263. (12) Regnault, Ann. 33, 317-319 (1840). (13) Staedel, Ann. 195, 183-185 (1879). (14) I.G., Ger. 523,436, April 23, 1931; Cent. 1931, I 3607. (15) Nutting, Huscher (to Dow Chem. Co.), U.S. 2,209,000, July 23, 1940; C.A. 35, 140 (1941). (16) I.G., Brit. 349,872, July 2, 1931; French 702,361, July 7, 1931; Cent. 1931, II 1191. (17) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994; C.A. 26, 2747 (1932). (18) Britton, Reed (to Dow Chem. Co.), U.S. 1,870,601, Aug. 9, 1932; Cent. 1932, II 3305. (19) Henne, Renoll, J. Am. Chem. Soc. 58, 889-890 (1936). (20) Cope, J. Am. Chem. Soc. 57, 572-574 (1935).
- (21) Rubin, Levedahl, Yost, J. Am. Chem. Soc. 66, 279-282 (1944). (22) Staverman, Rec. trav. chim. 60, 836-841 (1941); Cent. 1942, I 1352; C.A. 37, 2638 (1943). (23) Smyth, Ind. Eng. Chem. Anal. Ed. 8, 379 (1936).

```
3:5100 CARBON TETRACHLORIDE
                                                              CCL
                                                                              Beil. I - 64
           (Tetrachloromethane)
                                                                                    I_{1}-(12)
                                                                                    I_{2}-(22)
  B.P.
                                         F.P.
                                                            D_4^{30} = 1.57480 \quad (7)
  77.4°
                  at
                       774 mm.
                                  (1)
                                         -22° (28) (51)
                                                                   n_{\rm D}^{25.2} = 1.45767
  77.2°
                       766 mm.
                  at
                                  (2)
                                         -22.3^{\circ}
                                                     (52)
                                                                                       (65)
  76.9°
                  at
                       760 mm.
                                  (3)
                                         -22.5^{\circ}
                                                     (17)
                                                                           1.45707
                                                                                       (65)
                                                            D_{\perp}^{25} = 1.5850 \quad (54)
                                 (20)
                                                     (29)
                       749 mm. (4)
  76.87°
                 at
                                         -22.6^{\circ}
                                                    (30)
                                                                   1.58472 (55)
  76.83°
                  at
                       760 mm. (83)
                                                    (83)
                                                                   1.58469 (22)
  76.8°
                             (5)(87)
                                         -22.7^{\circ}
                                                     (31)
                                                                   1.58447 (5)
  76.75°
                 at
                       760 mm.
                                         -22.81°
                                  (6)
                                                                   1.58445 (13)
                                                     (15)
                              (7) (19)
                                         -22.83^{\circ}
                                                     (32)
                                                                   1.58443 (7)
  76.74°
                 at
                       760 mm.
                                  (8)
                                         -22.86^{\circ}
                                                     (33)
                                                                   1.58434 (56)
                                  (9)
                                                     (34)
                                                                   1.58426 (57)
  76.71°
                 at
                       760 mm. (10)
                                         -22.87^{\circ}
                                                    (35)
                                                                   1.58414 (58)
  76.70-76.74° at
                       760 mm. (11)
                                                                   1.5835 (23)(59)(166)
                                                     (36)
  76.7° u.c.
                 at
                       754 mm. (12)
                                         -22.89^{\circ}
                                                    (37)
                                                                    n_{\rm D}^{25} = 1.45930
                                                                                      (21)
  76.69°
                 at
                       760 mm. (55)
                                         -22.9°
                                                    (38)
                                                                           1.45759
                                                                                       (13)
  76.686°
                 at
                       760 mm. (13)
                                               (39)(53)
                                                                            1.4574
                                                                                       (66)
                       760 mm. (14)
                                         -22.95^{\circ}
  76.685°
                 at
                                                     (7)
                                                                           1.45732
                                                                                       (67)
                       760 mm. (15)
  76.66°
                 at
                                           (40) (41) (42)
                                                                           1.45724 (166)
  76.6°
                       760 mm. (48)
                 at
                                         -22.968° (87)
                                                                           1.4549
                                                                                       (68)
                                                                   n_{\rm D}^{23.8} = 1.45786
  76.58-76.60° at
                       761 mm. (16)
                                         -23.0(43)(44)
                                                                                       (69)
                       760 mm. (49)
                                                            D_4^{20} = 1.59472 (60)
  76.52°
                 at
                                              (45) (153)
                       759 mm. (17)
  76.5°
                 at
                                         -23.4°
                                                    (46)
                                                                   1.5944
                                                                             (11)
                       760 mm. (19)
  76.5° (18)
                                        -23.5^{\circ}
                 at
                                                    (47)
                                                                   1.5942
                                                                             (61)
  76.45-76.50° at
                       760 mm. (21)
                                                                   1.59407
                                                                               (7)
  76.4°
                            (50) (73)
                                        See also Notes
                                                                   1.5940 (61)
  76.22-76.38° at
                       741 mm. (22)
                                        4, 5, and 6.
                                                                         (62) (63)
 76.2°
                      745 mm. (56)
                                                                   1.5924 (64)
 76.1°
                      743 mm. (23)
                 at
                                                                   1.46023 (50)
 76°
                 at
                      733 mm. (24)
                                                                     n_{\rm D}^{20} = 1.4630
                                                                                       (70)
                      760 mm. (19)
  75.55°
                 at
                                                                           1.461
                                                                                       (15)
 75.4°
                 at
                      760 mm. (25)
                                                                           1.46048
                                                                                      (11)
                                (19)
                                                                           1.46044
                                                                                       (13)
 75.3-75.4°
                 at
                      729 mm. (56)
                                                                           1.46041
                                                                                       (10)
                 at 751.4 mm. (26)
 75.2°
                                                                           1.46040
                                                                                       (55)
 74.95°
                 at
                      720 mm. (10)
                                                                           1.46026 (165)
                      709 mm. (30)
 74.4-74.5°
                 at
                                                                           1.46023
 73.50°
                 at
                      687 mm. (27)
                                                           D_4^{15} = 1.60370 \quad (7)
 72.0°
                 at 643.2 mm. (2)
                                                                   1.6011
                                                                             (23)
                      663 mm. (23)
 71.0°
                 at
                                                           See also Note 7.
                                                                  n_{\rm D}^{19.68} = 1.46094 (10)
 65.0°
                 at
                      559 mm. (23)
                      506 mm. (23)
 62.0°
                 at
                                                                  n_{\rm D}^{16.80} = 1.46266 (10)
 60.0°
                 at
                      415 mm.
                                (2)
                      443 mm. (23)
 58.5°
                 at
 59.5°
                 at 398.85 mm.
                                (2)
                                                                    n_D^{15} = 1.46325 (168)
                      386 mm. (23)
 54.8°
                 at
                                                                           1.46305
                                                                                        (7)
 50.0°
                 at
                      328 mm. (23)
                                                                           1.4629 (167)
```

B.P. (Cont.)					
46.3°	at	282 mm.	(23)	$n_{\rm D}^{12.3}=1.4656$	(71)
42.0°	at	236 mm.	(23)		
36.0°	at 1	70.95 mm.	(2)	$n_{\rm D}^{12} = 1.4674$	(71)
31.0°	at	149 mm.	(23)		
25.0°	at	116 mm.	(23)	$n_{\rm D}^{11.19}=1.46589$	(10)
				$n_{\rm D}^{10.5} = 1.4661$	(10)

See also Notes 1, 2, and 3.

Note 1. For studies of vap. press. of \bar{C} over range -20° to $+283^{\circ}$ (72) and range +19.2 to 76.4° (73) see indic. refs.

Note 2. For studies of effect on b.p., vap. press., vapor density of very intensive drying see (74) (75) (76) (77) (79) (80).

Note 3. For study of detn. of b.p. range of \bar{C} as method of estimation of impurities see (81).

Note 4. For studies on effect of prior history of sample on detn. of f.p. of \bar{C} see (82) (52) (51).

Note 5. For studies of influence of high press. of f.p. see (41) (83).

Note 6. Solid \bar{C} has a transition point variously determined as follows: -47° (85) cf. (17), -47.55° (33), -47.63° (15), -47.66° (32) (36), -47.84° (39), -48.1° (47), -48.5° (86), -48.54° (87).

Note 7. For studies of density of \overline{C} over ranges -186° to -80° (88), 0° to 283° (crit. temp.) (72), and -18° to $+60^{\circ}$ (89) see indic. refs.

[See also methylene (di)chloride (3:5020) and chloroform (3:5050).]

MISCELLANEOUS PHYSICAL PROPERTIES OF C VARIOUS SOLUBILITY RELATIONS

With water. \bar{C} is only very slightly sol. aq. and is eas. volatile with steam; e.g., 100 g. aq. at 0° dis. 0.097 g. \bar{C} (91), at 10° 0.083 g. (91), at 15° 0.081 g. (8), at 20° 0.080 g. (91), at 30° 0.077 g. (8), 0.085 g. (91); for study of salting-out effect of KCl or MgSO₄ see (92). — For studies of soly. of aq. in \bar{C} at 0° (93), 10° (94), 20° (94), 25° (93), and 30° (93) (94) see indic. refs.; for study of reciprocal soly. of \bar{C} + aq. see (95).

With various inorganic compounds. [For data on soly. in \bar{C} of H_2 (96), O_2 (97) (98), O_3 (99) (100), air (96), N_2 (at high pressure) (101), NO (107), NO_2 (102), N_2O (96), NH_3 (103), H_2S (103), SO_2 (96) (116), HCl (103) (104) (105) (106), HBr (106), Cl_2 (108) (109) (110), or CO_2 (111) (112) see indic. refs. — For data on soly. of I_2 in \bar{C} see (113) (121) (122) (123) (124) (125); for study of nature of I_2 solns. in \bar{C} see (114); for soly. of I_2 in CCl_4 vapor see (115). — For data on soly. of sulfur in \bar{C} see (128) (129) (130). — For data on soly. of $AlCl_3$ in \bar{C} see (135).]

With various organic compounds. [For data on soly. in \bar{C} of ethane (116), ethylene (116) under high press. (101), acetylene (116), dimethyl ether (117), CH₃Cl (117) (118), COCl₂ (119) (120) see indic. refs.]

Binary Systems Containing Č

(See also azeotropes containing C)

 \tilde{C} with various inorganic compounds. $\tilde{C} + Cl_2$: for f.p./compn. data and diag. (note that 5 different cpds. are formed) see (29) cf. (17) (126). $- \tilde{C} + Br_2$: for f.p./compn. data and diag. (eutectic has f.p. about -47.6° and conts. about 82.7 mole % \tilde{C} (38)) see (38) cf. (125). $- \tilde{C} + I_2$: see above under soly. of I_2 in \tilde{C} . $- \tilde{C}$ + I - Cl: for f.p./compn. data and

diag. (series of solid solns.) see (31) cf. (127). — $\bar{C} + SO_2$: for f.p./compn. data and diag. see (131). — $\bar{C} + H_2S$: for f.p./compn. diag. see (132). — $\bar{C} + N_2O_4$: for f.p./compn. data and diag. see (133). — $\bar{C} + PCl_5$: for formn. of compd. 2PCl₅·CCl₄ see (134). — $\bar{C} + PBr_5$: for formn. of 2 cpds. see (134). — $\bar{C} + TiCl_4$: for f.p./compn. data and diag. see (53); for b.p. and liq. vapor compn. see (48).

 \bar{C} with org. cpds. of Order 1. \bar{C} + n-heptane (1:8575): for study of ht. of mixing see (136); for n_D^{20} /compn. see (165). — \bar{C} + C_6H_6 (1:7400): for f.p./compn. data and diag. see (137) (138) (90); for data on D_{20}^{20} (12), D_{23}^{22} (12), D_{25}^{22} (12), D_{25}^{25} (57) (140) (166), and D_{30}^{30} (141) versus compn. see indic. refs.; for $n_D^{1.8}$ (142), n_D^{20} (10), or n_D^{25} (65) (68) (166) versus compn. see indic refs.; for refractive indices at various wave lengths see (67); for data on b.p. at 720 mm. (10), vap. press. (2) (58) (10) (65) (143) (163), heat of mixing (141) (144), liq-vapor equil. (145), or study of distn. through packed column (139) see indic. refs. — \bar{C} + toluene (1:7405): for data on vap. press. (4) (143), D_{20}^{20} (12) cf. (4), D_4^{25} (166), n_D^{18} (146), and n_D^{25} (4) (166) see indic refs. — \bar{C} + cyclohexane (1:8405): for f.p./compn. data (147), D_4^{20} (62), D_4^{25} (140) (58), n_D^{25} (140) see indic. refs.

 $\bar{C} + MeOH$ (1:6120): for D_4^{25} and n_4^{25} /compn. see (151). $-\bar{C} + EtOH$ (1:6130): for vap. press. data/compn. see (148) (149); for D_4^{25} (59) (166) and n_D^{15} (167) or n_D^{25} (166) see indic. refs. $-\bar{C} + n\text{-}PrOH$ (1:6150): for n_D^{25} /compn. see (66). $-\bar{C} + n\text{-}BuOH$ (1:6180): for n_D^{20} /compn. see (165). $-\bar{C} + isoAmOH$ (1:6200): for D_4^{25} and n_4^{25} versus compn. see (166). $-\bar{C} + cyclohexanol$ (1:6415): for f.p./compn. data see (150)

 \bar{C} + dicthyl ether (1:6110): for data on f.p./compn. (152), D_4^{20} (62), D_4^{25} (166), and n_D^{25} (166) see indic. refs. — \bar{C} + disopropyl ether (1:6125): for D_2^{20} /compn. see (62). — \bar{C} + disoane-1,4 (1:6400): for D_4^{20} /compn. see (62). — \bar{C} + anisole (1:7445): for f.p./compn. data and diag see (153). — \bar{C} + diphenyl ether (1:7125): for f.p./compn. data and diag. see (153).

 \bar{C} + acctone (1:5400): for f.p./compn. data and diags. see (90) (147); for D_4^{20} (62), D_4^{25} (59), and n_D^{25} (166) versus compn. see indic refs.

 $\bar{C} + MeOAc$ (1:3005): for D_4^{25} and n_D^{25} versus compn. see (166). — $\bar{C} + EtOAc$ (1:3015): for f.p./compn. data and diag. see (152); for data on vap. press. (65) (192), D_4^{25} (166), n_D^{20} (27), n_D^{25} (166) cf. (65) versus compn. see indic. refs. — $\bar{C} + EtOBz$ (1:3721): for D_4^{20} compn. see (61). — $\bar{C} + diethyl$ carbonate (1:3150): for D_D^{25} /compn. see (5).

 $\tilde{\mathbf{C}}$ with org. cpds. of Order 2. \tilde{C} + nitrobenzene: for f.p./compn. data and diag. (eutectic, f.p. -34.5° , conts. 84.5 wt. % $\tilde{\mathbf{C}}$ (44)) see (44) cf. (138); for D_{-}^{20} , D_{-}^{44} , and n_{D}^{20} versus compn. see (154). — \tilde{C} + aniline: for f.p./compn. data (147) and D_{-}^{25} /compn. (155) see indic. refs. — \tilde{C} + quinoline: for D_{-}^{20} /compn. see (62).

 $ar{C}$ with org. cpds. of Order 3. $ar{C}+CH_2Cl_2$ (3:5020): for data on b.p., D_4^{20} , and liqvapor equilibria see (156). $-ar{C}+CHCl_3$ (3:5050): for f.p./compn. data and diag. (eutectic, f.p. -81.4°, conts. 49.4 wt. % $ar{C}$ (46)) (38) (147) (157) cf. (125) see indic. refs.; for D_4^{20} /compn. see (156) (158) cf. (12); for n_D^{25} compn. see (166); for b.p. and liq.-vapor equil. see (156). $-ar{C}+1$,1-dichloroethane (3:5035): for b.p., D_4^{20} , and liq.-vapor equil. see (156). $-ar{C}+1$,2-dichloroethane (3:5130): for data on b.p. (49) (159), liq.-vapor equil. (49) (159) (160), D_2^{20} /compn. (49) see indic. refs. $-ar{C}+p$ entachloroethane (3:5880): for f.p./compn. data and diag. see (157). $-ar{C}+1$,1,2,2-tetrachloroethylene (3:5460): for f.p./compn. data (45), vap. press. (3) and liq.-vapor equil. (3) see indic. refs. $-ar{C}+2$,2-dichloropropane (3:7140): for f.p./compn. data see (45). $-ar{C}+t$ er-butyl chloride (3:7045): for f.p./compn. data and diags. (complete series of solid solns.) see (47) (161). $-ar{C}+c$ hlorobenzene (3:7903): for D_4^{20} /compn. see (61).

 \tilde{C} with org. cpds. of higher orders. $\tilde{C}+CBr_4$: for extensive study of this system see (162); for D_4^{25} /compn. see (54). — $\tilde{C}+C_2H_5Br$: for D_4^{20} /compn. see (158). — $\tilde{C}+1$,2-dibromoethane: for f.p./compn. data and diag. see (138).

 $\ddot{C}+CHI_3$: for f.p./compn. data see (45). — $\ddot{C}+EtI$: for vap. press., liq.-vapor equil., and $n_0^{25.2}$ see (65).

 \bar{C} + CS_2 : for f.p./compn. data (147), study of distn. (164) (168), D_{20}^{20} /compn. (164), D_{25}^{25} /compn. (12), and n_D^{15} /compn. (168) see indic. refs.

TERNARY SYSTEMS CONTAINING C (See also azeotropes containing C)

 \bar{C} + MeOH (1:6120) + aq.: for studies of phase relations (169) cf. (170) and colloidal character (171) see indic. refs. $-\bar{C}$ + EtOH (1:6130) + aq.: for data on soly. relations incl. density and refractive indices see (173) cf. (170). $-\bar{C}$ + EtOH (1:6130) + C_6H_6 (1:7400): for data on vap. press. see (148). $-\bar{C}$ + EtOH (1:6130) + glycerol (1:6540): for study of soly. relations see (172). $-\bar{C}$ + n-PrOH (1:6150) + aq.: for data and diags. of soly. relations at 20°, and n_D^{25} /compn, see (66) cf. (170). $-\bar{C}$ + AcOH (1:1010) + C_6H_6 (1:7400): for data on density and n_D^{25} see (68); for vap. press. data see (2). $-\bar{C}$ + toluene (1:7405) + 1,2-dibromoethane: for extensive study see (4) (174). $-\bar{C}$ + Cl_2Cl_2 (3:5020) + $CHCl_3$ (3:5050): for f.p./compn. data (ternary cutectic, f.p. -111.4° , conts. 13 wt. % \bar{C} + 60 wt. % CH₂Cl₂ + 27 wt. % CHCl₃) see (46).

BINARY AZEOTROPES CONTAINING C

 $\overline{C} + MeOH$ (1:6120): \overline{C} forms with MeOH a const.-boilg. mixt., b.p. 55.70° at 760 mm., contg. 79.44 wt. % = 44.5 mole % \bar{C} (175), b.p. 54.4° at 734 mm., contg. 77 wt. % \bar{C} (176), b.p. 54.2° at 718 mm., contg. 79 wt. % \bar{C} (176); cf. also (177) (178). $-\bar{C} + EtOH$ (1:6130); C forms with EtOH a const.-boilg mixt, b p. 64.95° (175), 65 08° (179) at 760 mm., contg. 84.15 wt. % = 61.3 mole % (175) \overline{C} ; cf. also (180) (181); for effect of press. on this azeotrope see (182). $-\bar{C} + n\text{-}PrOH$ (1:6150): \bar{C} forms with n-PrOH a const-boilg. mixt., b.p. 72.8° (175), 73.1° (179) at 760 mm., contg. 88.5 wt. % = 75 mole % (175) \overline{C} ; cf. also (183). — \bar{C} + isoPrOH (1:6135): \bar{C} forms with isopropyl alc. a const.-boilg. mixt., b.p. 67.5° (175), 68.95° (184), contg. about 82 wt. % (175) (184) = 64 mole % \bar{C} ; cf. also (183) $-\bar{C}$ + n-BuOH (1:6180): C forms with n-butyl alc. a const.-boilg. mixt., b.p. 76.55° at 760 mm., contg. 97.5 wt. % \bar{C} (179). — $\bar{C} + isoBuOH$ (1:6165): \bar{C} forms with isobutyl alc. a const.boilg. mixt., b.p. 75.8° at 760 mm., contg. 94 5 wt. % = 89 mole % C (175) cf. (183) (186). — \ddot{C} + ter-BuOH (1:6140): \ddot{C} forms with ter-butyl alc. a const.-boilg mixt., b.p. 69 5° (175), 70.5° (185) at 760 mm., contg. 83 wt. % (175), 76 wt. % (185) \overline{C} . \overline{C} + ter-AmOH (1:6160): C forms with dimethyl-ethyl-carbinol a const.-boilg. mixt., b.p. about 76° at 760 mm., contg. about 95 wt. % C (185). — \ddot{C} + allyl alcohol (1:6145): \ddot{C} forms with allyl alc. a const.-boilg. mixt., b.p. 72.5°, contg. 79.5 mole % C (187).

 \bar{C} + acetone (1:5400): \bar{C} forms with acetone a const.-boilg. mixt, b.p. 55.9° at 763 mm. (188), about 56° at 760 mm. (185), contg. about 11.5 wt. % (185) \bar{C} . — \bar{C} + methyl ethyl ketone (1:5405): \bar{C} with methyl ethyl ketone forms a const.-boilg. mixt., b.p. 73.8° at 760 mm., contg. 71 wt. % = 53.4 mole % (175) \bar{C} .

 $\bar{C} + AcOH$ (1:1010): \bar{C} forms with AcOH a const.-boilg. mixt., b.p. about 77° at 760 mm., contg. about 97 wt. % \bar{C} (189).

 \ddot{C} + EtOAc (1:3015): \ddot{C} forms with ethyl acetate a const.-boilg. mixt., b.p. 74.75° at 760 mm. (175) (190), contg. 57 wt. % \ddot{C} (190); b.p. 76.15° at 789.2 mm. contg. 55.6 mole % \ddot{C} (191); b.p. 71.56° at 685.0 mm. contg. 58.2 mole % \ddot{C} (27); b.p. 66.72° at 583.7 mm. contg. 60.75 mole % \ddot{C} (191); b.p. 61.32° at 484.5 mm. contg. 63.75 mole % \ddot{C} (191); b.p. 55.22° at 385.2 mm. contg. 67.75 mole % \ddot{C} (191); b.p. 47.36° at 285.7 mm. contg. 72.6 mole % \ddot{C} (191): for study of thermodynamics of system see (193). — \ddot{C} + methyl propionate (1:3020): \ddot{C} forms with methyl propionate a const.-boilg. mixt., b.p. 75.5° at 760 mm.,

contg. 60 wt. % = 46 mole % (175); b.p. 76° at 760 mm. contg. about 75 wt. % (194) \overline{C} . — \overline{C} + n-Pr formate (1:3030): \overline{C} forms with n-propyl formate a const.-boilg. mixt., b.p. 74.6° at 760 mm., contg. about 69 wt. % \overline{C} (184).

 \bar{C} + nitromethane: \bar{C} forms with nitromethane a const.-boilg. mixt., b.p. 71.3° at 760 mm., contg. about 83 wt. % \bar{C} (184). — \bar{C} + 1,2-dichloroethane (3:5130): \bar{C} forms with ethylene dichloride a const.-boilg. mixt., b.p. 75.30° at 760 mm., contg. about 70 mole % \bar{C} (49) cf. (159); b.p. about 76° at 760 mm. contg. 79 wt. % \bar{C} (185).

TERNARY AZEOTROPES CONTAINING Č

 $\bar{C} + EtOH~(1:6130) + aq.$: this system forms a ternary two-phase const.-boilg. mixt., b.p. 61.8° at 760 mm. (181) (175), contg. 86.3 wt. % = 57.6 mole % $\bar{C} + 10.3$ wt. % = 23.0 mole % EtOH~+ 3.4 wt. % = 19.4 mole % aq.; for use of this azeotrope in detn. of water content of wood see (195). $-\bar{C} + n-PrOH~(1:6150) + aq$: this system forms a ternary two-phase const.-boilg. mixt., b.p. 54 4° at 760 mm , contg. 54 4 mole % $\bar{C} + 18.0$ mole % n-propyl alc. + 27.6 mole % aq. (175). $-\bar{C} + allyl~alc.~(1:6145) + aq.$: this system forms a const.-boilg. mixt., b.p. 65.4° at 760 mm., contg. 90.43 wt. % = 64.5 mole % $\bar{C} + 5.44$ wt. % = 10 4 mole % allyl alc. + 4.13 wt. % = 25.1 mole % aq. (187); b.p. 65.15° at 760 mm. contg. 53 8 mole % $\bar{C} + 18.7$ mole % allyl alc. + 27.5 mole % aq. (175). $-\bar{C} + ter-BuOH~(1:6140) + aq$: this system forms a const.-boilg. mixt., b.p. 64.7° at 768 mm., contg. about 85 wt. % $\bar{C} + 11.9$ wt. % ter-BuOH + 3.1 wt. % aq. (188).

 \ddot{C} + methyl ethyl ketone (1:5405) + aq: this system gives a const.-boilg. mixt., b.p. 65.7° at 760 mm, contg. 76 9 wt. % \ddot{C} + 20.1 wt. % methyl ethyl ketone + 3.0 wt. % aq. (188); for use of this azeotrope in detn. of water in wood see (195).

OTHER SELECTED PHYSICAL CHARACTERISTICS OF C

[For studies of thermal conductivity of \bar{C} see (196) (197) (198); for studies of heat capacity of \bar{C} (39) (15) (183) as calcd. from spectroscopic data (199) (200) see indic. refs.; for studies of specific heat of \bar{C} see (21); for studies of heat of fusion and/or of transition see (39) (15) (36) (86) (157); for studies on ebullioscopic const. of \bar{C} , viz., 4.88° (201), 4.68° (202) per mole solute in 1000 g. \bar{C} , see indic. refs.; for studies on cryoscopic const. of \bar{C} , viz., 29.9° (203), 29.8° (204) per mole solute in 1000 g. \bar{C} , see indic. refs.]

[For studies of adsorption of \bar{C} on various carbons (205) (206) (207) (208) (209) (210) (211) (212) (213) at low press. (214) (215), animal charcoal (216), wood or cocoanut charcoal (217) (218) (219) (220) (221) (222) (223) (224), alumina gel (225) (226), silica gel (227) (224) (228), Fe (OH)₃ gel (229) (230), Cr (OH)₃ gel (231), TiO₂ gel (232), or mica (233) see indic. refs.]

PHYSIOLOGICAL ASPECTS OF C

 \bar{C} (as vapor) does not cause acute poisoning until exposure for 30 min. to concns. of 1000–1500 p.p.m. (234) but constant exposure to concns. above 100 p.p.m. (234) (235) or even 50 p.p.m. (236) will cause serious physiological disturbances. The least concn. of \bar{C} in air detectable by odor is 71.8 p.p.m. (237). For further studies of toxicity and industrial hygiene of \bar{C} see (238) (239) (240); for study of comparative toxicity of \bar{C} and 1,1,2-trichloroethylene (3:5170) see (241).

USES OF C

 \bar{C} is widely used as solvent, fire extinguisher, fumigant, anthelmintic, etc.; although any detailed survey of these aspects is beyond the scope of this book, a few special uses are cited. [For study of use of \bar{C} as solvent for ozonization see (24); for use in concn. of HNO₃ (242)

or AcOH (243) or in drying of higher alcs. (244) see indic. refs.; for use of molecular compound (245) of \tilde{C} with rotenone in extraction (245) and detn. (246) (247) (248) of rotenone see indic. refs.]

DETECTION OR DETERMINATION OF C

Detection of \bar{\mathbb{C}}. [For detection of $\bar{\mathbb{C}}$ in pres. of CHCl₃ (3:5050) q.v. by methods based on differences in aq. soly. (249), or on solv. power for papaverine HCl (250) or quinine sulfate (251), or on color reactions with pyrocatechol (1:1520) (252) (253), α -naphthol (1:1500) (254) cf. (255), or 2,7-dihydroxynaphthalene (255) cf. (254) (for further details on last two see at end of text of this compd. under \mathfrak{P}), see indic. refs. For review of literature of tests for $\bar{\mathbb{C}}$ see (256).]

Note that C does not (251) reduce Fehling soln. [dif. from CHCl₃ (3:5050)].

Determination of \bar{C} . Methods for the detn. of \bar{C} are based upon both physical and chemical procedures or combinations of the two.

Physical methods include those based upon adsorption of \bar{C} , e.g., on activated carbon (257) or silica gel (258); by thermal conductivity of vapor of \bar{C} (259); by measurement of vapor press. (260); or on interference refractrometry (234).

Chemical methods include those based upon decompn. of \bar{C} by combustion and/or hydrolysis followed by detn. of HCl or of chloride ion, or those based upon color reactions. [For examples of methods based upon combustion followed by detn. of HCl (261) (262) (263) (264) (265) (266) (267) (268) (279) (for combustion in H_2 see (269)); methods based upon hydrolysis with alc. alk. (270) (271) (272) or reduction with Na + ethanolamine (273) (274) followed by detn. of chloride ion; or methods based upon use of color (Fujiwara) reaction with pyridine + alkali (275) (276) (277) (278) see indic. rcfs.]

DETECTION OF OTHER COMPOUNDS IN C

[For studies on removal of CHCl₃ (3:5050) from \bar{C} by digestion with Fehling soln. at 60-70° for several hrs. (280); on detection in \bar{C} of CS₂ by addn. of MeOH (1:6120) and formn. of CS₂/MeOH azeotrope of b.p. 37.1° at 751 mm. (188) or by use of xanthate reaction (281); on removal of CS₂ from \bar{C} by use of alc. hydrazine hydrate (282) see indic. refs.; for detection in \bar{C} of carbonyl chloride see (283) (284) (285) (286) and also under phosgene (3:5000).]

PREPARATION OR FORMATION OF C

The principal methods of prepn. of \tilde{C} are those involving chlorination of CS_2 or of hydrocarbons, but many other procedures have been studied as exemplified below.

From carbon disulfide. [Prepn. of \tilde{C} from CS_2 by action of Cl_2 was first effected (287) by passage through red-hot tube; in subsequent development of this method use of various catalysts has been found to reduce the required temperature. The overall reaction is believed to occur in two stages, viz., (1) $CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$ and (2) $CS_2 + 2S_2Cl_2 \rightarrow CCl_4 + 6S$. The resultant sulfur may be recovered and used again in prepn. of CS_2 .]

[For an extensive account of prepn. of \bar{C} prior to 1906 see monograph of Margosches (288); for longer summary as of 1938 see (289); for still later patents and articles on use of Cl₂ (290) (291) (292) (293) (294) (295) or various sulfur chlorides (296) (297) (298) (299) see indic refs.]

[For studies on use of various catalysts, e.g., Br₂ (300), I₂ (301), I₂ + Fe (302), MoCl₅ (303), SbCl₅ (304), or FeCl₃ (304), see indic. refs.; note that CS₂ reacts with SbCl₅ even without addn. of Cl₂ to give \bar{C} (305).]

[Note that in chlorination of CS₂ with restricted amts. Cl₂ various intermediate carbon chlorosulfides have been detected (306) (307).]

From methane. The formation of \bar{C} , together with CH₃Cl (3:7005), CH₂Cl₂ (3:5020), CHCl₃ (3:5050), and other products, has been very extensively studied from many viewpoints. The literature of this reaction is diffuse and interlocked with that of methane and of the various other chlorination products. For this reason and because detailed treatment of this topic is beyond the scope of this book, the following citations must be regarded only as leading references.

[The form. of \bar{C} from CH_4 by action of Cl_2 was first discovered in 1840 by Dumas (308). For examples of more recent technical papers ((309)–(317), incl.) and patents ((318)–(332), incl.) see indic. refs.]

From other hydrocarbons. [For examples of patents on prepn. of \tilde{C} from aliph. hydrocarbons higher than methane (including in some cases also their halogen derivatives) see (313) (333) (334) (335) (336) (337). — For prepn. of \tilde{C} from acetylene + Cl_2 + cat. at 100-200° (338) or with Cl_2 + eutectic of $AlCl_3/NaCl/FeCl_3$ at 175-200° (339) see indic. refs. (see also below under prepn. of \tilde{C} from tetrachloroethylene). — For prepn. of \tilde{C} from naphthalene by destructive chlorination see (340).]

From various chloro and polychloro compounds. [For technical papers on prepn. of Č from chlorinolysis of various chloro and polychloroparaffins (341) or chloropentanes (342) see indic. refs.]

[For patents on prepn. of \bar{C} from tetrachloroethylene (3:5460) with Cl_2 at 700-800° (343) or with Cl_2 over activated carbon at 600-650° (337) see indic. refs.; for study of this reaction see (344). For formn. of \bar{C} from hexachloroethane (3:4835) pyrolyzed in air at 550-600° see (342).]

[For prepn. of \bar{C} from CHCl₃ (3:5050) by chlorination with Cl₂ in sunlight (first prepn. of \bar{C}) (345) or u.v. light (346) (347) (348) (349), at 260-300° (350), or in pres. of FeCl₃ (351) or of aq. (352), or from CHCl₃ with ICl at 165° (353), or with NaOCl (reaction very slow and incomplete (354)), see indic. refs.]

[For formn. of C from CFCl₃ with AlCl₃ see (355); from CBrCl₃ with Cl₂ in dark at 100° (356) or in light (357) (358) see indic. refs.]

From miscellaneous sources. [For formn. of C from charcoal or other form of carbon + Cl₂ see patents (359) (361) and technical papers (344) (360); from trichloroacetyl chloride (3:5420) on htg. with AlCl₃ (362) or pyrolysis through glass tube at 600° (363), from trichloromethyl chloroformate (3:5515) on htg. with AlCl₃ (364), from chloral (3:5210) with Cl₂ in sunlight (365), or from acetone (1:5400) with NaOCl soln. (366) cf. (354), or from phosgene (3:5000) on htg. with cat. (344) cf. (372), see indic. refs.]

[For formn. of \bar{C} from dimethyl sulfide [Beil. I-288, I₁-(144), I₂-(276)] with Cl₂ + I₂ at 100-120° in daylight see (367) (368) (369); from trichloromethyl sulfur chloride ("perchloromethyl mercaptan") [Beil. III-135, III₁-(63), III₂-(106)] on htg. with Fe filings or ZnF₂ (370) cf. (307) (371) or with Cl₂ + I₂ in sunlight (370) see indic. refs.; from thiophosgene [Beil. III-134, III₁-(63), III₂-(105)] with Fe at 37° for many months or from "trichloromethyl dithiochloroformate" [Beil. III-215, III₂-(155)] with Fe in s.t. at 100° see (307).]

CHEMICAL BEHAVIOR OF C

Pyrolysis of Č. [C̄ on pyrolysis at 600-1500° (373) (374) cf. (344) (375) (376) gives tetrachloroethylene (3:5460) (80% yield (374)), hexachloroethane (3:4835), and other products. C̄ by action of electric arc (377) cf. (378), dark electric discharge (in H₂) (379), radium emanation (380), gives hexachloroethane (3:4835) and various other products.]

[Note also that \bar{C} in X-radiation (381) (382) or ultrasonic radiation (383) splits off some Cl₂. For action of X-radiation on mixts. of \bar{C} with aq., CHCl₃, CHI₃, lgr., or cyclohexane see (381) (384); for decompn. of \bar{C} in u.v. light below 2750 Å see (385).]

Oxidation of C. C under various oxidizing conditions yields phosgene and other products. [E.g., C with O₂ in light of 2537 Å (386) or with atomic oxygen (387) gives carbonyl chloride (3:5000); C with O₂ over white-hot Pt (375), or with air over CuCl₂ or FeCl₃ at elev. temp. (388), or C over GeO₂ (389), or C with pyrosulfuryl chloride (1 mole) + sulfuric acid monohydrate (2 moles) on warming (390) (391) (392) (393) gives phosgene (3:5000). For formn. of phosgene (3:5000) q.v. during thermal decompn. of C (as in use as fire extinguisher) see (394), also below under behavior of C with metals.] [Note that C, unlike CHCl₃ (3:5050), is not oxidized by Fehling soln.]

Reduction of C. [\bar{C} with K/Hg + aq. gives (395) methane; \bar{C} with Fe(OH)₂ + aq. alk. gives (396) CH₂Cl₂ (3:5020) + CHCl₃ (3:5050); \bar{C} with Zn + H₂SO₄ (397) (398), finely divided Fe + aq. (399) + cat. (400) (401), or on electrolytic reduction (402) gives CHCl₃ (3:5050). For behavior of \bar{C} with atomic hydrogen see (403).]

[Note that $\tilde{C} + H_2$ over pumice in hot tube gives (404) CHCl₃ (3:5050), CH₂Cl₂ (3:5020), tetrachloroethylene (3:5460) + hexachloroethane (3:4835), and at red heat (395) methane and ethylene. \tilde{C} with excess H_2 over reduced Ni at 270° gives (405) hexachloroethane (3:4835) + HCl.]

Substitution of \bar{C} . \bar{C} by reaction with F_2 , metallic fluorides, or HF, etc., each in the presence of appropriate catalysts, undergoes replacement of one or more of its chlorine atoms by fluorine and consequent formation of mixed derivatives such as CCl_3F , CCl_2F_2 ("Freon" = "Freon-12" "F-12"), $CClF_3$, etc., to whose properties as refrigerants, etc., much attention is currently being given. [Detailed analysis of the conversion of \bar{C} to these materials is far beyond the scope of this book, but for examples of leading technical papers (406) (407) (408) (409) (410) (411) and patents ((412)-(429)) see indic. refs.] (See also below under behavior of \bar{C} with inorganic salts.)

Hydrolysis of \tilde{C} . [\tilde{C} with aq. on long exposure (e.g., 7 months (430)) to sunlight gives $CO_2 + HCl$; \tilde{C} with large excess of aq. in s.t. at 250° also gives $CO_2 + HCl$, but \tilde{C} with very small proportion of aq. under same conditions gives (431) some phosgene (3:5000). At ord. temp. hydrolysis of \tilde{C} by pure aq. is scarcely perceptible, but in presence of Fe, Cu, acid, or alkali, hydrolysis is strongly accelerated especially at higher temperatures (432). \tilde{C} is hydrolyzed by aq. + reduced Fe but not by aq. NaHCO₃ (342) under reflux.]

[\bar{C} with boilg. alc. alk. is eventually completely hydrolyzed (use in detn. of \bar{C} by estimation of resultant chloride ion (see above)); however, reaction is slow and with N aq. or alc. KOH or NaOEt at 60° is very slight in 2 hrs. (433). For study of rate of hydrolysis of \bar{C} with KOH in 95% alc. (434) cf. (435), or with Ba(OH)₂ or TlOH in 50% alc. (436), see indic. refs.]

Behavior of \bar{C} with inorganic salts. [\bar{C} with AlBr₃ at room temp. for 3 days gives (358) CBrCl₃ [Beil. I-67, I₂-(31)], b.p. 104.2-104.35° at 758.5 mm. (358), but \bar{C} with AlBr₃ at 60° gives (437) cf. (438) CBr₄ [Beil. I-68, I₁-(17), I₂-(35)], m.p. 94°, b.p. 189.5° at 760 mm. with slight decompn. (439).]

[\bar{C} with AlI₃ (440), Al + I₂ in CS₂ (441), CaI₂ + 2H₂O or LiI + 1.5H₂O in evacuated s.t. at 90-92° for 5 days (50-55% yield (442)) (443), with BI₃ (444), or \bar{C} (1 mole) + C₂H₅I (4 moles) + AlCl₃ (0.1 mole) (445), or best \bar{C} (0.7 mole) with CH₃I (2.94 moles) + AlCl₃ (0.015 mole) at 40° (92% yield (446)) gives carbon tetraiodide, CI₄ [Beil. I-74, I₁-(19), I₂-(39)].]

Č with alc. AgNO₃ does not react even after several days; note that in this respect Č behaves like CH₂Cl₂ (3:5020) and CHCl₃ (3:5050) while CH₃Cl (3:7005) gives a ppt. within 3 hrs. (446).

Behavior of $\tilde{\mathbb{C}}$ with metals. $\tilde{\mathbb{C}}$ with alkali or even alkaline-earth metals undergoes explosive decompn. on htg. or even at room temp. if subjected to sufficient mechanical shock. [For studies on the explosion of $\tilde{\mathbb{C}}$ with alkali metals see (477) (448); for further studies on explosion of $\tilde{\mathbb{C}}$ with Li, Na, K, Ca, Sr, Ba, Mg, Al, and Tl, expecially with reference to sensitivity to mechanical shock, see (449). — For behavior of $\tilde{\mathbb{C}}$ with Na vapor see (450); for rate of reaction of $\tilde{\mathbb{C}}$ with Na atoms see (451); for study of $\tilde{\mathbb{C}}$ + Na/Hg as means of sepn. of isotopes of chlorine see (452) cf. (453).]

[For study of hazards of behavior of $CCl_4/CHCl_3$ mixts. with Mg (454) (455) or Al (454) see indic. refs.; note also that \bar{C} refluxed with Al powder (456) or Al/Hg (457), or \bar{C} with Al + AlCl₃ at 60-75° (458), or \bar{C} with Cu powder at 120° (458) or molecular Ag at 200° (431) gives (yields: 80% (456), 65% (457)) hexachloroethane (3:4835).]

Note that C with Mg in boilg, ether does not react, even in the presence of various catalysts (459).

[For extensive study of corrosion of metals by \tilde{C} (460) cf. (461) (462) (463) (432) see indic. refs.]

Behavior of \bar{C} with other inorganic reactants. [\bar{C} is claimed to be unaffected by conc. H_2SO_4 at 237° (464) although over H_2SO_4 on pumice at 150° \bar{C} is reported (465) to give HCl, SO_2 , $COCl_2 + CO_2$.]

[For study of photochem. reaction of \tilde{C} with H_2S giving hexachloroethane (3:4835) + S + CCl_3SH see (466); for studies on photochem. decompn. of Cl_2O in \tilde{C} see (467) (468) (469) (470) cf. (471); for behavior of \tilde{C} with Br_2O giving phosgene (3:5000) + Cl_2 + Br_2 see (472).]

[\bar{C} with NH₃ under high press. in pres. of Cu + I₂ at 140° for 17 hrs. gives (35–40% yield (473)) guanidine hydrochloride [Beil. III 82, III₁-(39), III₂-(69)]. — \bar{C} with hydrazine hydrate in stream of NH₃ refluxed for several days gives (poor yield (474)) N,N',N''-triaminoguanidine [Beil. III-122, III₁-(57), III₂-(97)], as monohydrochloride, m.p. 228° dec.]

Behavior of \bar{C} with organic reactants. With carbon monoxide. $[\bar{C}$ with CO + AlCl₃ at 200° and 250 atm. for 6 hrs. gives (37% yield (475)) trichloroacetyl chloride (3:5420).]

With hydrocarbons. [Č (excess) with octene-1 (1.8375) in pres. of small amts. (0.02 mole) of dibenzoyl peroxide (or diacetyl peroxide) adds to unsatd. linkage giving (476) 1,1,1,3-tetrachlorononane; under similar conditions C adds to one of the unsatd. linkages of diallyl (1:8045) giving 5,7,7,7-tetrachloroheptene-1 or to both giving 1,1,1,3,6,8,8,8-octachloro-octane. — For other addns of C to olefin linkages see below.]

[\bar{C} with C_6H_6 in pres. of AlCl₃ gives according to conditions triphenylchloromethane (3:3410) (477), triphenylmethane (1:7220) (478), or benzophenone (1:5150) (479). Other arom, hydrocarbons and aryl halides behave similarly but cannot be detailed here.]

With saturated halohydrocarbons. Č (0.7 mole) with MeI (2.94 moles) + AlCl₃ (0.015 mole) at 40° gives (92% yield (446)) carbon tetraiodide (see also above under behavior of Č with inorganic salts). — Č with CBr₄ in pres. of slightly moistened AlCl₃ at 170° for 7 hrs. undergoes a redistribution reaction giving (480) an equil. mixt. of CCl₄, CCl₃Br, CCl₂Br₂, CClBr₃, and CBr₄.]

With unsaturated halohydrocarbons. [C with ord. 1,2-dichloroethylene (3:5030) + AlCl₃ gives (481) (482) cf. (483) 1,1,1,2,3,3-hexachloropropane (3:6460); for reaction of this system yielding heptachloropentenes see (483).]

[\bar{C} with trichloroethylene (3:5170) + AlCl₃ at 20-30° for 48 hrs. gives (49% yield (484)) (481) (482) 1,1,1,2,3,3,3-heptachloropropane (3:6860).]

With alcohols or alcoholates. [C with MeOH over cat. at 200-350° gives (485) MeCl (3:7005); C with EtOH under similar circumstances gives EtCl (3:7015).]

[C with NaOCH₃ would be expected to yield tetramethyl orthocarbonate [Beil. III₂-(4)],

b.p. 112-113° at 724 mm. (486), $n_D^{19} = 1.3841$ (486), but this reaction is unreported, the expected prod. having been made only by other methods. — \bar{C} with NaOC₂H₅ would be expected to yield tetraethyl orthocarbonate [Beil. III-5, III₁-(4), III₂-(5)], b.p. 157-158° (487), 59.6-60° at 14 mm. (486), $D_4^{18.5} = 0.9197$ (488), $n^{18.5} = 1.39354$ (488), but this reaction is unreported cf. (505); however, the prod. has been prepd. from CBr₄ with NaOEt in dry ether in s.t. at 170° (487), from "thiocarbonyl tetrachloride," CSCl₄ cf. (489) refluxed in dry ether with NaOEt, and in other ways]

With mercaptans or mercaptides. [\bar{C} with NaSCH₃ might be expected to give tetramethyl tetrathioorthocarbonate, C(SCH₃)₄, but this appears to be unreported; \bar{C} with NaSCH₃ has been found (492) to react differently giving trimethyl trithioorthoformate [Beil. II₁-(39)], m.p. 16° (493), b.p. 220° dec. (493), 103–104° at 12 mm. (492), 96° at 9 mm. (493), $n_D^{15} = 1.5696$ (492), and dimethyl disulfide, b.p. 39–41° at 18 mm. (492). — \bar{C} with NaSC₂H₅ is claimed (491) to give the expected homologous tetracthyl tetrathioorthocarbonate C(SC₂H₅)₄, but this material was not well characterized, and \bar{C} with NaSC₂H₅ has subsequently (492) been found to give triethyl trithioorthoformate [Beil. II-95, II₁-(39)], b.p. 235° dec. (493), 174° at 760 mm. (494), $D_D^{20} = 1.053$ (495), $n_D^{15} = 1.5410$ (492). — For behavior of \bar{C} with salts of n-propyl, n-butyl, and ter-butyl mercaptans see (492).]

With phenols or phenolates. [\bar{C} with phenol (1:1420) in pres. of $ZnCl_2 + ZnO$ at 120° gives (496) diphenyl carbonate (1:2335), various dihydroxybenzophenones, and other products; for analogous study of \bar{C} with o-cresol (1:1400) see (497).

[C with K phenolate at 170° gives mainly (498) aurin (pararosolic acid) (4',4''-dihydroxy-fuchsone) [Beil. VIII-361, VIII₁-(671)]; for analogous behavior of C with K o-cresolate and K m-cresolate see (498).]

With diacyl peroxides. [C refluxed with di-n-butyryl peroxide for 17 hrs. gives (499) n-propyl chloride (3:7040) + hexachloroethane (3:4835) + ethyl n-butyrate (1:3127); C refluxed similarly with di-n-isobutyryl peroxide gives (499) isopropyl chloride (3:7025) + hexachloroethane (3:4835) + ethyl isobutyrate (1:3095).]

[$\bar{\mathbf{C}}$ with di- α -naphthyl peroxide under reflux gives (500) CO₂, α -chloronaphthalene (3:6878), α -naphthoic acid (1:0785), and other products; $\bar{\mathbf{C}}$ with di- β -naphthyl peroxide under reflux gives (500) CO₂, β -chloronaphthalene (3:1285), β -naphthoic acid (1:0800), and other products.]

[Č with dibenzoyl peroxide under reflux gives (501) (502) (503) 4-(trichloromethyl)-benzoic acid, hexachloroethane (3:4835), phosgene (3:5000), chlorobenzene (3:7903), and other products; for study of kinetics of reaction see (504).]

With salts of enolic esters. [\bar{C} with diethyl sodio-malonate (505) (507) or with diethyl disodio-malonate (506) (507) (508) (509) gives the Na enolate of tetraethyl α,γ -dicarboxy-glutaconate, (C₂H₅OOC)₂C=CH—CH(COOC₂H₅)₂ [Beil. II-876, II₁-(336), II₂-(710)], b.p. 208-210° at 23 mm. (510), 200-204° at 18 mm. (510); note that this product is also obtd. from CHCl₃ (3:5050) with diethyl sodio-malonate (505) (511) (512) (513) (514) (515) (516) (517).]

[C with 4 moles of Na enolate of ethyl cyanoacetate in alc. at 100° gives (505) cf. (508) the sodium enolate of diethyl α , γ -dicyanoglutaconate, C_2H_5OOC —C(CN)—CH—CH- $(CN)COOC_2H_5$ [Beil. II-878, II₂-(712)], also obtd. from $CHCl_3$ (3:5050) with the Na enolate of ethyl cyanoacetate (518) (519) (520).]

With amines. The behavior of \bar{C} with amines has been little studied. [For studies on the behavior of \bar{C} with aniline (521) and also with other aromatic amines in pres. of Cu powder (522) or I₂ (523) see indic. refs.]

Color reaction with α-naphthol/cyclohexanol. C
 (1 drop) with 2 ml. of a 2% soln. of α-naphthol (1:1500) in cyclohexanol (1:6415) + 1 pellet of solid NaOH, boiled

- 25 seconds and cooled, gives (254) blue color; one portion of this blue solution underlaid with equal volume 85% $\rm H_2SO_4$, stood 1 min. and shaken, remains blue; a second portion of the alkaline blue soln. acidified with equal vol. AcOH (1:1010), stood 1 min. and shaken, becomes red. [Note that the alkaline boilg. also gives a blue color with $\rm CH_2Cl_2$ (3:5020) and with CHCl₃ (3:5050), while other chlorinated solvents (254) give yellow-brown, gray, or brown; in the $\rm H_2SO_4$ acidification $\rm CH_2Cl_2$ (3:5020) gives greenish blue, while both CHCl₃ (3:5050) and $\rm \bar C$ give intense blue; in the AcOH acidification $\rm CH_2Cl_2$ (3:5020) gives yellow while CHCl₃ (3:5050) gives an orange-yellow color.]
- ② Color test with 2,7-dihydroxynaphthalene/cyclohexanol. C

 ☐ (1 drop) with 2 ml. pure cyclohexanol (1:6415) + 1 pellet NaOH + a few mgms. 2,7-dihydroxynaphthalene htd. at 197° (b.p. of ethylene glycol) for 45 seconds, decanted from undissolved NaOH, cooled, and shaken with 2 ml. AcOH + 4 ml. 96% EtOH, gives a pale yellow-brown color (255). [Note that under these conditions CH₂Cl₂ (3:5020) gives a steel-blue color while CHCl₃ (3:5050) gives a deep red color.]
- ② Color test with cyclopentanol. C (1 drop) in 1 ml. cyclopentanol (1:6412) + 1 pellet NaOH boiled 25 seconds, then shaken vigorously for 35 seconds, and treated with 4 ml. 96% EtOH and shaken, gives an intense brown color (255). [Note that, after addition of alc., CH₂Cl₂ (3:5020) gives a more intense red or becomes reddish brown while CHCl₃ (3:5050) gives only a pale citron-yellow. By comparing with authentic known samples, this test is claimed (255) to be able to detect as little as 5% C in CHCl₃.]
- 3:5100 (1) Biltz, Sapper, Z. anorg. allgem. Chem. 203, 283, 285 (1932). (2) McMillan, McDonald, J. Phys. Chem. 49, 10-20 (1945). (3) McMillan, McDonald, Ind. Eng. Chem. 36, 1175-1176 (1944). (4) Schultze, J. Am. Chem. Soc. 36, 498-513 (1914). (5) Bowden, Butler, J. Chem. Soc. 1939, 79-83. (6) Timmermans, Bull. soc. chim. Belg. 24, 244-269 (1910); Cent. 1910, II 442. (7) Timmermans, Martin, J. chim. phys. 23, 766-768 (1926). (8) Gross, Saylor, J. Am. Chem. Soc. 53, 1747-1748 (1931). (9) Thorpe, J. Chem. Soc. 37, 199 (1880). (10) Grimm, Z. physik. Chem. A-140, 326-329 (1929).
- (11) Mathews, J. Am. Chem. Soc. 48, 570 (1926). (12) Linebarger, Am. Chem. J. 18, 439-442 (1896). (13) Zmaczynski, Roczniki Chem. 16, 486-501 (1936); C.A. 31, 3355 (1937): Svensk Kem. Tid. 48, 268-273 (1936); Cent. 1937, I 2762; [C.A. 31, 2056 (1937)]. (14) Wcjciechowski, Nature 138, 1096 (1936). (15) Stull, J. Am. Chem. Soc. 59, 2726-2733 (1937). (16) Wood, J. Am. Chem. Soc. 59, 5151 (1937). (17) Biltz, Meinecke, Z. anorg. allgem. Chem. 131, 1-21 (1923). (18) Earp, Glasstone, J. Chem. Soc. 1935, 1711. (19) Young, J. Chem. Soc. 59, 912 (1891). (20) Perkin, J. Chem. Soc. 45, 532 (1884).
- (21) Williams, Daniels, J. Am. Chem. Soc. 46, 903-917, 1569-1577 (1924). (22) Hartung, Chem. News 116, 274 (1917). (23) Herz, Rathmann, Chem. Zig. 36, 1417 (1912). (24) Greenwood, J. Org. Chem. 10, 414-418 (1945). (25) Pawlewski, Ber. 16, 2633 (1883). (26) Schiff, Ann. 223, 72 (1884). (27) Schutz, J. Am. Chem. Soc. 61, 2691-2693 (1939). (28) Wald, Z. physik. Chem. 88, 141 (1914). (29) Wheat, Browne, J. Am. Chem. Soc. 60, 371-372 (1938). (30) Moles, Gomez, Z. physik. Chem. 80, 526 (1912).
- (31) Cornog, Olson, J. Am. Chem. Soc. 62, 3328-3330 (1940); Proc. Iowa Acad. Sci. 46, 198 (1939). (32) Phipps, Reedy, J. Phys. Chem. 40, 97-98 (1936). (33) Skau, Meier, J. Am. Chem. Soc. 51, 3517-3519 (1929). (34) Skau, J. Phys. Chem. 37, 612 (1933). (35) Keyes, Townshend, Young, J. Math. Phys. 1, 305, 310 (1922). (36) Johnston, Long, J. Am. Chem. Soc. 56, 31-35 (1934). (37) Timmermans, van der Horst, Onnes, Cent. 1923, IV 377. (38) Sameshima, Hiramatsu, Bull. Chem. Soc. Japan 9, 260-262 (1934). (39) Hicks, Hooley, Stephenson, J. Am. Chem. Soc. 66, 1064-1067 (1944). (40) Timmermans, Bull. soc. chim. Belg. 25, 300-327 (1911), Cent. 1911, II 1015.
- (41) Deffet, Bull. soc. chim. Belg. 44, 62-63 (1935). (42) Michel, Bull. soc. chim. Belg. 48, 138 (1939). (43) Linard, Bull. soc. chim. Belg. 34, 369, 371 (1925). (44) Hrynakowski, Szmyt, Z. physik. Chem. A-182, 405-412 (1938). (45) van de Vloed, Bull. soc. chim. Belg. 48, 260, 262 (1939). (46) Kanolt, Sci. Papers U.S. Bur. Standards 20, 619-633 (1926). (47) Turkevich, Smyth, J. Am. Chem. Soc. 62, 2468-2474 (1940). (48) Nasu, Bull. Chem. Soc. Japan 8, 392-399 (1933); Science Repts. Tohoku Imp. Univ. (1) 22, 987-996 (1933). (49) Young, Nelson, Ind. Eng. Chem., Anal. Ed. 4, 67-69 (1932). (50) Stearn, Smyth, J. Am. Chem. Soc. 56, 1667 (1934).

(51) Brüll, Z. Electrochem. 38, 601-611 (1932).
(52) Nieuwenhuis, Z. Elektrochem. 39, 727-731 (1933).
(53) Nasu, Bull. Chem. Soc. Japan 8, 195-207 (1933); Science Repts. Tohoku Imp. Univ. (1) 22, 972-986 (1933).
(54) Hammick, Wilmut, J. Chem. Soc. 1934, 33.
(55) Grimm, Z. physik. Chem. B-2, 184-188 (1929).
(56) Kailan, Z. physik. Chem. 88, 86 (1914).
(57) Seatchard, Wood, Mochel, J. Am. Chem. Soc. 62, 712-716 (1940).
(58) Scatchard, Wood, Mochel, J. Am. Chem. Soc. 61, 3206-3210 (1939).
(59) Graffinder, Heymann, Z. Physik. 72, 755 (1932).
(60) Patterson, Thomson, J. Chem. Soc. 93, 371 (1908).

(61) Goss, J. Chem. Soc. 1937, 1920.
(62) Earp, Glasstone, J. Chem. Soc. 1935, 1709-1723.
(63) Biron, J. Russ. Phys.-Chem. Soc. 42, 169 (1910); Cent. 1910, I 1913.
(64) Grunert, Z. anorg. allgem. Chem. 164, 257 (1927).
(65) Zawidski, Z. physk. Chem. 35, 129-203 (1900).
(66) Denzler, J. Phys. Chem. 49, 358-365 (1945).
(67) Hubbard, Z. physk. Chem. 74, 228-229 (1910).
(68) McMillan, McDonald, Ind. Eng. Chem., Anal. Ed. 15, 114-116 (1943).
(69) Schwers, Bull. acad. roy. Belg., Classe des sci. 1912, 629; Cent. 1913, I 211.
(70) Beythien, Hennicke,

Pharm. Zentralhalle 48, 1006 (1907).

(71) Gladstone, J. Chem. Soc. 59 292-293 (1891).
(72) Young, Sci. Proc. Roy. Dublin Soc. 12, 427 (1909/10); C.A. 5, 406 (1911).
(73) Smyth, Engel, J. Am. Chem. Soc. 51, 2649 (1929).
(74) Baker, J. Chem. Soc. 121, 569-574 (1922); 1927, 949-958; 1928, 1051-1055; 1929, 1661-1664; J. Am. Chem. Soc. 53, 1810 (1931).
(75) Mali, Z. anoro. allgem. Chem. 149, 150-156 (1925).
(76) Balarew, J. prakt. Chem. (2) 116, 57-58 (1925).
(77) Lenher, Daniels, Proc. Natl. Acad. Sci. U.S. 14, 606-609 (1928).
(78) Lenher, J. Am. Chem. Soc. 51, 2948-2550 (1929).
(79) Lenher, J. Phys. Chem. 33, 1579-1582 (1929).
(80) Greer, J. Am. Chem. Soc. 52, 4191-4201 (1930).

(81) Williams, Ind. Eng. Chem., Anal. Ed. 18, 157-160 (1946). (82) Brull, Z. Elektrochem. 40, 8-10 (1934). (83) Brudgman, Phys. Ren. (2) 3, 175-180 (1914). (84) Bugarszky, Z. physik. Chem. 71, 710 (1910). (85) Wahl, Z. physik. Chem. 88, 141 (1914). (86) Latimer, J. Am. Chem. Soc. 44, 93 (1922). (87) McCullough, Phipps, J. Am. Chem. Soc. 50, 2213-2216 (1928). (88) Isnardi, Z. Physik 9, 158, 171-173 (1922). (89) Stranathan, Phys. Rev. (2) 31, 664 (1928).

(90) Wyatt, Trans. Faraday Soc. 25, 48-53 (1929).

(91) Rex, Z. physik. Chem. 55, 363, 365 (1906).
(92) Gross, Z. physik. Chem. B-6, 215-220 (1930).
(93) Staverman, Rec. trav. chim. 60, 836-841 (1941).
(94) Rosenbaum, Walton, J. Am. Chem. Soc. 52, 3568-3573 (1930).
(95) Niini, Suomen Kemistlehti II-A, 19-20 (1938); Cent. 1939, II 614; C.A. 32, 4861 (1938).
(96) Horiuchi, Bull. Inst. Phys. Chem. Research (Tokyo) 7, 119-172 (1928); English Ed. 1, 11-17 (1928); Cent. 1928, I 2770; C.A. 22, 3332 (1928), cf. ibid. 17, 125-256 (1931); C.A. 26, 2104-2105 (1932).
(97) Fischer, Pfleiderer, Z. anorg. allgem. Chem. 124, 68 (1922).
(98) Metschl, J. Phys. Chem. 28, 426, 428 (1924).
(99) von Wartenberg, von Podjaski, Z. anorg. allgem. Chem. 148, 395 (1925).
(100) Fischer, Tropsch, Ber. 50 765-767, (1917).

(101) Frölich, Tauch, Hogan, Ind. Eng. Chem. 23, 548-550 (1931). (102) Hamai, Science Repts. Tohoku Imp. Univ. (1) 25, 344-356 (1936); Cent. 1936, II 3784. (103) Bell, J. Chem. Soc. 1931, 1376-1377. (104) Hamai, Science Repts. Tohoku Imp. Univ. (1) 25, 357-363 (1936); Cent. 1936, II 3784. (105) Hamai, Bull. Chem. Soc. Japan 10, 5-16 (1935). (106) Howland, Miller, Willard, J. Am. Chem. Soc. 63, 2807-2811 (1941). (107) Klemenc, Spitzer-Neumann, Monatsh. 53/54, 417 (1929). (108) Jones, J. Chem. Soc. 99, 399 (1911). (109) Taylor, Hildebrand, J. Am. Chem. Soc. 45, 683 (1923). (110) Schwab, Hantko, Z. physik. Chem. 114, 251-256 (1925).

(111) Just, Z. physik. Chem. 37, 354 (1901). (112) Kunerth, Phys. Rev. (2) 19, 520 (1922). (113) Hildebrand, J. Phys. Chem. 43, 109-112 (1939). (114) Eugen Chirnoaga, Eugenia Chirnoaga, Z. anorg. allgem. Chem. 218, 273-300 (1934). (115) Brull, Ellerbrock, Z. anorg. allgem. Chem. 218, 273-300 (1934). (115) Brull, Ellerbrock, Z. anorg. allgem. Chem. 216, 353-366 (1934). (116) Horiuchi, Bull. Inst. Phys. Chem. Research (Tokyo) 9, 697-730 (1930); Abstracts, 69-75 (in English); C.A. 25, 3543 (1931). (117) Horiuchi, Bull. Inst. Phys. Chem. Research (Tokyo) 10, 374-401 (1931); Abstracts 41 (in English); C.A. 25, 5609 (1931). (118) Mamedaliev, Musakhanly, J. Applied Chem. (U.S.S.R.) 13, 735-737 (1940); C.A. 35, 314 (1941). (119) Baskerville, Cohen, J. Ind. Eng. Chem. 13, 333-334 (1921). (120) Kireev, Kaplan, Vasneva, J. Gen. Chem. (U.S.S.R.) 6, 799-805 (1936); Cent. 1937, II 755; C.A. 30, 7013 (1936).

(121) Jakowkin, Z. physik. Chem. 18, 590 (1895). (122) Hildebrand, Jenks, J. Am. Chem. Soc. 42, 2185 (1920). (123) Andre, Bull. soc. chim. (4) 33, 1643 (1923). (124) Margosches, Hinner, Friedmann, Z. anorg. allgem. Chem. 137, 81-90 (1924). (125) Biltz, Jeep, Z. anorg. allgem. Chem. 162, 44-45 (1927). (126) Waentig, McIntosh, Trans. Roy. Soc. Can. 9, III 203-209 (1916). (127) Oddo, Gazz. chim. ital. 32, II 149 (1901). (128) Hofmann, Kirmreuther, Thal, Ber. 43, 188 (1910). (129) Delaplace, J. pharm. chim. 26, 139-140 (1922); C.A. 16, 4110 (1922). (130) Hildebrand, Jenks, J. Am. Chem. Soc. 43, 2172-2175 (1921).

(131) Bond, Beach, J. Am. Chem. Soc. 48, 352-353 (1926); Proc. Iowa Acad. Sci. 32, 328 (1925). (132) Bilts, Bräutigam, Z. anorg. allgem. Chem. 162, 55-56 (1927). (133) Pascal, Bull. soc. chim.

(4) 33, 539-543 (1923). (134) Krakowiecki, Roczniki Chem. 10, 197-198 (1930); Cent. 1930, I 3424; C.A. 24, 2686 (1930). (135) Lloyd, J. Phys. Chem. 22, 302 (1918). (136) Bykov, J. Phys. Chem. (U.S.S.R.) 13, 1013-1019 (1939); C.A. 34, 4653 (1940). (137) Baud, Ann. chim. (8) 29, 135-138 (1913). (138) Linard, Bull. soc. chim. Belg. 34, 382-391 (1925). (139) Duncan, Koffolt, Withrow, Trans. Am. Inst. Chem. Engrs. 38, 259-281 (1942); C.A. 36, 3399 (1942). (140) Pesce, Tuozzi, Evdokimoff, Gazz. chim. ital. 70, 721-723 (1940); C.A. 35, 5367 (1941).

(141) Wood, Brusie, J. Am. Chem. Soc. 65, 1891-1895 (1943). (142) Anasov, Ann. secteur anal. phys. chim., Inst. chim. gén. (U.S.S.R.) 9, 255-270 (1936); Cent. 1937, I 3942; C.A. 30, 7994 (1936). (143) Schmidt, Z. physik. Chem. 121, 239, 240, 243 (1926). (144) Boissonnas, Cruchaud, Hels. Chim. Acta 27, 994-1006 (1944). (145) Stage, Schultze, Oel u. Kohle 40, 90-95 (1944); C.A. 38, 6134 (1944). (146) Lehfeldt, Phil. Mag. (5) 46, 42-59 (1898). (147) Timmermans, Bull. soc. chim. Belg. 37, 415-419 (1928). (148) Schreinemakers, Z. physik. Chem. 47, 446-470 (1904). (149) Ishikawa, Yamaguchi, Bull. Inst. Phys. Chem. Research (Tokyo) 17, 246-255 (1938); Cent. 1938, II 517; C.A. 32, 7807 (1938). (150) Wilson, Heron, J. Soc. Chem. Ind. 69, 168-171 (1941); C.A. 35, 7269 (1941).

(151) Pesce, Evdokimoff, Gazz. chim. ital. 70, 723-725 (1940); C.A. 35, 5367 (1941). (152) Wystt, Trans. Faraday Soc. 25, 43-48 (1929). (153) Sisler, Cory, J. Am. Chem. Soc. 69, 1515-1519 (1947). (154) Soucek, Collectron Czechoslov. Chem. Commun. 10, 459-465 (1938). (155) Hartung, Trans. Faraday Soc. 12, 66-85 (1916). (156) Kaplan, Monakhova, J. Gen. Chem. (U.S.S.R.) 7, 2499-2512 (1937); Cent. 1938, II 1572; C.A. 32, 2404 (1938). (157) Verstraete, Bull. soc. chim. Belg. 43, 521-527, 530 (1934). (158) Goss, J. Chem. Soc. 1940, 758. (159) Kireev, Monakhova, J. Phys. Chem. (U.S.S.R.) 7, 71-76 (1936); Cent. 1937, II 755, C.A. 31, 25 (1937). (160) Kireev, Skvortsova, J. Phys. Chem. (U.S.S.R.) 7, 63-70 (1936); Cent. 1937, II 755, C.A. 31, 25 (1937).

(161) Conner, Smyth, J. Am. Chem. Soc. 63, 3424-3428 (1941). (162) Sohier, Bull. soc. chim. Belg. 40, 403-426 (1931). (163) Schulze, Z. physik. Chem. 86, 317-323 (1914). (164) Brown, J. Chem. Soc. 33, 304-319 (1881). (165) Smyth, Engel, Wilson, J. Am. Chem. Soc. 61, 1736-1744 (1929). (166) Krchma, Williams, J. Am. Chem. Soc. 49, 2408-2416 (1927). (167) Grimm, Z. angew. Chem. 41, 99 (1928). (168) Pahlavouni, Bull. soc. chim. Belg. 36, 542 (1927). (169) Showalter, Trans. Roy. Soc. Cam. (3) 27, III 183-185 (1933); Cent. 1934, I 2874; C.A. 28, 2983 (1934). (170) Bonner, J. Phys. Chem. 14, 738-789 (1910).

(171) Sata, Niwase, Bull. Chem. Soc. Japan 12, 90-95 (1937); Cent. 1937, II 1527; C.A. 31, 3760 (1937). (172) McDonald, Kluender, Lane, J. Phys. Chem. 46, 946-948 (1942). (173) Curtis, Titus, J. Phys. Chem. 19, 739-752 (1915). (174) Rosanoff, Schulze, Dunphy, J. Am. Chem. Soc. 36, 2480-2495 (1914). (175) Lecat, "L'Azeotropisme" (1918). (176) Soday, Bennett, J. Chem. Education 7, 1336-1340 (1930). (177) Young, J. Chem. Soc. 83, 77-83 (1903). (178) Brown, J. Chem. Soc. 35, 544-547 (1879). (179) Lecat, Rec. trav. chim. 47, 15 (1928). (180) Tyrer, J. Chem. Soc. 101, 1104-1113 (1912).

(181) Hill, J. Chem. Soc. 101, 2467-2470 (1912). (182) Prigogine, Bull. soc. chim. Belg. 52, 95-99 (1943); C.A. 40, 4576 (1946). (183) Zhdanov, J. Gen. Chem. (U.S.S.R.) 11, 471-482 (1941); C.A. 35, 7275 (1941). (184) Lecat, Rec. trav. chim. 45, 623-624 (1926). (185) Lecat, Ann. soc. sct. Bruxelles 47, I 66, I 10, I I (1927). (186) Zhdanov, J. Gen. Chem. (U.S.S.R.) 11, 483-492 (1941); C.A. 36, 961 (1942). (187) Hands, Norman, Ind. Chemist 21, 307-315 (1945). (C.A. 39, 4273 (1945). (188) Atkins, J. Chem. Soc. 117, 218-220 (1920). (189) Lecat, Ann. soc. sci. Bruxelles 49, I 10 (1929). (190) de Kolossowsky, Alimow, Bull. soc. chim. (5) 2, 688 (1935).

sci. Bruxelles 49, 110 (1929). (190) de Kolossowsky, Alimow, Bull. soc. chim. (5) 2, 688 (1935). (191) Schutz, Mallonee, J. Am. Chem. Soc. 62, 1491-1492 (1940). (192) Litvinov, J. Phys. Chem. (U.S.S.R.) 14, 562-570 (1940); 13, 119-123 (1939); C.A. 35, 2046 (1941); 34, 299 (1940). (193) Redlich, Schutz, J. Am. Chem. Soc. 66, 1007-1011 (1944). (194) Lecat, Rec. trav. chim. 46, 243 (1927). (195) Atkins, Nature 151, 449 (1943). (196) Bates, Hazzard, Palmer, Ind. Eng. Chem. 33, 375-376 (1941). (197) Hutchinson, Trans. Faraday Soc. 41, 87-90 (1945). (198) Davis, Phyl. Mag. (6) 47, 972-975 (1924). (199) Vold, J. Am. Chem. Soc. 57, 1192-1195 (1935). (200) Spencer, Flanagan, J. Am. Chem. Soc. 64, 2511-2513 (1942).

(201) Beckmann, Z. physik. Chem. 58, 555-556, 559 (1907). (202) Carroll, Rollefson, Mathews, J. Am. Chem. Soc. 47, 1798 (1925). (203) Waentig, Z. physik. Chem. 68, 547 (1909). (204) Beckmann, Waentig, Z. anorg. allgem. Chem. 67, 30-31 (1910). (205) Patryn, Pilat, Caoutchouc and Rubber (U.S.S.R.) 1940, No. 10, 14-16; C.A. 35, 2029 (1941). (206) Alekseevski, Musin, J. Applied Chem. (U.S.S.R.) 12, 704-719 (1939); C.A. 34, 2652 (1940). (207) Alekseevski, Vaskovskii, J. Applied Chem. (U.S.S.R.) 8, 779-801 (1935); Cent. 1936, I 2982; [C.A. 39, 4375 (1936)]. (208) Swietoslawski, Ann. chim. (10) 16, 269 (1931). (209) Lemcke, Hofmann, Angew. Chem. 47, 37-43 (1934). (210) Burrage, Trans. Faraday Soc. 29, 445-457, 458-476, 564-569, 570-576, 665-672, 673-676 (1933); 30, 317-325 (1934).

(211) Burrage, J. Phys. Chem. 37, 33-39 (1933). (212) Allmand, Burrage, Chaplin, Trans.

Faraday Soc. 28, 218-226 (1932). (213) Allmand, Burrage, J. Phys. Chem. 35, 1692-1703 (1931).
(214) Allmand, Puttick, Proc. Roy. Soc. (London) A-130, 197-209 (1930). (215) Allmand, Chaplin, Proc. Roy. Soc. (London) A-129, 235-251, 252-266 (1930). (216) Driver, Firth, J. Chem. Soc. 121, 2409-2414 (1922). (217) Pearce, Reed, J. Phys. Chem. 35, 905-914 (1931). (218) Pearce, Johnstone, J. Phys. Chem. 34, 1260-1279 (1930). (219) Pearce, McKinley, J. Phys. Chem. 32, 360-379 (1928). (220) Coolidge, J. Am. Chem. Soc. 46, 596-627 (1924).

(221) Lamb, Coolidge, J. Am. Chem. Soc. 42, 1146-1170 (1920). (222) Migal, J. Gen. Chem. (U.S.S.R.) 5, 197-210 (1935); Cent. 1936, I 1590; C.A. 29, 5006 (1935). (223) Baughan, Razouk, Trans. Faraday Soc. 33, 1463-1472 (1937). (224) Chambers, King, J. Chem. Soc. 1949, 156-166. (225) Perry, J. Phys. Chem. 29, 1462-1468 (1925). (226) Munro, Johnson, Ind. Eng. Chem. 17, 88-92 (1925). (227) Grimm, Raudenbusch, Wolff, Z. angew. Chem. 41, 106 (1928). (228) Rao, J. Phys. Chem. 45, 517-521 (1941). (229) Perry, Ind. Eng. Chem. 19, 746-748 (1927). (230)

Rao, J. Phys. Chem. 45, 522-531 (1941).

(231) Habard, King, J. Chem. Soc. 1940, 19-29. (232) Higuti, Bull. Inst. Phys. Chem. Research (Tokyo) 18, 675-684 (1939); C.A. 34, 4959 (1940). (233) Bangham, Mosallam, Proc. Roy. Soc. (London) A-165, 565-567 (1938); A-166, 564 (1938). (234) H. F. Smyth, H. F. Smyth, Jr., C. F. Carpenter, J. Ind. Hyg. Toxicol. 18, 277-298 (1936). (235) Davis, J. Am. Med. Assoc. 103, 962-966 (1934). (236) Elkins, J. Ind. Hyg. Toxicol. 24, 233-234 (1942). (237) Sayers, Dallavalle, Ind. Eng. Chem. 26, 1251 (1934). (238) von Oettingen. J. Ind. Hyg. Toxicol. 19, 374-384 (1937). (239) Hammes, J. Ind. Hyg. Toxicol. 23, 111-117 (1941). (240) Lehman, Schmidt, Kehl, Arch. Hyg. Bakt. 116, 131-268 (1936), [C.A. 31, 477 (1937)].

(241) Barrett, MacLean, Cunningham, J. Ind. Hyg. Toxicol. 20, 360-379 (1938). (242) Ernst (to A. Wacker Soc. Elektrochem. Ind.), Ger. 639,623, Dec. 10, 1936; Cent. 1937, I 1502; C.A. 21, 4064 (1937). (243) Clarke, Othmer (to Eastman Kodak Co.), U.S. 1,861,841, June 7, 1932; Cent. 1933, II 2192; [C.A. 26, 4067 (1932)]. (244) Taylor, J. Soc. Chem. Ind. 53, 193-1947 (1934); Cent. 1935, I 3127; C.A. 28, 5400 (1934). (245) Jones, U.S. 1,942,104, Jan. 2, 1934; Cent. 1934, I 2185; [C.A. 28, 1810 (1934)]. (246) Worsley, J. Soc. Chem. Ind. 55, 349-3577 (1936); Cent. 1937, I 1744; C.A. 21, 1729 (1937). (247) Begtrup, Dansk. Tids. Farm. 11, 6-12 (1937); Cent. 1937, I 1744; C.A. 31, 2342 (1937). (248) "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," 6th ed., 74-76 (1945). (249) Höst-Madsen, J. pharm. chim. (8) 21, 246-247 (1935); Cent. 1935, II 1216; C.A. 29, 4899 (1935). (250) Rozeboom, Pharm. Weekblad 72, 689 (1935); Cent. 1935, II 2096, C.A. 29, 5386 (1935).

(251) Schoorl, Pharm. Weekblad 72, 751 (1935); Cent. 1935, II 3954; [C.A. 29, 5986 (1935)]. (252) Sivadjian, J. pharm. chim. (8) 9, 434-437 (1929); Cent. 1929, II 1830, C.A. 23, 5544 (1929). (253) Ciogolea, J. pharm. chim. (8) 19, 377-383 (1934); Cent. 1934, II 1502; C.A. 28, 4537 (1934). (254) Weber, Chem. Ztj. 57, 836 (1933); Cent. 1933, II 3889; C.A. 28, 727 (1934). (255) Weber, Chem. Ztj. 61, 807-808 (1937); Cent. 1938, I 950; C.A. 32, 74 (1938). (256) Ciaravino, Boll. chim. farm. 74, 741-748 (1935); Cent. 1936, I 2156; [C.A. 30, 409 (1936)]. (257) Fieldner, Katz, Kinney, Longfellow, J. Franklin Inst. 190, 543-565 (1920). (258) L. V. Cralley, T. E. Shea, L. J. Cralley, J. Ind. Hyg. Toxicol. 25, 172-173 (1943). (259) Robbins, Lamson, J. Pharmacol., Proc. 31, 220 (1927); [C.A. 21, 3978 (1927)]. (260) Nuckolls et al., Underwriter's Labs., Miscellaneous Hazards No. 2375, 118 pp. (1933); C.A. 28, 2079 (1934).

(261) Schayer, Ackerman, J. Ind. Hyg. Toxicol. 28, 237-240 (1946). (262) Thomas, Ivie, Abersold, Hendricks, Ind. Eng. Chem., Anal. Ed. 15, 287-290 (1943). (263) Moran, J. Ind. Hyg. Toxicol. 25, 243-248 (1943). (264) Olsen, Smyth, Ferguson, Scheflan, Ind. Eng. Chem., Anal. Ed. 8, 260-263 (1936). (265) Smyth, Ind. Eng. Chem., Anal. Ed. 8, 379 (1936). (266) Winteringham, J. Soc. Chem. Ind. 61, 190-192 (1942); C.A. 37, 1951 (1943). (267) Tebbens, J. Ind. Hyg. Toxicol. 19, 204-211 (1937). (268) Dudley, U.S. Pub. Health Repts. 56, 1021-1027 (1941); C.A. 35, 4637 (1941). (269) Treadwell, Zürcher, Hetr. Chim. Acta 23, 1371-1380 (1939). (270) "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," 6th ed., 710-711 (1945).

(271) Matchett, J. Assoc. Official Agr. Chem. 14, 360-367 (1931). (272) Kunke, J. Assoc. Official Agr. Chem. 12, 264-276 (1929). (273) Rauscher, Ind. Eng. Chem., Anal. Ed. 9, 296-299 (1937). (274) Winteringham, J. Soc. Chem. Ind. 61, 186-187 (1942); C.A. 37, 1950 (1943). (275) Webb, Kay, Nichol, J. Ind. Hyg. Toxicol. 27, 249-255 (1945). (276) Barrett, Cunningham, Johnston, J. Ind. Hyg. Toxicol. 21, 487-488 (1939). (277) Habgood, Powell, Brit. J. Ind. Med. 2, 39-40 (1945); C.A. 39, 5273 (1945). (278) Daroga, Pollard, J. Soc. Chem. Ind. 60, 218-222 (1941); C.A. 35, 7882 (1941). (279) Kohn-Abrest, Ann. chim. anal. chim. appl. 15, 199-207 (1933); Cent. 1933, II 580-581; [C.A. 27, 3193 (1933)]. (280) C. J. H. Staverman-Pekelder, A. J. Staverman, Rec. trav. chim. 59, 1084 (1940).

(281) Bishop, Wallace, Ind. Eng. Chem., Anal. Ed. 17, 563-564 (1945). (282) Davidis (to

E. Davidis and O. Adler), Ger. 702,889, date unreported; C.A. 36, 786 (1942). (283) Anger, Wang, Mikrochim. Acta 3, 24-26 (1938). (284) Yant, Olsen, Storch, Littlefield, Schefian, Ind. Eng. Chem., Anal. Ed. 8, 20-25 (1936). (285) Matuszak, Ind. Eng. Chem., Anal. Ed. 6, 374-375 (1934). (286) Olsen, Ferguson, Sabetta, Schefian, Ind. Eng. Chem., Anal. Ed. 3, 189-191 (1931). (287) Kolbe, Ann. 45, 41-46 (1843), 54, 146 (1845). (288) Margosches, Ahrens' Sammlung chemischer und chem.-techn. Vortrage 16, 243-358 (1906). (289) Roffey, "Thorpo's Dictionary of Applied Chemistry," 4th ed. II, 353-356 (1938). (290) Beanblossom (to Hooker Electrochemical Co.), U. S. 2,287,225, June 23, 1942; C.A. 37, 143 (1943).

(291) Hennig (to General Aniline and Film Corp.), U.S. 2,223,448, Dec. 3, 1940; C.A. 35, 1708 (1941). (292) Nichols (to Westvaco Chlorine Products, Inc.), U.S. 2,016,804, Oct. 8, 1935; Cent. 1936, I 2206; C.A. 29, 8005 (1935). (293) Firma Stabilimenti di Rumianca, Ger. 604,347, Oct. 19, 1934; Cent. 1935, I 307; C.A. 29, 817 (1935). (294) Izgaryshev, Polikarpov, Compt. rend. acad. sci. U.R.S.S. 27, 950-955 (1940); C.A. 35, 2798 (1941). (295) Elmanovich, Maiofis, Shusterovich, Trans. State Inst. Applied Chem. (Leningrad) No. 15, 8-36 (1932); Cent. 1933, I 503; [C.A. 27, 3038 (1933)]. (296) Beanblossom, Scott (to Hooker Electrochemical Co.), U.S. 2,316,736, April 13, 1943; C.A. 37, 5737 (1943). (297) Reilly (to Dow Chem. Co.), U.S. 2,110,174, March 8, 1938; Cent. 1938, II 174; C.A. 32, 3422 (1938): Brit. 484,888, June 9, 1938, Cent. 1938, II 3157; [C.A. 32, 7480 (1938)]. (298) Petrov, Russ. 48,232, Aug. 31, 1936, Cent. 1937, II 119; not in C.A. (299) Brallier, Dunlap, Muggleton (to Niagara Smelting Corp.), U.S. 1,817,123, Aug. 4, 1931; Cent. 1932, I 1827; C.A. 25, 5522 (1931). (300) Crump, Chem. News 14, 154,216 (1866).

(301) Morel, Compt. rend. 84, 1460 (1877). (302) Serra, Gazz. chim. ital. 29, II 353-354 (1899). (303) Aronheim, Ber. 9, 1788-1789 (1876). (304) Ochi, J. Chem. Ind. (Tokyo) 22, 877-890 (1919); C.A. 14, 1671 (1920). (305) Hofmann, Ann. 115, 264-267 (1860). (306) Klason, Ber. 20, 2376-2383 (1887). (307) Delépine, Giron, Bull. soc. chim. (4) 33, 1785-1792 (1923). (308) Dumas, Ann. 33, 187-191 (1840). (309) McBee, Hass, Neher, Strickland, Ind. Eng. Chem. 34, 296-300 (1942). (310) Padovani, Magaldi, Giorn. chim. ind. applicata 15, 1-7 (1933); Cent. 1933, 13056; C.A. 27, 3443 (1933): Inst. Ind. Chem. Fuels, Polytechnicum, Milan 4, 193-208 (1932/1933); (C.A. 29, 1229 (1935)].

(311) Kiprianov, Kusner, J. Applied Chem. (U.S.S.R.) 8, 673-684 (1935); Cent. 1936, I 3907; C.A. 30, 1735 (1936). (312) Tomasık, Przemsyl Chem. 18, 598-605 (1934); Cent. 1935, I 2156; C.A. 29, 6206 (1935). (313) Boswell, McLaughlin, Can. J. Research 1, 240-254 (1929); Cent. 1930, I 358; [C.A. 24, 53 (1930)]. (314) Jones, Allison, Ind. Eng. Chem. 11, 639-643 (1919). (315) Bedford, J. Ind. Eng. Chem. 8, 1090-1094 (1916). (316) Jones, Allison, Meighan, U.S. Bur. Mines, Tech. Paper 255, 44 pp. (1921); C.A. 15, 1983-1984 (1921). (317) Baskerville, Riederer, J. Ind. Eng. Chem. 5, 5-8 (1913). (318) Pie (to Darco Corpn.), U.S. 2,280,928, April 28, 1942; C.A. 36, 5484 (1942). (319) Bender (to Dow Chem. Co.), U.S. 2,170,801, Aug. 29, 1939; C.A. 34, 117 (1940). (320) Bender (to Great Western Electro-Chemical Co.), U.S. 2,089,937, Aug. 17, 1937; Cent. 1937, II 3494; C.A. 31, 6936 (1937).

(321) I.G., French 816,990, Aug. 21, 1937; Cent. 1937, II 3380, C.A. 32, 2142 (1938). (322) I.G., French 816,957, Aug. 21, 1937; Cent. 1937, II 3380; C.A. 32, 2142 (1938). (323) Soil, Runkel (to I.G.), Ger. 491,316, Dec. 20, 1932; Cent. 1933, I 1013; C.A. 27, 991-992 (1933). (324) Imperial Chem. Ind. Ltd., Wheeler, Mason, U.S. 1,918,624, July 18, 1933; not in Cent.; C.A. 27, 4816 (1933): Brit. 342,329, Feb. 26, 1931; Cent. 1931, II 629; C.A. 25, 4890 (1931). (325) McKee, Salls, U.S. 1,765,601, June 24, 1930; Cent. 1930, II 1439, C.A. 24, 4051 (1930). (326) Boswell, McLaughlin, Canadian 301,542; July 1, 1930; Cent. 1933, II 2454; C.A. 24, 4127 (1930). (327) Ayres (to B.A.S. Co.), U.S. 1,717,136, June 11, 1929; Cent. 1939, I 3237; C.A. 23. 3713 (1929): French 657,518, May 23, 1929; Cent. 1930, I 285; [C.A. 23, 4228 (1929)]. Tizard, Chapman, Taylor, Brit. 214,293, Dec. 14, 1922; C.A. 18, 2523 (1924); not in Cent. Carter, Coxe (to S. Karpen and Bros., U.S. 1,572,513, Feb. 9, 1926; Cent. 1926, I 2838; C.A. 20, 1243 (1926): Brit. 245,991, Sept. 11, 1926; Cent. 1926, I 2838; C.A. 21, 415 (1927): Ger. 472,421, Feb. 28, 1929; Cent. 1929, I 2818; [C.A. 23, 2448 (1929)]: French 597,678, Nov. 26, 1925; Cent. 1926, I 2838; not in C.A.; Canadian 251,763, July 14, 1925; not in Cent.; C.A. 19, 3272 (1925). (330) Ernst, Wahl (to I.G.), Ger. 486,952, Nov. 30, 1929; Cent. 1930, I 3829; C.A. 24, 1393 (1930). (331) Polish 11,909 and 11,910, June 25, 1930; Cent. 1931, II 2512. (332) Polish 10,462

Sept. 25, 1929; Cent. 1939, II 1642. (333) Bender (to Dow Chem. Co.), U.S. 2,200,254 and 2,200,255, May 14, 1940; C.A. 34, 5854 (1940). (334) Hass, McBee (to Purdue Research Foundation), U.S. 2,105,733, Jan. 18, 1938; Cent. 1938, I 4533; C.A. 32, 2142 (1938). (335) Grebe, Reilly, Wiley, U.S. 2,034,292, March 17, 1936; Cent. 1936, II 2611; [C.A. 30, 3178 (1936)]. (336) Hennig (to I.G.), Ger. 712,492, Sept. 25, 1941; C.A. 37, 4407 (1943). (337) I.G., Brit. 513,235, Oct. 6, 1939; [C.A. 35, 1808 (1941)]: French 836,979, Jan. 31, 1939; Cent. 1939, II 226; C.A. 33, 5869 (1939). (338) Klein (to Ruhrchemie, A. G.), Ger. 613,607, May 23, 1935; Cent. 1935, II

1256; [C.A. 29, 8007 (1935)]. (339) Reilly (to Dow Chem. Co.), U.S. 2,140,551, Dec. 20, 1938; Cent. 1939, I 3625; C.A. 33, 2540 (1939). (340) Shvemberger, Gordon, J. Gen. Chem. (U.S.S.R.) 8, 1353-1360 (1938); Cent. 1939, II 3690; C.A. 33, 4232 (1939).

(341) McBee, Hass, Bordenca, Ind. Eng. Chem. 35, 317-320 (1943). (342) McBee, Hass, Chao, Welch, Thomas, Ind. Eng. Chem. 33, 176-181 (1941). (343) Mugdan, Wimmer (to Consortium für Elektrocheni. Ind.), U.S. 2,305,821, Dec. 22, 1942; C.A. 37, 3108 (1943): Brit. 519,220, March 19, 1940; C.A. 35, 7981 (1941): Ger. 680,659, Sept. 9, 1939; Cent. 1939, II 3486; [C.A. 36, 1951 (1942)]: French 844,300, July 21, 1939; C.A. 34, 7300 (1940). (344) Fink, Bonilla, J. Phys. Chem. 37, 1141-1145 (1933). (345) Regnault, Ann. 33, 332-334 (1840). (346) Gault, Truffault, Compt. rend. 179, 467 (1924). (347) Schumacher, Wolff, Z. physik. Chem. B-25, 161–176 (1934). (348) Schwab, Heyde, Z. physik. Chem. B-8, 147–158 (1930). (349) Schwab, Heyde, J. Phys. Chem. (U.S.S.R.) 2, 460-467 (1931); Cent. 1933, I 20; not in C.A. (350) Taylor,

Hanson, J. Chem Phys. 7, 418-425 (1939).

(351) S. S. Bhatnagar, N. A. Yajnik, P. L. Kapur, A. S. Bhatnagar, J. Indian Chem. Soc. 18, 350-358 (1941). (352) Aschan, Cent. 1919, I 220, C.A. 13, 2868 (1919). (353) Friedel, Silva, Bull. soc. chim. (2) 17, 537-539 (1872). (354) Dehn, J. Am. Chem. Soc. 31, 1225-1226 (1909). (355) Croco (to Kinetic Chemicals, Inc.), U.S. 1,994,035, March 12, 1935; Cent. 1935, II 2580; [C.A. 29, 2974 (1935)]. (356) von Ranke, Z. Elektrochem. 27, 365-367 (1921); Cent. 1921, III 917-918; C.A. 15, 3256 (1921). (357) Nernst, Physik. Z. 21, 602-605 (1920). (358) Vesper, Rollefson, J. Am. Chem. Soc. 56, 1455-1461 (1934). (359) Hennig (to I.G.), Ger. 693,414, June 13, 1940; [C.A. 35, 4693 (1941)]: French 826,875, April 12, 1938; Cent. 1938, II 411-412; C.A. 32, 8088 (1938). (360) Stock, Lux, Wustrow, Z. anorg. allgem. Chem. 195, 149-157 (1931). (361) A. C. Combes, P. R. Combes, Ger. 204,942, Dec. 17, 1908; Cent. 1909, 326-327; C.A. 3, 1450 (1909). (362) Boeseken, Rec. trav. chim. 29, 112 (1910). (363) Simons, Sloat, Meunier. J. Am. Chem. Soc. 61, 435-436 (1939). (364) Hentschel, J. prakt. Chem. (2) 36, 308-309 (1887). (365) Gautier, Compt. rend. 101, 1161 (1885); Bull. Soc. chim. (2) 45, 86-88 (1886). (366) Robineau, Rollin, Ber. 27, Referate 396-397 (1894). (367) Hallstein (to Chem. Fabrik Schering), Ger. 416,603, July 21, 1925; Cent. 1925, II 1795-1796; not in C.A. (368) Hallstein (to Chem. Fabrik Schering), Ger. 417,970, Aug. 20, 1925, Cent. 1926, I 226; not in C.A. (369) Hallstein (to Chem. Fabrik Schering), Ger. 432,849, Aug. 14, 1926, Cent. 1926, II 1688; not in C.A. (370) Helfrich, Reid, J. Am. Chem. Soc. 43, 591-594 (1921).

(371) Frankland, Garner, Challenger, Webster, J. Soc. Chem. Ind. 39, 313-315T (1920); Cent. 1921, I 937; C.A. 15, 509 (1921). (372) Stock, Wustrow, Z. anorg. allgem. Chem. 195, 129-139 (1931). (373) Strosacker, Schwegler (to Dow Chem. Co.), U.S. 1,930,350, Oct. 10, 1933; Cent. 1934, I 124; [C.A. 28, 180 (1934)]. (374) Weiser, Wightman, J. Phys. Chem. 23, 415-439 (1919). (375) Bodenstein, Günther, Hofmeister, Z. angew. Chem. 39, 875-880 (1926). (376) Bodenstein, Gunther, Nagai, Z. angew. Chem. 43, 423-425 (1930). (377) Tarczynskki, Z. Elektrochem. 22, 252-254 (1916). (378) Urbain, Scal, Compt. rend. 168, 887 (1919). (379) Besson,

Fournier, Compt. rend. 150, 1119 (1910). (380) Kailan, Monatsh. 38, 543-549 (1917).

(381) Gunther, van der Horst, Cronheim, Z. Elchtrochem. 34, 619 (1928). (382) Roffo, Correa, Strahlentherapie 33, 537-541 (1929); Cent. 1929, II 2019; C.A. 24, 4525 (1930). (383) Schmitt, Johnson, Olson, J. Am. Chem. Soc. 51, 372 (1929). (384) Gunther, Z. angew. Chem. 41, 1360 (1928). (385) Gillam, Morton, J. Soc. Chem. Ind. 46, 419-T (1927); Cent. 1928, I 96; C.A. 22, 1540 (1928). (386) Lyons, Dickinson, J. Am. Chem. Soc. 57, 443-446 (1935). (387) Harteck, Kopsch, Z. physik. Chem. B-12, 327-347 (1931). (388) Biesalski, Z. angew. Chem. 37, 315-317 (1924). (389) Dede, Russ, Ber. 61, 2462 (1928). (390) Lepin, J. Russ. Phys.-Chem. Soc. 52, 1-17 (1920); Cent. 1923, III 823; C.A. 17, 1395 (1923).

(391) Oddo, Sconzo, Gazz. chim. ital. 57, 91, 99-102 (1927). (392) Erdmann, Ber. 26, 1993-1994 (1893). (393) Armstrong, J. prakt. Chem. (2) 1, 245-248 (1870). (394) Hamilton, Ind. Eng. Chem. 25, 539-541 (1933). (395) Berthelot, Ann. chim. (3) 51, 48-50 (1857). (396) Soc. Chim. des Usines du Rhone, Ger. 416,014, July 7, 1925; French 586,006, March 13, 1925, Cent. 1925, II 1795; not in C.A. (397) Geuther, Ann. 107, 214-217 (1858). (398) Coupin, J. pharm. chim. (6) 3, 314-315 (1896); Cent. 1896, II 15; cf. Cent. 1896, I 362. (399) Smith, U.S. 753,325, March 1, 1904; not in either Cent. or C.A. (400) Coleman, Hadler (to Dow Chem. Co.), U.S. 2,095,240, Oct. 12, 1937; Cent. 1938, I 1218; C.A. 31, 8549 (1937).

(401) Coleman, Hadler, Zuckermandel (to Dow Chem. Co.), U.S. 2,104,703, Jan. 4, 1938; Cent. 1938, I 3387, C.A. 32, 1718 (1938). (402) Byers, van Ardsel, U.S. 1,534,027, April 21, 1925; Cent. 1925, II 91; [C.A. 19, 1667 (1925)]. (403) Smyser, Smallwood, J. Am. Chem. Soc. 55, 3498-3499 (1933). (404) Besson, Compt. rend. 118, 1347 (1894). (405) Sabatier, Mailhe, Compt. rend. 138, 409 (1904). (406) McBee, Hass, Frost, Welch, Ind. Eng. Chem. 39, 404-409 (1947). (407) Simons, Bond, McArthur, J. Am. Chem. Soc. 62, 3477-3480 (1940). (408) Booth, Swinehart, J. Am. Chem. Soc. 54, 4751-4753 (1932). (409) Bigelow, Pearson, Cook, Miller, J. Am. Chem. Soc. 55, 4616 (1933). (410) Ruff, Keim, Z. anorg. allgem. Chem. 201, 245-258 (1931).

(411) Thompson, Ind. Eng. Chem. 24, 620-623 (1932). (412) Leicester (to Imperial Chem. Ind. Ltd.), U.S. 2,110,369, March 8, 1938; Cent. 1938, II 174; C.A. 32, 3422 (1938); Brit. 468.447. Aug. 5, 1937; Cent. 1937, II 2900, C.A. 32, 587 (1938) (413) Daudt, Youker (to Kinetic Chemicals, Inc.), U.S. 2,062,743, Dec. 1, 1936; Cent. 1937, I 4557; C.A. 31, 700 (1937). (414) Daudt, Youker, Reynolds (to Kinetic Chemicals, Inc.), U.S. 2,024,095, Dec. 10, 1935; Cent. 1936, I 4212; C.A. 30, 1067 (1936). (415) Daudt, Youker (to Kinetic Chemicals, Inc.), U.S. 2,005,710. June 18. 1935; Cent. 1936, I 1501; C.A. 29, 5123 (1935). (416) Daudt, Youker (to Kinetic Chemicals, Inc.), U.S. 2,005,709, June 18, 1935; Cent. 1936, I 2630; C.A. 29, 5123 (1935). (417) Daudt. Youker (to Kinetic Chemicals, Inc.), U.S. 2,005,707, June 18, 1935; Cent. 1936, I 876; C.A. 29, 5123 (1935). (418) Daudt, Youker (to Kinetic Chemicals, Inc.), U.S. 2,005,706; June 18, 1935; not in Cent.; C.A. 29, 5123 (1935). French addition 43,972, Sept. 25, 1934; Cent. 1935, I 2255; C.A. 29, 1593 (1935): Brit. 428,445, May 7, 1935, not in Cent.; C.A. 29, 6901 (1935). (419) Daudt, Youker (to Kinetic Chemicals, Inc.), U.S. 2,005,705, June 18, 1935; not in Cent., C.A. 29, 5123 (1935): Brit. 391,168, not in Cent.; C.A. 27, 4813 (1933): Ger. 552,919, June 21, 1932; Cent. 1932. II 1832; [C.A. 26, 5967 (1932)]: French 720,474, Feb. 19, 1932; Cent. 1932, II 1832; [C.A. 26, 3805 (1932)] French addition, 46,349, April 30, 1936; Cent. 1936, II 3358; C.A. 30, 7290 (1936). (420) Daudt, Youker, Jones (to Kinetic Chemicals, Inc.), U.S. 2,004,932, June 18, 1935; Cent. 1936, I 875-876; C.A. 29, 5123 (1935).

(421) Daudt, Mattison (to Kinetic Chemicals, Inc.), U.S. 2,004,931, June 18, 1935; Cent. 1936. I 875; C.A. 29, 5123 (1935). (422) Henne (to General Motors Corp.), U.S. 1,990,692, Feb. 12, 1935; Cent. 1935, II 435-436; C.A. 29, 2174 (1935). (423) Henne (to General Motors Corp.), U.S. 1,978,840, Oct. 30, 1934, Cent. 1935, I 1934, C.A. 29, 175 (1935). (424) Henne (to General Motors Corp.), U.S. 1,973,069, Sept. 11, 1934; Cent. 1935, I 790-791; C.A. 28, 6723 (1934). (425) Nutting, Petrie (to Dow Chem. Co), U.S. 1,961,622, June 5, 1934; Cent. 1934, II 2284; C.A. 28, 4746 (1934). (426) Midgely, Henne, McNary (to Frigidaire Corp.), U.S. 1,930,129; Oct. 10, 1933; not in Cent.; C.A. 28, 179 (1934). (427) Lacy (to du Pont Co.), U.S. 1,914,135, June 13, 1933; not in Cent.; C.A. 27, 4252 (1933): French 730,874, Aug. 25, 1932; Cent. 1933, II 605; C.A. 27. 304 (1933): Canadian 330,907, March 14, 1933, C.A. 27, 3485 (1933). (428) I.G., Brit. 370,356, April 28, 1932; Cent. 1932, II 612; C.A. 27, 2966 (1933): French 727,952, Dec. 7, 1931; not in Cent.; C.A. 26, 5574 (1932). (429) Frigidaire Corp., French 701,324, March 14, 1931; Cent. 1931. II 120; C.A. 25, 4011 (1931). (430) Benrath, Ann. 382, 223-224 (1911).

(431) Goldschmidt, Ber. 14, 928 (1881). (432) Doughty, J. Am. Chem. Soc. 39, 2685-2691 (1917). (433) Treadwell, Kohl, Helv. Chim. Acta 9, 689 (1926). (434) P. Petrenko-Kritschenko. D. Talmud, B. Talmud, W. Butmy-de-Katzman, A. Gandelman, Z. physik. Chem. 116, 313-318 (1925). (435) Petrenko-Kritschenko, Opotzky, Ber. 59, 2132 (1926). (436) Petrenko-Kritschenko, Ber. 61, 847, Note 3 (1928). (437) Harlow, Ross (to Dow Chem. Co.), U.S. 1,891,415, Dec. 20, 1932; Cent. 1933, I 1683, C.A. 27, 1890 (1933). (438) Gustavson, J. Russ. Phys.-Chem. Soc. 13, 286 (1881). (439) Bolas, Groves, J. Chem. Soc. 24, 780 (1871). (440) Gustavson, Ann. **172**, 173-176 (1874).

(441) Biltz, Sapper, Z. anorg. allgem. Chem. 203, 279-280 (1932). (442) Lantenois. Compt. rend. 156, 1385 (1913): J. pharm. chim. (7) 10, 185-190 (1914); Cent. 1915, I 652-653; C.A. 9, 953 (1915). (443) Spindler, Ann. 231, 264-265 (1885). (444) Moissan, Compt. rend. 113, 20 (1891). (445) Walker, J. Chem. Soc. 85, 1090 (1904). (446) Tchakiran, Compt. rend. 196, 1026-1028 (1933). (447) Staudinger, Z. Elektrochem. 31, 549-552 (1925). (448) Staudinger, Z. angew. Chem. 35, 658-659 (1922). (449) Lenze, Metz, Z. ges. Schiess- u. Sprengstoffw. 27, 255-258, 293-296, 337-340, 373-376 (1932). (450) von Hartel, Meer, Polanyi, Z. physik. Chem. **B-19**, 139-163 (1932).

(451) Haresnape, Stevels, Warhurst, Trans. Faraday Soc. 36, 465-472 (1940). (452) Bradley, Nature 137, 403-404 (1936). (453) Stedman, Can. J. Research 13-B, 114-121 (1935); Cent. 1936, I 269: C.A. 30, 337 (1936). (454) Clogston, Underwriters' Lab., Bull. Research No. 34, 5-15 (1945); C.A. 40, 210 (1946). (455) Pearce, Scheflan, Schrenk, Ferguson, Brown, U.S. Bur. Mines, Rept. Investigations 3686, 18 pp. (1943); C.A. 37, 2578 (1943). (456) Ray, Dutt, J. Indian Chem. Soc. 5, 107-108 (1928). (457) Hofmann, Seiler, Ber. 38, 3058 (1905). (458) Bartlett, U.S. 1,800,371, April 14, 1931; Cent. 1931, II 629; C.A. 25, 3362 (1931). (459) Tseng, Natl. Cent. Univ. (Nanking) Sci. Repts. A-1, No. 2, 1-4 (1931); Cent. 1938, I 53; C.A. 26, 2166 (1932): Trans. Sci. Soc. China 7, 233-237 (1932). (460) Staub, Ann. chim. (12) 1, 105-156 (1946).

(461) Formanek, Chem. Obzor 5, 57-59 (1930); Cent. 1930, II 976; C.A. 24, 4492 (1930). (462) Milbauer, Collection Czechoslov. Chem. Commun. 3, 73-75 (1931). (463) Dubrisay, Arditti, Compt. rend. 204, 1568-1570 (1937). (464) Milbauer, Chem. Obzor 12, 57-62 (1937); Cent. 1937, II 1507; C.A. 31, 6093 (1937). (465) Senderens, Aboulenc, Compt. rend. 202, 1548-1550 (1936). (466) Avery, Forbes, J. Am. Chem. Soc. 60, 1005-1011 (1938). (467) Schumacher, Wagner, Z. physik. Chem. B-5, 199-208 (1929). (468) Dickinson, Jeffreys, J. Am. Chem. Soc. 53, 4288-

Beil. I - 199

4297 (1930). (469) Moelwyn-Hughes, Hinshelwood, Proc. Roy. Soc. (London) A-131, 177-186

(1931). (470) Nagai, Goodhue, Trans. Faraday Soc. 27, 508-513 (1931).

(471) Yost, Felt, J. Am. Chem. Soc. 56, 68-69 (1934). (472) Brenschede, Schumacher, Z. anorg. allgem. Chem., 226, 370-384 (1936). (473) Stähler, Ber. 47, 909-910 (1914). (474) Stöllé, Ber. 37, 3548 (1904). (475) Theobald (to du Pont Co.), U.S. 2,378,048, June 12, 1945; C.A. 38, 4085 (1945). (476) Kharasch, Jensen, Urry, Science 102, 128 (1945). (477) Hauser, Hudson, Org. Syntheses 23, 102-107 (1943). (478) Norris, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 548-550 (1941); (1st ed.), 532-534 (1932); 4, 81-83 (1925). (479) Marvel, Sperry, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 95-98 (1941); (1st ed.), 89-92 (1932); 8, 26-29 (1928). (480) Forbes, Anderson, J. Am. Chem. Soc. 66, 931-933 (1944).

(481) Prins, J. prakt. Chem. (2) 89, 415, 417, 421 (1914). (482) Prins, Ger. 261,689, July 2, 1913; Cent. 1913, II 394; [C.A. 7, 3641 (1913)]. (483) Kirkbride (to Imperial Chem. Ind., Ltd.), U.S. 2,297,564, Sept. 29, 1942; C.A. 37, 1450 (1943). (484) Henne, Ladd, J. Am. Chem. Soc. 60, 2494-2495 (1938). (485) I.G., French 793,731, Jan. 30, 1936; Cent. 1936, I 4074; [C.A. 30, 4514 (1936)]. (486) Reitz, Sabathy, Z. physik. Chem. B-41, 156 (1938). (487) Ponzio, Gazz. chim. ital. 36, II 149 (1906). (488) Brühl, Ber. 30, 159 (1897). (489) Connolly, Dyson, J. Chem. Soc.

1934, 822. (490) Connolly, Dyson, J. Chem. Soc. 1937, 828.

(491) Claesson, J. prakt. Chem. (2) 15, 212-213 (1877). (492) Backer, Stedehouder, Rec. trav. chim. 52, 438-443 (1933). (493) Houben, Schultze, Ber. 44, 3235-3241 (1911). (494) Post, J. Org. Chem. 5, 247 (1940). (495) Holmberg, Ber. 40, 1740-1743 (1907). (496) Gomberg, Snow, J. Am. Chem. Soc. 47, 198-211 (1925). (497) Gomberg, Anderson, J. Am. Chem. Soc. 47, 2022-2033 (1925). (498) Baines, Driver, J. Chem. Soc. 123, 1214-1218 (1923). (499) Kharasch, Kane, Brown, J. Am. Chem. Soc. 63, 526-528 (1941). (500) Kharasch, Dannley, J. Org. Chem. 10, 406-413 (1945).

(501) Böeseken, Gelissen, Rec. trav. chim. 43, 869-871 (1924). (502) Gelissen, Hermans, Ber.,
58, 286, Note 7 (1925). (503) Gelissen, Ger. 480,362, Aug. 7, 1929; Cent. 1929, II 2831-2832;
[C.A. 23, 4950 (1929)]. (504) Nozaki, Bartlett, J. Am. Chem. Soc. 68, 1686-1692 (1946). (505)
Ingold, Powell, J. Chem. Soc. 119, 1222-1231 (1921). (506) Zelinski, Doroschewski, Ber. 27, 3374-3376 (1894). (507) Bischoff, Ber. 28, 2829-2832 (1895). (508) Dimroth, Ber. 35, 2881-2884 (1902). (509) Dimroth, Feuchter, Ber. 36, 2239, Note 5 (1903). (510) Stobbe, Wildensee, J. prakt. Chem. (2) 115, 177 (1927).

(511) Faltis, Pirsch, Ber. 60, 1623-1625 (1927). (512) Faltis, Ruiz de Roxas, Monatsh. 42, 461 (1921). (513) Ingold, Perren, J. Chem. Soc. 119, 1591 (1921). (514) Mereshkowski, J. Russ. Phys.-Chem. Soc. 46, 521 (1914); Cent. 1914, II 1266. (515) Guttzeit, Hartmann, J. prakt. Chem. (2) 81, 347-348 (1910). (516) Coutelle, J. prakt. Chem. (2) 73, 49-100 (1906). (517) Conrad, Guthzeit, Ber. 15, 2841-2844 (1882); Ann. 222, 249-262 (1883). (518) Urushibara, Bull. Chem. Soc. Japan 2, 26-36, 236-241 (1927); Cent. 1927, I 2061; Cent. 1927, II 2278. (519) Ruhemann, Browning, J. Chem. Soc. 73, 282-284 (1898). (520) Errera, Gazz. chim. ital. 27, II 393-397 (1897); Ber. 31, 1241-1242 (1898).

(521) Hartung, J. Chem. Soc. 113, 163-168 (1918). (522) Shah, J. Indian Inst. Sci. 7, 205-223, (1924); Cent. 1925, I 659-661; [C.A. 19, 645-646 (1925)]. (523) Desai, J. Indian Inst. Sci. 7, 235-251 (1925); Cent. 1925, I 1297-1298; [C.A. 19, 2645-2646 (1925)].

[See also the higher-boilg. stereoisomer (3:5150).]

3:5110 1,2-DICHLOROPROPENE-1

[For prepn. of C from 1,2,2-trichloropropane (3:5475) with MeOH/NaOMe or EtOH NaOEt at ord. temp. (55-58% yield (1)), or with alc. KOH (2) or with aq. on htg. in s.t. (3), see indic. refs.]

 \tilde{C} with abs. MeOH (1:6120) forms a const.-boilg. mixt., b.p. 56.5-56.8° at 760 mm., $n_D^{25} = 1.4030$, contg. 75 wt. % \tilde{C} (1).

 \tilde{C} with Cl₂ at 0° in strong light adds 1 mole halogen giving (1) 1,1,2,2-tetrachloropropane (3:5825).

Č with Br₂ at 0° slowly adds 1 mole halogen giving (1) (3) 1,2-dibromo-1,2-dichloro-propane, b.p. 190° (3).

 $\ddot{\mathbf{C}}$ with O_3 in CCl₄ at -15° followed by aq. gives (1) acetic acid (1:1010) and formic acid (1:1005).

3:5110 (1) Huntress, Sanchez-Nieva, unpublished work. (2) Friedel, Silva, Bull. soc. chim. (2) 17, 386 (1872); Jahresber, 1872, 322; Compt. rend. 74, 805-809 (1872); 75, 81-85 (1872). (3) Friedel, Silva, Jahresber, 1871, 322, 329.

3:5120 1,1-DICE	LOROPROPENE-1	CH ₃ .CH=CCl ₂	$\mathrm{C_{8}H_{4}Cl_{2}}$	Beil. I - 199 I ₁
B.P. 79–80° 78° 77.15–77.3 77° 76.5°	(1) (2) (3) (4) (5) 5 (6) (7) (8)		$D_0^{19.5} = 1.1$ $D_0^0 = 1.2$	I ₂

Colorless oil insol. in aq.

[For prepn. of \bar{C} from 1,1,1-trichloropropanol-2 (3:0846) with Zn dust + AcOH see (6) (5); from corresp. acetate with Zn dust + alc. see (8); from butylchloral $(\alpha,\alpha,\beta$ -trichloro-n-butyraldehyde) (3:5910) (1) (2) (9) or its alcoholate (10) with KOH see indic. refs.; from Ag 2,2,3-trichlorobutyrate on boilg. with aq. (3) or Na 2,2,3-trichlorobutyrate on distn. (4) see (3) (4); for prepn. from 1,1,2-trichloropropane (3:5630) + aq. or alc. alk. or aq. Ca(OH)₂ see (11) (14).]

 $\ddot{\mathbf{C}}$ on oxidn. with $K_2Cr_2O_7 + H_2SO_4$ gives (7) AcOH (1:1010).

 $\ddot{\mathbf{C}}$ adds $\mathbf{Br_2}$ very easily giving (9) 1,1-dichloro-1,2-dibromopropane [Beil. I-111], b.p. 188° (9). — $\ddot{\mathbf{C}}$ with $\mathbf{Cl_2}$ at 0-30° yields (12) 1,1,1,2-tetrachloropropane (3:5270), b.p. 153°.

 \tilde{C} with HCl + AlCl₃ at 5-10° yields (13) (14) 1,1,1-trichloropropane (ethylchloroform) (3:5270), b.p. 106-107°.

3:5120 (1) Kramer, Pinner, Ber. 3, 388-389 (1870). (2) Kramer, Pinner, Ann. 158, 47-49 (1871). (3) Judson, Ber. 3, 789 (1870). (4) Valentin, Ber. 28, 2663 (1895). (5) Wohl, Roth, Ber. 40, 215 (1907). (6) Bruyne, Davis, Gross, Physik. Z. 33, 720 (1932). (7) Lieben, Zeisel, Monatsh. 4, 536 (1883). (8) Faworski, Jozitsch, J. Russ. Phys.-Chem. Soc. 30, 998-1003 (1898); Cent. 1899, I 778. (9) Pinner, Ann. 179, 44-45 (1875). (10) Freundler, Bull. soc. chim. (4) 1, 501-503 (1907).

(11) Cass (to du Pont), U.S. 2,134,102, Oct. 25, 1938; Brit. 471,186, Sept. 30, 1937. (12) Cass (to du Pont) U.S. 2,097,442, Nov. 2, 1937; Brit. 471,187, Sept. 30, 1937, Cent. 1938, 1218. (13) Levine, Cass (to du Pont), U.S. 2,179,218, Nov. 7, 1939; Brit. 503,615, May 11, 1939; Cent. 1939, II 1572. (14) Henne, Whaley, J. Am. Chem. Soc. 64, 1157 (1942).

```
CH2-CH2
                                                               C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>
                                                                             Beil. I - 84
3:5130 1,2-DICHLOROETHANE
          (Ethylene (di)chloride;
                                                                                   I_{1}-(24)
                                                  Ċī
                                           ĊL
                                                                                   I_{2}-(52)
          sym.-dichloroethane)
 B.P.
                             F.P.
  84.1° cor. at 760 mm. (1) [-32.5^{\circ} (28)] D_4^{25} = 1.2525
                                                                     n_{\rm D}^{25} = 1.4430
                                                              (40)
                                                                                      (47)
  84.08°
                              -35.3° (35)
                                                    1.2463
                                                              (41)
                                                                           1.4427
                                                                                      (91)
        cor. at 760 mm.(2)
  84° at 760 mm.
                                                                           1.4423
                        (3)
                                36°
                                      (11)
                                                    1.24571 (44)
                                                                                      (14)
  83.9° at 766 mm.
                                                                           1.44118 (48)
                        (4)
                             -35.5° (23)
                                                    1.24554 (23)
  83.8°
                    (5)(6)
                                                    1.2455
                                                              (42)
                                       (5)
                             -35.8° (24)
  83.75° at 760 mm.
                        (7)
                                                    1.2445
                                                              (43)
  83.7-84.3°
                             -35.9^{\circ} (37)
                        (8)
                                                    1.2444
                                                              (4)
  83.7-83.9°
                             -36.0° (34)
        cor. at 772 mm.(9)
                                      (38)
                                             D_4^{20} = 1.2569
                                                                     n_{\rm D}^{20} = 1.44507 (49)
  83.7° at 760 mm.
                       (10)
                                                              (10)
      (11) (12) (111) (112) [-42.0^{\circ} (39)]
                                                         (22) (34)
                                                                           1.44505 (50)
  83.65-83.70° at 760 mm. (13)
                                                    1.2541
                                                              (12)
                                                                           1.44476 (18)
  83.65°
                 at 760 mm. (14)
                                                    1.25295 (44)
                                                                                 (19)(20)
                                                    1.25277 (23)
  83.6-83.8°
                             (15) (16) (17)
                                                                           1.4447
                                                                                      (51)
 83.5-83.7°
                             (18) (19) (20)
                                                    1.2521
                                                              (45)
                                                                           1.4446
                                                                                      (52)
 83.5°
                 at 760 mm. (21)
                                                    1.252
                                                              (3)
                                                                                      (79)
                   (22) (23) (34)
                                                    1.2515
                                                              (4)
                                                                           1.4444
                                                                                      (53)
 83.5°
                             (24)
                                                   1.2501
                                                              (46)
                                                                           1.44439 (46)
 83.481° cor.
                 at 760 mm. (25)
                                                                           1.44432 (45)
 83.45°
                 at 760 mm. (26)
                                                                           1.4443 (201)
 83.43-83.48°
                             (27)
                                                                           1.4440
                                                                                      (54)
 83.4-83.6°
                             (28)
                                                                           1.444
                                                                                      (34)
 83.3°
                 at 749 mm. (29)
                                                                           1.44268 (13)
 83°
                             (30)
                                            D_4^{15} = 1.26000 (23) n_D^{15} = 1.44759 (23)
 82.85°
                 at 760 mm.(100)
 82.6-82.8°
                 at 743 mm. (31)
                                                                            See note 3.
 82.4°
                 at 747 mm. (32)
 82.3-82.6°
                             (33)
 81.47° cor.
                 at 700 mm. (2)
 79.325° cor.
                at660.8mm.(25)
 76.63° cor.
                at 600 mm. (2)
                at 500 mm. (2)
 75.05° cor.
 64.73° cor.
                at 400 mm. (2)
 See also Notes 1 and 2.
```

Note 1. For b.p. of Č at press. 660-860 mm. (25), 400-1080 mm. (2), see indic. refs.; Č has b.p. 84.9-85.5° at 777 mm. (53).

Note 2. For vap. press. of \bar{C} over range -30 to 100° (1), or $0-30^{\circ}$ (8), or $0-25^{\circ}$ (55) see indic. refs.; for relation between vap. press. and temp. see (56) (25).

Note 3. For values of n^{18} at 14 different wave lengths see (57).

Care must be taken to avoid confusion of $\bar{\mathbf{C}}$ with either cis (3:5042) or trans (3:5028) 1,2-dichloroethylene.

MISCELLANEOUS PHYSICAL PROPERTIES

Various solubility relations. \bar{C} is almost insol. aq., but easily volatile with steam (see under azeotropes); soly. of \bar{C} in 100 g. aq. at 0° is 0.873 g. (58), 0.922 g. (8); at 10° = 0.885 g. (8); at 15° = 0.872 g. (59); at 20° = 0.869 g. (8), 0.849 g. (58); at 25° = 0.865 g. (15); at 30° = 0.90 g. (59), 0.894 g. (8); at 35° = 0.895 g. (58); at 56° = 1.030 g. (58). — [For influence of added salts in diminishing soly. of \bar{C} in aq. see (16). — Note that \bar{C} with aquander press. forms a solid hydrate which can be maintained up to +18° under 100 atm. but which at ord. press. decomposes below 0° (60). — For soly. of aq. in \bar{C} at 0°, 25°, and 30° (as detd. by Karl Fischer reagt.) see (61).]

[For soly. in \tilde{C} of NH₃ at 20° and 1 atm. (62), of H₂S at 20° and 1 atm. (62), of HCl at various temps. and press. (62) (63), of ethylene at 0-40° (4), or of chlorine at -9° to +40° (4) see indic. refs.]

[For soly. in \bar{C} of I_2 over range 11-25° (and comparison with other chlorinated solvents) see (64).]

[For study of industrial recovery of \bar{C} by countercurrent absorption in kerosene see (65).] Adsorption of \bar{C} by solids. [For studies on adsorption of \bar{C} by activated carbon (66) (67) (68) (69) (70), by silica gel (67), or by alumina gel (71) see indic. refs. — For patent on sepn. of \bar{C} from other solvents by adsorption on carbon see (72).]

Other properties. [For study of thermal conductivity of \bar{C} see (73); for study of diffusion of vapors of \bar{C} through films of various cellulose esters see (74).]

Binary systems contg. C. (See also azeotropes (below).)

 \bar{C} with hydrocarbons — \bar{C} + n-heptane (1:8575): use in testing of distg. columns (detn. of number of theoret. plates) see (75). — \bar{C} + cyclohexane (1:8405): for values of D_0^{20} and n_D^{20} (49), for use in detn. of number of theoret. plates in distg. columns (75), or for sepn. of \bar{C} from system by forming azeotrope of cyclohexane with McOH (76), see indic. refs. (see also below under azeotropes).

 \ddot{C} + benzene (1:7400): note that because of the proximity of the b.p.'s of the components, because of the importance of both as industrial solvents, and because they are not readily separable by chemical means (such as H_2SO_4 , etc.) a great deal of study has been given to the system from various viewpoints.

For f.p./compn. data on system $\ddot{\mathbf{C}}$ + $\mathbf{C}_6\mathbf{H}_6$, eutectic, f.p. -54.2° , contg. about 67 mole % $\ddot{\mathbf{C}}$ see (24) cf. (77); for D_{20}^{20} (78) (79), n_D^{20} (78) (79) (49), or n_D^{25} (80) (89) cf. (81) see indic. refs. — For use of this system as test liq. for studying efficiency of distn. columns see (81) (78) (79) (82); for study of distn. of the system see (78) (79) (81) (82) (83) (84) (85); for use in detn. number of theoret. plates see (75) (78); for data on vap. press. of system, vapor liq. compn., etc., see (86) (87) (88) (80) (49) (89) (90).

 \bar{C} + toluene (1:7405): for n_D^{25} for system see (91) (92); for vapor-liq. equil. data and study of distn. of system see (83) (91) (92) (93).

 \bar{C} with other cpds. of Order I. \bar{C} + acetic acid (1:1010): for values of D and n for the system see (94); for vapor-liq. equil. see (95); see also under uses of \bar{C} (below). — \bar{C} + phenol (1:1420): for vap. press. of system see (96). — \bar{C} + acetime (1:5400): for D and n_D^{2D} see (49) (94), for vapor-liquid equil. see (49). — \bar{C} + diethyl ether (1:6110): for f.p./compn. data and diag. see (24); for D_0^t over range 0-40° see (97). — \bar{C} + ethylene axide (1:6105): for soly. and vap. press. (98) and vapor-liq. equil. (106) see indic. refs.

 \bar{C} with cpds. of Order III. $\bar{C}+CHCl_3$ (3:5050): for b.p./compn. diag. see (99). — $\bar{C}+CCl_4$ (3:5100): for D_{20}^{20} (100) and vapor-liq. compn. data and diagrams (100) (99) (88) (see also below under azeotropes).

 $\ddot{C}+1,1$ -dichloroethane (3:5035): for b.p. at 760 mm., D_4^{20} , and vapor-liq. equil. data see (101). $-\ddot{C}+1,1,2$ -trichloroethane (3:5330): for f.p./compn. data, eutectic f.p. -79°

(102), and for D and vapor-liq. equil. (4) see indic. refs. $-\bar{C}+1,1,2,2$ -tetrachloroethane (acetylene tetrachloride) (3:5750): this system forms a 1:1 cpd., m.p. abt. -31.3° (102); for f.p./compn. data and diagrams see (102); for $n_{\rm H\alpha}^{25}$ /compn. and $n_{\rm H\alpha}^{t}$ for range $t=14-27^{\circ}$ see (30). $-\bar{C}+p$ entachloroethane (3:5880): for f.p./compn. data, eutectic, f.p. -62°, see (102).

 \bar{C} + cis-dichloroethylene (3:5042): for f.p./compn. data see (103). — \bar{C} + trans-dichloro-

ethylene (3:5028): for f.p./compn. data see (103).

 $\bar{C}+1,2,4,5$ -tetrachlorobenzene (3:4115): for f.p./compn. data see (35). — $\bar{C}+carbonyl$ chloride (phosgene) (3:5000): for soly. relations at 20°, 0°, and -15° (104) and b.p., vaporliq. equil. (105) see indic. refs. — $\bar{C}+2$ -chloroethanol-1 (ethylene chlorohydrin) (3:5552): for D and liq.-vapor equil. data and diag. see (106).

 \bar{C} with miscellaneous cpds. of orders other than I or III. \bar{C} + ethylene dibromide: for f.p./compn. data (the two form solid solns.) see (103) (102) cf. (107); for D_{25}^{25} and n_{D}^{25} for system see (48) cf. (108). $-\bar{C}+1,1,2,2$ -tetrabromoethane (sym.-acetylene tetrabromide): for f.p./compn. data see (102). $-\bar{C}+c$ carbon disulfide: for f.p./compn. data and diag. see (28). $-\bar{C}+s$ succino(di)nitrile: for f.p./compn. data, eutectic at -48° , see (102), cf. (109).

Azeotropes (const.-boilg. mixts.) contg. \bar{C} . \bar{C} with aq. forms a heterogeneous const.-boilg. mixt., b.p. 72°, contg. 80.5 wt. % \bar{C} (110).

Azeotropes with hydrocarbons. \bar{C} with cyclohexane (1:8405) forms a const.-boilg. mixt., b.p. 74.4° at 760 mm., $n_0^{20} = 1.42879$, contg. 45.5 wt. % \bar{C} (49).

Azeotropes with other chlorohydrocarbons. \bar{C} with CCl_4 (3:5100) forms a const.-boilg. mixt., b.p. 75.6° at 760 mm. (7), 75.3° at 760 mm. (100), contg. 21 wt. % (7) or 30 mole % (100) \bar{C} . $-\bar{C}$ with trichloroethylene (3:5170) forms a const.-boilg. mixt., b.p. 82.9° at 760 mm., contg. 82 wt. % \bar{C} (7).

Azeotropes with alcohols. \bar{C} with MeOH (1:6120) forms a const.-boilg. mixt., b.p. 60.95° at 760 mm., contg. 68 wt. % \bar{C} (111). $-\bar{C}$ with EtOH (1:6130) forms a const.-boil. mixt., b.p. 70.5° at 760 mm., contg. 63 wt. % \bar{C} (111). $-\bar{C}$ with n-propyl alc. (1:6150) forms a const.-boilg. mixt., b.p. 80.65° at 760 mm., contg. abt. 81 wt. % \bar{C} (111). $-\bar{C}$ with isopropyl alc. (1:6135) forms a const.-boilg. mixt., b.p. 74.7° at 760 mm., contg. 56.5 wt. % \bar{C} (111). $-\bar{C}$ with isobutyl alc. (1:6165) forms a const.-boilg. mixt., b.p. 83.45° at 760 mm., contg. 93.5 wt. % \bar{C} (112). $-\bar{C}$ with ter-amyl alc. (1:6160) forms a const.-boilg. mixt., b.p. 83° at 760 mm., contg. 94 wt. % \bar{C} (113).

Azeotropes with acids. \bar{C} with formic acid (1:1005) forms a const.-boilg. mixt., b.p. 77.4° at 760 mm., contg. 86 wt. % \bar{C} (114). [Note that no data on any azeotrope of \bar{C} with AcOH can be found; however, for use of \bar{C} in dehydration or concn. of AcOH see below under uses of \bar{C} .]

USES OF C

Because of its valuable solvent props. and high volatility \tilde{C} is widely used in a great many different connections, some of which involve its mixture with one or more other organic compounds. — Although no review of its uses could hope to be complete, the following examples are intended to be helpful in suggesting typical cases.

[For general reviews which include uses see (115) (34) (116); for an important annotated and indexed bibliography contg. 469 titles see (117).]

References on the use of \tilde{C} (or of its mixts, with CCl₄) as a furnigant for grain or as an insecticide or fungicide are beyond the scope of this work; however, a few citations on some aspects of this use are given as lead articles.—[E.g., for general articles on this aspect see (118) (119) (120) (121) (122); for study of combustibility of \tilde{C}/CCl_4 mixts, used

for fumigation (123), for study of extinction of flames from \ddot{C} with CO₂ (124), for effect of \ddot{C}/CCl_4 on metals during its use for fumigation (125).]

[For use of \bar{C} in concn. (dehydration) of AcOH see (126) (127) (128) (129) (130); for similar use with propionic acid, butyric acid, and valeric acid see (131), for use in dehydration of EtOH see (132).]

[For use of system \bar{C} (40%) + CCl₄ (3:5100) (60%) as dry cleaner's solvent (133) and removal of scavenged impurities with carbon (134) see indic. refs.; for use of system \bar{C} (75%) + trichloroethylene (3:5170) (25%) as dry cleaner and metal degreesing solvent see (135) (136) (137).]

[For use of \tilde{C} in extraction of oils (138) (139) (140) (141) (142) (143), in purifn. of vitamincontg. oils (144), in extractn. of soybean oil (incl. n_D^{25} for system) (47), in wool degreasing (145) (146) see indic. refs.]

[For use of C in lacquer and varnish industry see (147) (148) (149).]

[For study of \bar{C} as solvent for cellulose acetates see (150) (151), for use of \bar{C} + EtOH as solv. for cellulose acetate see (152); for use of \bar{C} in sepn. of simple from mixed cellulose esters see (153); for use of a mixt. of \bar{C} (90–40%) + an alc. (10–60%) (154) or a mixt. of \bar{C} (40–50%) + an alkyl acetate (60–50%) (155) as solv. for cellulose ethers see indic. refs.]

[For use of \tilde{C} in dewaxing of mineral oil (156) (157), as solvent for rubber (158), for removal of caffeine from coffee (159), as component of refrigerant liq. (160), in purifn. of triphenyl phosphate (161), in dentrifices (162), in hair-wash (163) see indic. refs.]

[For use of C in sepn. of olefins and diolefins from alkanes see (164).]

[For patents on sepn. of mixts. of $\bar{C}+1,2$ -dichloropropane (3:5200) + n-butyl alc. (1:6180) (165), or of $\bar{C}+aq$. sol. alcs. and /or ketones (166), see indic. refs.]

 \bar{C} also serves as a raw material for the comml. manufacture of other prods.; this topic cannot be fully explored here, but attention is called to two important examples. — For use of \bar{C} as starting point for the prepn. of elastothiomers (167) such as "Thiokol A" (168) (169) (170) (from \bar{C} + alkali polysulfide) or elastoplastics (167) of the polyarylethylene type such as AXF (171) (172) (from \bar{C} + aromatic hydrocarbons + AlCl₃) see indic. refs. (and also below under chem. behavior of \bar{C}). — For use of \bar{C} as starting point for prepn. of ethylene glycol (1:6465) by hydrolysis, ethylenediamine by ammonation, or vinyl chloride by dehydrohalogenation see below under chem. behavior of \bar{C} .

TOXICITY AND PHYSIOLOGICAL ACTION OF C

Full treatment of this topic is beyond the scope of this work; however, for lead references on toxicity of \bar{C} see (390) (391) + (173)-(180) incl. (references earlier than 1934 will be found in the cited articles).

[For study of \bar{C} as anthelmintic see (181) (182); for antiseptic and disinfectant actn. see (183) (184); for actn. of \bar{C} on yeast see (185).]

DETERMINATION OF C

Some methods for detn. of \bar{C} involve conversion of all of its halogen to chloride ion and subsequent volumetric or gravimetric detn. of the latter: e.g., for methods based on initial pyrolytic decompn. see (186), for methods involving initial combustion of \bar{C} with MnO₂ at 300° (187), with air (188), in a modified sulfur lamp (189), or (for high conens.) by an explosion pipet method (190) see indic. refs. — For methods based on conversion of halogen to chloride ion by reactn. with Na + ethanolamine in dioxane (191) (192) (latter discussed application to mixts. of \bar{C} with CCl₄ (3:5100) and with tetrachloroethylene (3:5460)), or with alc. NaOEt (193) (194) (195) (note that this method gives CH₂=CHCl + NaCl), see indic. refs.

Note that oxidn. of \bar{C} with CrO_3/H_2SO_4 in pres. of Hg yields CO_2 quantitatively (196) (dif. from many polychloro cpds.). — Note also that \bar{C} does *not* respond to the R + H "Tri-Per Analyzer" (a recording ultra-violet photometer) (197).

For detn. of C in organs and tissues see (198).

PREPARATION OF C

The most-studied method for prepn. and manufacture of \bar{C} is that from ethylene by addn. of chlorine; this method is also of historical interest as leading to the discovery of \bar{C} in 1795 (199) and its initial designation as "oil of the four Dutch chemists." — Various other modes of forms, of \bar{C} have since been discovered and will be indicated below.

Preparation from ethylene. By use of chlorine. Ethylene with chlorine under certain conditions adds chlorine quant. yielding only \bar{C} ; under other conditions, however, the system gives 1,1,2-trichloroethane (3:5330) + HCl. — In the absence of catalysts, the substitution reactn. is avoided by use of very low temperatures; in the presence of catalysts addition (rather than substitution) is facilitated even at the higher temperatures (e.g., 120°) resulting from heat of reactn.

For general articles discussing the various factors involved see (200) (201) (53) (202) (203) (204) (205) (69); for articles discussing the reaction from the viewpoint of utilization of the ethylene of industrial gases see (206)–(214) incl.; for patents on prepn. of \bar{C} from ethylene + Cl_2 see (215)–(236) incl. [For prepn. of "heavy" \bar{C} contg. one C^{13} atom see below under miscell. prepns.]

By use of HOCl ($Cl_2 + H_2O$, etc.). Although ethylene with HOCl solns, gives mainly ethylene chlorohydrin (3:5552) nevertheless some \bar{C} is formed; for studies of this reactn. see (237) (238) (239) (240) (241).

By other miscellaneous reagts. [For formn. of \tilde{C} (together with other prods.) from ethylene with Cl_2 in AcOH or Ac₂O soln. (242), with HCl + air over pumice contg. CuCl₂ at 300° (243), with aq. ICl (244), with NCl₃ in CCl₄ soln. at 20-25° for 7 days (245), with nitryl chloride (ClNO₂) (246), with SbCl₅ or CuCl₂ (247), or with N-chlorourea (253) see indic. refs.]

Formation of \tilde{C} from ethane or acetylene. [For formn. of \tilde{C} from ethane with NOCl at 300° (248) or with $Cl_2 + O_2 + cat.$ at 300-650° (249) see indic. refs.; for formn. of \tilde{C} (together with other prods.) from acetylene with HCl gas in pres. of NO₂ (250), or with Cl_2 in pres. of $CCl_4 + AlCl_3/NaCl/FeCl_3$ at 175-250° (251) cf. (252), see indic. refs.]

Formation of C from miscellaneous sources and by various methods. [For formn. of C (together with other prods.) from methyl chloride (3:7005) in dark elec. discharge (254); from ethyl chloride (3:7015) with Cl₂ in light (255), with NCl₃ (256), or with SbCl₅ in s.t. at 100° (257); from 1,2-dibromoethane (ethylene dibromide) (1 mole) with SbCl₅ (2 moles) (note that use of only 1 mole SbCl₅ yields ethylene chlorobromide) (258); from 1-chloro-2-iodoethane (ethylene chloro-iodide) with finely divided Ag at 160° (259) see indic. refs.]

[For formn. of \tilde{C} (together with other prods.) from ethylene glycol (1:6465) with excess fumg. HCl in s.t. at 100° (260), with PCl₃ + ZnCl₂ (57% yield (261)), with PCl₅ (262), or PCl₅ + ZnCl₂ (37% yield (261)), with SOCl₂ + pyridine (62% yield (261)) see indic. refs.; from ethylene oxide (1:6105) with S₂Cl₂ (263); from 1,4-dioxane (1:6400) with Zn + acid chlorides (264); from 2-chloroethanol-1 (ethylene chlorohydrin) (3:5552) by disproportionation in s.t. at 184° for 10 hrs. (265) or during reactn. with HBr (266); from bis-(β -chloroethyl) sulfate with Cl₂ (267); from bis-(β -chloroethyl) sulfate with conc. aq. HCl (268) or with alk. chloride + dil. HCl (269) see indic. refs.]

[For form. of C (together with other prods.) from diazomethane with ZnCl₂ in ether (270), from ethylenediamine with NOCl in xylene (271), see indic. refs.]

[For prepn. of "heavy" \bar{C} contg. 1 C^{13} atom (from NaC¹³N via CH₃C¹³N, CH₃.C¹³-H₂NH₂, CH₃.C¹³H₂N(CH₃)₃OH, CH₂=C¹³H₂) and its reactn. with Cl₂ see (272).]

CHEMICAL BEHAVIOR OF C

Pyrolysis of C. C on suitable htg. especially in pres. of dehydrohalogenating cat. loses 1 mole HCl yielding vinyl chloride (3:7010) [e.g., C over activated carbon at 230-250° (273), or with aq. vapor over cat. at 800-1000° (274), or over pumice at 600° (275) cf. (276) (277), or over alumina at low red heat (278) yields vinyl chloride (3:7010)].

BEHAVIOR OF C WITH INORGANIC REACTANTS

Reaction of C with Cl₂. C with Cl₂ gives according to the conditions chlorinated derivatives either of the ethylene or ethane series.

[E.g., \bar{C} with Cl₂ in pres. of AlCl₃/NaCl/FeCl₃ at 400–480° gives (279) a mixt. contg. 20% 1,1-dichloroethylene (3:5005) + 22% 1,2-dichloroethylene (3:5030) + 29% trichloroethylene (3:5170) + 29% higher chlorination prods.; \bar{C} with Cl₂ over suitable cat. at 300–500° gives (280) tetrachloroethylene (3:5460).]

[On the other hand, \tilde{C} with Cl_2 in ultra-violet light at 50° (281) (282), or 25° (283), or \tilde{C} with Cl_2 + suitable cat. at not above 60° (284), or \tilde{C} (as liquid) with Cl_2 (285), or \tilde{C} with Cl_2 in pres. of $AlCl_3/NaCl/FeCl_3$ at 300–425° as directed (279), or \tilde{C} with SO_2Cl_2 + trace of dibenzoyl peroxide refluxed 2 hrs. in dark (286) gives (yields: 80% (284), 70% (283) (286), 50% (279)) 1,1,2-trichloroethane (3:5330). — Furthermore, \tilde{C} with Cl_2 as directed (287) (288) or Cl_2 + $AlCl_3$ at 70–80° (289) (327) gives 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750). — Finally \tilde{C} (in vapor phase) with Cl_2 + cat. (290) cf. (285) or \tilde{C} with Cl_2 at elev. temp. and press. (291) yields hexachloroethane (3:4835).]

Reaction of \bar{C} with alkalies. \bar{C} with alkalies or substances behaving as such may according to circumstances undergo either (or both) of two reactions: on the one hand \bar{C} may lose HCl (1 mole) (dehydrohalogenation) yielding vinyl chloride (3:7010); on the other \bar{C} may be hydrolyzed to ethylene glycol (1:6465).

Dehydrohalogenation. C with aq. alk. at elev. temp. and press. (292) especially in press of tetramethylene glycol, etc. (293), or C with MeOH/alk. (294), or EtOH/alk. (53) (295), loses HCl giving (91-93% yield (53)) vinyl chloride (3·7010). — [For study of rate of reactn. of C with KOH in 95% EtOH at 90° and 100° (296) (297), with NaOEt or KOEt in 95% EtOH or 48% EtOH at 90° (296) (297), or with MeOH/NaOMe at 17-19° (298) see indic. refs. — Note that C with alc. NaOEt at 100° under press. gives 90% yield (299) ethyl vinyl ether (1:7810).]

Hydrolysis. C under appropriate conditions hydrolyses to ethylene glycol (1:6465); for general articles from this viewpoint see (110) (214) (314).

[For hydrolysis of \bar{C} to ethylene glycol with aq. vapor over cat. at 550-850° (300), with aq. at 200° under press. in absence of any acid acceptor (301), or with aq. at 120° under press. (302) see indic. refs. cf. (110).]

[For hydrolysis of \bar{C} to ethylene glycol with aq. KOH at elevated temp. and press. see (110). — For study of use of Na₂CO₃ and/or NaHCO₃ in aq. (214) (303) (304) (305) (306) or in 85% EtOH (307) cf. (214) see indic. refs. — For use of aq. CaCO₃ in pres. of NH₄ salts (308) (309), or aq. BaCO₃ (310) at elev. temp. and press., see indic. refs. — For use of sodium formate in MeOH at 165° under press. (311) cf. (214), aq. + PbO in s.t. at 170° (312), or Fe₂O₃ (?) (313) see indic. refs.]

For use of hydrolysis with alk. followed by KMnO₄ oxidn. of resultant ethylene glycol to oxalic acid as means of distinction between \bar{C} and the isomeric 1,1-dichloroethane (3:5035) see (256).

Reaction of \tilde{C} with alk. sulfides or polysulfides, etc. [\tilde{C} with aq. NaSH at 100° under press. gives (65% yield (315)) 1,2-dimercaptoethane ("ethylene dimercaptan") [Beil. I-471, I_1 -(244), I_2 -(529)].]

C with aq. (316) or boilg. alc. (317) Na₂S yields 1,4-dithiane [Beil. XIX-3, XIX₁-(609)],

cryst. from hot alc., m.p. 110-111° (318).

[C with alk. or alk.-earth tetrasulfides yields elastothiomers (167) such as "Thiokol A" (168) (169) (170); for very important compact survey of this reactn. and field see (319); for lecture experiment illustrating prepn. of "Thiokol A" see (320).]

Reaction of \bar{C} with metals. [For studies of \bar{C} from viewpoint of corrosion of metals see (321) (322) (323). — \bar{C} on warming with K loses HCl yielding (295) vinyl chloride (3:7010) and H_2 ; note, however, that \bar{C} with Na or K or their alloys, or even with alkaline-earth metals, may (like many other polychloro cpds.) explode under certain conditions; for extensive studies of this behavior including sensitivity to mechanical shock see (324).]

[C with Na in liq. NH₃ loses both atoms of chlorine yielding (325) (326) ethylene +

NaCl; note that little, if any, (325) ethylenediamine is formed.]

Reaction of Č with various metal salts (of inorganic acids). [Č with anhydrous AlCl₃ at 45-55° loses 1 HCl yielding (53) polymerization prods. of vinyl chloride; at 80-85° the reactn. involves loss of 2 HCl yielding (327) some acetylene.]

[$\bar{\mathbf{C}}$ with anhydrous AlBr₃ yields (328) ethylene dibromide (see also below under reactn. of $\bar{\mathbf{C}}$ with organic cods.).]

Č with boilg. conc. aq. KI gives a little ethylene (329) (dıf. from ethylene dibromide which reacts quant.).

[\bar{C} with aq. alc. Na₂SO₃ refluxed in Cu vessel gives (80-85% yield (330)) of the sodium salt of 2-chloroethanesulfonic acid-1. — For reactn. of \bar{C} with boilg. aq./alc. Na₂S₂O₃ see (331).]

C with alc. AgNO₃ reacts slowly (332); for study of rate see (297).

Reaction of \tilde{C} with misc. non-nitrogenous inorganic reagts. [\tilde{C} with air over CuO at 450° gives (333) phosgene (3:5000). — \tilde{C} with fumg. H₂SO₄ (65–80% SO₃) with or without HgSO₄ yields (334) β -chloroethyl chlorosulfonate + a little bis-(β -chloroethyl) sulfate. — \tilde{C} with dry O₂ in ultra-violet light yields (335) chloroacetic acid (3:1370).]

Reaction of \bar{C} with NH₃ (for reactn. with amines see below). $[\bar{C}$ with conc. aq. NH₃ (336) (337) (338) (339) under press. (340) (341) (342) in pres. of cat. (343) (for use of glass-stoppered press. vessels see (344)), or \bar{C} with dry NH₃ under high press. (345), or \bar{C} with liq. NH₃ (346), yields ethylenediamine [Beil. IV-230, IV₁-(398), IV₂-(676)] always accompanied by higher condens. prods. such as diethylenetriamine, triethylenetetramine, etc. — For rate of reactn. of \bar{C} with NH₃ in 95% EtOH see (296).]

BEHAVIOR OF C WITH ORGANIC REACTANTS

Reactn. of \tilde{C} with aromatic hydrocarbons, aryl halides, or aromatic ethers. [\tilde{C} with aromatic hydrocarbons in the pres. of AlCl₃ leads to various elastoplastics (167) of the polyarylethylene type: e.g., for use in prepn. of AXF type plastics see (171) (172) (347) (348). — For analogous reactn. of \tilde{C} + AlCl₃ with various polychlorobenzenes (249), with xylene (350), with naphthalene (1:7200) (351), or with diphenyl ether (1:7125) (352) see indic. refs.]

Reactn. of \tilde{C} with alcohols, mercaptans, or phenols. \tilde{C} with Na phenolate (271), or with aq. K phenolate refluxed 48 hrs. (353), gives (70-85% yield (353)) ethylene glycol diphenyl ether (1:7235), lfts. from alc., m.p. 98°; note, however, that reactn. of only 1 of the 2 chlorine atoms may (354) lead to β -chloroethyl phenyl ether (3:0165), m.p. 28°, b.p. 217-220° at 760 mm. (355); also that under certain conditions, e.g., \tilde{C} with alc. NaOH + phenol in s.t. at 180-200° for 5 hrs. (356), gives 80% yield phenyl vinyl ether, b.p. 155-

156° (356). — [For reactn. of \tilde{C} with aq. 2,4-dichlorophenol (3:0560) or with 2,4,6-trichlorophenol (3:1673) at 73-98° for 24-66 hrs. giving respectively 1,2-bis-(2,4-dichlorophenoxy)ethane, m.p. 132-133°, and 1,2-bis-(2,4,6-trichlorophenoxy)ethane, m.p. 167-167.5°, see (357).]

[For reactn. of C with 50% NaOH + cellulose see (358). — C with MeOH over Al₂O₈ at 280° loses HCl yielding (359) vinyl chloride (3:7010) + MeCl (3:7005).]

[For reactn. of "heavy" C, viz., ClCH₂.Cl³H₂Cl, with "heavy" benzyl mercaptan, viz., C₆H₅.CH₂.S³⁴H, see (272).]

Reaction of \bar{C} with salts of organic acids. \bar{C} with salts of acids yields the corresp. ethylene glycol esters; note, however, that reactn. of only 1 chlorine atom can lead to β -chloroethyl esters and that loss of HCl and subsequent formn. of vinyl esters (or their polymers) can sometimes occur.

[E.g., Č with NaCN yields (360) succino (di)nitrile [Beil. II-615, II₁-(265), II₂-(554)], m.p. 53-54° (for rate of reactn. of Č with alc. KCN see (296)). — Č with anhydrous alkali or alk.-earth acetate at 230° in glycol diacetate (361) or monoacetate (364), or in alc. at 160-180° under press. (362), or in pres. of an amine salt as cat. at 175-225° (363), yields ethylene glycol diacetate (1:3511), b.p. 190°.]

Reaction of \tilde{C} with miscellaneous non-nitrogenous org. cpds. [For reactn. of \tilde{C} + AlCl₃ (in CCl₄) with CO at 60-70° and 60-70° atm. press. yielding a mixt. of acid chlorides, ketones, etc., see (365). — For reactn. of \tilde{C} with CS₂ + aq. KOH yielding ethylene glycol trithiocarbonate see (366).]

[$\bar{\rm C}$ (0.5 mole) + ethylene dibromide (0.5 mole) + AlCl₃ (0.015 mole) refluxed 2 hrs. (367) or stood at 25° for 35 hrs. (368) undergoes a redistribution reaction giving a prod. contg. 49.8 mole % 1-bromo-2-chloroethane (ethylene chlorobromide) [Beil. I-89, I₁-(28), I₂-(61)], b.p. 107-108°, $n_D^{2D}=1.4908$ (369). — Similarly $\bar{\rm C}$ (1 mole) + ethyl bromide (2 moles) + AlCl₃ (3%) in steel bomb at 25° for 14 days gives a mixt. contg. five prods. in mole % as follows: $\bar{\rm C}$ 9%, EtCl 34%, ethylene chlorobromide 18%, ethylene dibromide 10%, and EtBr 29% (367).]

[For reactn. of \bar{C} with diethyl sodio-malonate leading to tetraethyl butane-1,1,4,4-tetracarboxylate [Beil. II-862, II₁-(333), II₂-(702)] together with various other prods. see (370) (371).]

Reactn. of \bar{C} with amines. \bar{C} with aniline (4 moles) boiled ¾ hr. yields (372) N,N'-diphenyl-ethylenediamine (1,2-bis-(phenylaminoethane)) [Beil. XII-543, XII₁-(282)], m.p. 64° (373) (corresp. bis-acetyl deriv. m.p. 158°), probably accompanied by some N,N'-diphenylpiperazine [Beil. XXIII-8, XXIII₁-(5)], m.p. 164°. [For nitration of 1,2-bis-(phenylaminoethane) see (372) (373); for nitration of N,N'-diphenylpiperazine see (374). — Note that \bar{C} with NaNHC₆H₅ (from aniline + NaNH₂ in dry ether) loses 2 HCl yielding (375) acetylene.]

[\bar{C} with 33% abs. alc. Me₃N stood 10 days gives (22.5% yield (376)) the corresp. monoquaternary salt, β -chloroethyl-trimethyl-ammonium chloride ("choline dichloride"); for study of rate of reactn. of \bar{C} with Me₃N in 90% acctone at 55° see (377). — For studies of rate of reactn. of \bar{C} with other amines, e.g., with benzylamine (296) (297), piperidine (296) (297) (298), pyridine (298) (378), see indic. refs.]

COLOR REACTIONS OF C

With Weber reagent. Č (2 drops) with 2% soln. of phenolphthalein in cyclohexanol (2 ml.) + trace solid NaOH htd. 5 min. at 190-200° (preferably in bath as directed (379)), then cooled and acidified with AcOH (1 ml.) gives lilac color. [Note that acetylene tetrachloride (3:5750) with this reagt. gives a somewhat similar result.]

Comment on NH₄OH/CuCl reagt. Note that \bar{C} with NH₄OH/CuCl does not (380) give any color (dif. from 1,1-dichloroethane (ethylidene (di)chloride) (3:5035) which in 10 min. gives cloudy amethyst coloration (380)).

Comment on Fehling's soln. Note that \bar{C} does not reduce Fehling's soln. even on htg. (dif. from ethylidene (di)chloride (3:5035)).

- **1,2-Diphenoxyethane** (ethylene glycol diphenyl ether) (1:7235). Lfts. from alc., m.p. 98°. [From \bar{C} with aq. K phenolate refluxed 48 hrs. (70-85% yield (353)); note, however, that if only one of the two chlorine atoms reacts some β -chloroethyl phenyl ether, m.p. 28°, b.p. 217-220° at 760 mm. (355), may be formed.]
- 1,2-Di- α -naphthoxyethane (ethylene glycol di- α -naphthyl ether) [Beil. VI-607]. Lfts. from alc., m.p. 127.5° (381). [From $\tilde{C} + \alpha$ -naphthol + aq. NaOH at 120° in s.t. for 8 hrs. (381). Note that the half reactn. prod., β -chloroethyl α -naphthyl ether, has m.p. 28° (355).]
- —— 1,2-Di- β -naphthoxyethane (ethylene glycol di- β -naphthyl ether) [Beil. VI-642]. Lfts. from C₆H₆, m.p. 217° (381). [From $\ddot{C} + \beta$ -naphthol + aq. NaOH at 120° in s.t. for 8 hrs. (381). Note that the half reactn. prod., β -chloroethyl β -naphthyl ether, has m.p. 83° (355).]
- DEthylene 1,2-bis-(isothiourea picrate): ndls. from alc., m.p. 260° (382), 259° (332). [From C with thiourea refluxed in alc. and subsequently treated with PkOH (332).]
- D 1,2-Diphthalimidoethane (ethylene diphthalimide) [Beil. XXI-492, XXI₁-(384)]. Ndls. from AcOH, dil. AcOH or alc., m.p. 236° (383), 232-233° (384), 232° (385). [From C + K phthalimide (2 moles) in s.t. at 200° (386); note that C in very large excess with K phthalimide in s.t. at 180-190° for 3 hrs. gives (387) the half reactn. prod., N-(β-chloroethyl)phthalimide, cryst. from CS₂ or alc., m.p. 81° (388), 79-81° (387) (389).]
- 1,2-Disaccharinoethane: m.p. 253-254° (392). [Not reported from C̄ itself, but obtd. (20% yield) from ethylene (di)bromide with sodium saccharin in aq. butylcarbitol (1:6517) contg. KI on refluxing for 3 hrs.; note that with shorter reflux (1 hr.) some half reactn. prod., viz., N-(β-bromoethyl)saccharin, m.p. 99°, is formed (392).]
- S:5130 (1) Pearce, Peters, J. Phys. Chem. 33, 873-878 (1929). (2) Staedel, Ber. 15, 2563 (1882).
 Mumford, Phillips, J. Chem. Soc. 1928, 159. (4) Partnov, Seferovich, Trans. State Inst. Applied Chem. (U.S.S.R.) 24, 81-89 (1935); C.A. 29, 7272 (1935). (5) Railing, J. Am. Chem. Soc. 61, 3349-3353 (1939). (6) White, Morgan, J. Chem. Phys. 5, 656 (1937). (7) Lecat, Ann. soc. soc. Bruxelles 47-B, I, 110 (1927); Cent. 1927, II 1677; not in C.A. (8) Rex, Z. physik. Chem. 55, 358, 364-365 (1906). (9) Bloom, Sutton, J. Chem. Soc. 1941, 729. (10) Richards, Mathews, J. Am. Chem. Soc. 30, 10 (1908); Z. physik. Chem. 61, 452 (1907).
- (11) Timmermans, Bull. soc. chim. Belg. 25, 310 (1911). (12) Timmermans, Bull. soc. chim. Belg. 24, 244 (1910); Cent. 1910, II 442. (13) Mathews, J. Am. Chem. Soc. 48, 569 (1926). (14) Jones, Schoenborn, Colburn, Ind. Eng. Chem. 35, 666-672 (1935). (15) Gross, J. Am. Chem. Soc. 51, 2362-2364 (1929). (16) Gross, Z. physik. Chem. B-6, 215-220 (1929). (17) Gross, Physik. Z. 32, 588 (1931). (18) Smyth, Dornte, Wilson, J. Am. Chem. Soc. 53, 4252 (1931). (19) Smyth, Hitchcock, J. Am. Chem. Soc. 54, 4634 (1932). (20) Stearn, Smyth, J. Am. Chem. Soc. 56, 1667 (1934).
- (21) Thorpe, J. Chem. Soc. 37, 182 (1880). (22) Curme, Chem. & Met. Eng. 25, 999-1000 (1921). (23) Timmermans, Martin, J. chim. phys. 25, 420-422 (1928). (24) Huettig, Smyth, J. Am. Chem. Soc. 57, 1523-1526 (1935). (25) Smith, Matheson, J. Research Natl. Bur. Standards 20, 641-650 (1938). (26) Tyrer, J. Chem. Soc. 105, 2538 (1914). (27) Sunier, Rosenblum, J. Phys. Chem. 32, 1052-1053 (1928). (28) Hammick, Howard, J. Chem. Soc. 1932, 2915-2916. (29) Schiff. Ann. 220, 96 (1883). (30) Hamai, Bull. Chem. Soc. Japan 8, 297-306 (1933).
- Key, Chem. 32, 1052-1053 (1928). (28) Hammick, Howard, J. Chem. Soc. 1832, 2915-2916.
 Schiff, Ann. 220, 96 (1883). (30) Hammick, Howard, J. Chem. Soc. 1832, 2915-2916.
 Fairbrother, J. Chem. Soc. 1933, 1541. (32) Kraus, Fuoss, J. Am. Chem. Soc. 55, 23 (1933). (33) Greene, Williams, Phys. Rev. (2) 42, 133 (1932). (34) Fife, Reid, Ind. Eng. Chem. 27, 513-514 (1930). (35) Timmermans, Bull. soc. chim. Belg. 43, 632 (1934). (36) Seward, J. Am. Chem. Soc. 56, 2610 (1934). (37) Pitzer, J. Am. Chem. Soc. 62, 332 (1940). (38) Schneider,

Z. physik. Chem. 19, 157 (1896). (39) Haase, Ber. 26, 1053 (1893). (40) Dunstan, Hilditch, Thole, J. Chem. Soc. 103, 137 (1913).

(41) Jaeger, Z. anorg. allgem. Chem. 101, 58 (1917). (42) Walden, Busch, Z. physik. Chem. A-140, 92 (1929). (43) Sugden, J. Chem. Soc. 1933, 772. (44) Götz, Z. physik. Chem. 94, 193 (1920). (45) Brühl, Ann. 203, 10 (1880). (46) Weegmann, Z. physik. Chem. 2, 231 (1888). (47) Johnstone, Spoor, Goss, Ind. Eng. Chem. 32, 834 (1940). (48) McFarlane, Wright, J. Chem. Soc. 1933, 116. (49) Pahlavouin, Bull. soc. chim. Belg. 36, 538, 542-545 (1927). (50) Davies, Phil. Mag. (7) 21, 1022-1025 (1936).

(51) Bragg, Richards, Ind. Eng. Chem. 34, 1088-1091 (1935). (52) Gallaugher, Hibbert, J. Am. Chem. Soc. 58, 815 (1936). (53) Waterman, Leendertse, Colthoff, Chem. Weekblad 32, 550-551 (1935). (54) Hoyt, J. Chem. Education 8, 538 (1931). (55) Radulescu, Alexa, Bul. Soc. Chim. România 20-A, 89-113 (1938); C.A. 34, 934 (1940). (56) Gallaugher, Hibbert, J. Am. Chem. Soc. 59, 2523 (1937). (57) Beynon, Phil. Mag. (7) 28, 558 (1939). (58) van Ackel, Vles, Rec. trav. chim. 55, 410 (1936). (59) Gross, Saylor, J. Am. Chem. Soc. 53, 1744-1751 (1931). (60) Villard, Ann. chim. (7) 11, 388 (1897).

(61) Staverman, Rec. trav. chim. 60, 836-841 (1941); Cent. 1942, I 1352; C.A. 37, 2638 (1943). (62) Bell, J. Chem. Soc. 1931, 1375-1377. (63) Hamai, Bull. Chem. Soc. Japan 10, 5-16 (1935). (64) Margosches, Hinner, Friedmann, Z. anorg. allgem. Chem. 137, 83-90 (1924). (65) Osborne, Simmons, Ind. Eng. Chem. 26, 856-857 (1934). (66) Alekseevskii, Musin, J. Applied Chem. (U.S.S.R.) 12, 704-718 (1939); C.A. 34, 2652 (1940). (67) Pokrovskii, Org. Chem. Ind. (U.S.S.R.) 2, 473-476 (1936); Cent. 1937, II 1242; C.A. 31, 2366 (1937). (68) Pearce, Eversole, J. Phys. Chem. 38, 383-393 (1934). (69) Alekseevskii, J. Russ. Phys.-Chem. Soc. 55, 403-432 (1924); Cent. 1925, II 642; C.A. 20, 2609 (1926); cf. C.A. 19, 2634 (1925). (70) Alekseevskii, J. Applied Chem. (U.S.S.R.) 1, 182-184 (1928); Cent. 1929, II 708; C.A. 23, 4390 (1929).

(71) Perry, J. Phys. Chem. 29, 1462-1468 (1925). (72) Malm, Nadeau (to Eastman Kodak Co.), U.S. 2,203,690, June 11, 1940; C.A. 34, 6860 (1940). (73) Bates, Hazzard, Palmer, Ind. Eng. Chem. 33, 375-376 (1941). (74) Pakshuer, Mankash, J. Phys. Chem. (U.S.S.R.) 11, 400-409 (1938); Cent. 1939, II 2410; C.A. 33, 4106 (1939). (75) Stage, Schultze, Oel u. Kohle 40, 90-95 (1944); C.A. 38, 6134 (1944). (76) Fisher (to Eastman Kodak Co.), U.S. 2,341,433, Feb. 8, 1944; C.A. 38, 4268 (1944). (77) Bury, Jenkins, J. Chem. Soc. 1934, 688-696. (78) Bragg, Richards, Ind. Eng. Chem. 34, 1088-1091 (1942). (79) Bragg, Ind. Eng. Chem., Anal. Ed. 11, 283-287 (1939). (80) Rosanoff, Easley, J. An. Chem. Soc. 31, 970, 979-981 (1909).

(81) Bruun, Shicktanz, J. Research Natl. Bur. Standards 7, 878-882 (1931). (82) Carlson, Colburn & Richards, Bragg, Ind. Eng. Chem. 34, 1533 (1942). (83) Johnstone, Pigford, Trans. Am. Inst. Chem. Engrs. 38, 25-51 (1942). (84) Bragg, Trans. Am. Inst. Chem. Engrs. 37, 19-50 (1941). (85) Bragg, Ind. Eng. Chem. 33, 279-282 (1941). (86) Litvinov, J. Phys. Chem. (U.S.S.R.) 13, 119-123 (1939); 14, 562-570 (1940); C.A. 34, 299 (1940), 35, 2046 (1941), respt. (87) Smoker, Rose, Trans. Am. Inst. Chem. Engrs. 36, 285-293 (1940). (88) Kircev, Skvortsova, J. Phys. Chem. (U.S.S.R.) 7, 63-70 (1936); Cent. 1937, II 755; C.A. 31, 25 (1937). (89) von Zawidzki, Z. physik. Chem. 35, 145, 148 (1900). (90) Schulze, Hock, Z. physik. Chem. 86, 446-449 (1914).

(91) Colburn, Stearns, Trans. Am. Inst. Chem. Engrs. 37, 291-309 (1941). (92) Jones, Schoenborn, Colburn, Ind. Eng. Chem. 35, 666-672 (1943). (93) Colburn, Schoenborn, Shilling, Ind. Eng. Chem. 35, 1250-1254 (1943). (94) Schwers, Bull. acad. roy. Belg., Classe sci. 1912, 610-654; Cent. 1913, I 211; C.A. 7, 2896-2897 (1913). (95) Othmer, Ind. Eng. Chem. 35, 614-620 (1943). (96) Neissenberger, Schuster, Zack, Z. angew. Chem. 39, 270-271 (1926). (97) Götz, Z. physik. Chem. 94, 192-198 (1920). (98) Kaplan, Reformatskaya, J. Gen. Chem. (U.S.S.R.) 7, 545-549 (1937); Cent. 1937, II 2332; C.A. 31, 4554 (1937). (99) Kireev, Monakhova, J. Phys. Chem. (U.S.S.R.) 7, 71-76 (1936); Cent. 1937, II 755; C.A. 31, 25 (1937). (100) Young, Nelson, Ind. Eng. Chem., Anal. Ed. 4, 67-69 (1932). (101) Kaplan, Monakhova, J. Gen. Chem. (U.S.S.R.) 7, 2499-2512 (1937); Cent. 1938, II

(101) Kaplan, Monakhova, J. Gen. Chem. (U.S.S.R.) 7, 2499-2512 (1937); Cent. 1938, II
1572; C.A. 32, 2404 (1938). (102) Timmermans, Vesselovsky, Bull. soc. chim. Belg. 48, 505-512 (1931). (103) Timmermans, Bull. soc. chim. Belg. 36, 184-186 (1927). (104) Kireev, Kaplan, Vasneva, J. Gen. Chem. (U.S.S.R.) 6, 799-805 (1936); Cent. 1937, II 755; C.A. 36, 7013 (1936). (105) Kireev, Kaplan, Zlobin, J. Applied Chem. (U.S.S.R.) 8, 949-951 (1935); Cent. 1937, I 3474; C.A. 36, 5484 (1936). (106) Kaplan, Grishin, Skvortsova, J. Gen. Chem. (U.S.S.R.) 7, 538-544 (1937); Cent. 1937, II 2332; C.A. 31, 4554 (1937). (107) Bruni, Gazz. chim. ital. 28, I 277-283 (1898). (108) Biron, J. Russ. Phys.-Chem. Soc. 41, 569-586 (1909); Cent. 1908, II 608; C.A. 5, 608 (1911). (109) Bruni, Manuelli, Z. Elektrochem. 11, 860-862 (1905). (110) Bahr, Zieler, Z. angew. Chem. 43, 286-289 (1930).

(111) Lecat, Rec. trav. chim. 45, 623-624 (1926). (112) Lecat, Rec. trav. chim. 47, 15 (1928). (113) Lecat, Ann. soc. sci. Bruxelles 47, I 152 (1927). (114) Lecat, Ann. soc. sci. Bruxelles 48-B,

I 56 (1928). (115) Killefer, Ind. Eng. Chem. 19, 636-639 (1927). (116) Putikov, Zimakov, J. Chem. Ind. (Moscow) 1932, No. 6, 36-44; Cent. 1933, I 2607; C.A. 26, 5290 (1932). (117) Gersdorff, U. S. Dept. Agr., Misc. Pub. 117 (1932). (118) Winteringham, J. Soc. Chem. Ind. 63, 144-150 (1944); C.A. 38, 5013 (1944). (119) Sherrard, U. S. Pub. Health Repts. 57, 753-759 (1942); C.A. 36, 4245 (1942). (120) Russ, Ind. Eng. Chem. 22, 844-847 (1930).

(121) Hoyt, Ind. Eng. Chem. 20, 835-837, 931-932 (1928). (122) Cotton, Roark, J. Econ. Entomol. 20, 636-639 (1927); C.A. 21, 3416 (1927). (123) Popov, Bezub, Trans. Sci. Inst. Fertilizers Insectofungicides (U.S.S.R.), No. 135, 98-102 (1939); C.A. 34, 5663 (1940). (124) Jones, Kennedy, Ind. Eng. Chem. 22, 963-964 (1930). (125) Popov, Lebedeva, Trans. Sci. Inst. Fertilizers Insectofungicides (U.S.S.R.) No. 135, 102-104 (1939); C.A. 34, 6210 (1940). (126) Rutkovskii, Gorbunova, Org. Chem. Ind. (U.S.S.R.) 3, 686-693 (1937); Cent. 1938 II 410; C.A. 31, 6926 (1937). (127) Othmer (to Eastman Kodak Co.), U.S. 1,917,391, July 11, 1933; Cent. 1933, II 2192; C.A. 27, 4544 (1933). (128) Kodak-Pathé, French 667,559, Oct. 18, 1929; Cent. 1930, I 435; C.A. 24, 123 (1930). (129) Eastman Kodak Co., Brit. 327,444, May 1, 1930; Cent. 1930, II 306; C.A. 24, 5045 (1930). (130) Holzverkohlungs Ind. A.-G., Ger. 472,399, Feb. 27, 1929; Cent. 1929, I 2819; C.A. 23, 2449 (1929).

(131) Stone (to Eastman Kodak Co.), U.S. 1,939,237, Dec. 12, 1933; Cent. 1934, I 1245; C.A. 28, 1363 (1934). (132) Kodak-Pathé, French 701,355, March 16, 1931; Cent. 1931, II 925; C.A. 25, 4084 (1931). (133) Mohn (to Rhodes-Perry-Martin, Inc.), U.S. 1,940,688, Dec. 26, 1933; Cent. 1934, I 2214; C.A. 28, 1552 (1934). (134) Stout, Tillmann, Ind. Eng. Chem. 28, 22-25 (1936). (135) Schmidt, Deutsch. Färber-Zig. 72, 159-160 (1936); Cent. 1936, II 394. (136) Compagnie des Prod. Chim. d'Alais, French 785,864, Aug. 21, 1935; Cent. 1935, II 3859; not in C.A. (137) Reid (to Union Carbide and Chem. Corp.), U.S. 2,070,962, Feb. 16, 1937; Cent. 1937, I 4040; C.A. 31, 2716 (1937). (138) Rapoport, Sbornik Dikhloretan 1939, 52-91; C.A. 37, 4225 (1942). (139) Rapoport, Sherstyanoe Delo 1939, No. 12, 20-22; C.A. 36, 6018 (1942). (140) Chernukhin, Maslobolno Zhirovoe Delo 13, No. 3, 7-8 (1937); Cent. 1938, I 769; C.A. 31, 8967 (1937).

(141) Bauer, Lauth, Chem. Umschau Fette, Oele, Wachse, Harze 35, 82-86 (1928); Cent. 1928, I 2675; C.A. 22, 2221 (1928). (142) Hassel, Seifensieder Zy. 56, 370-372 (1929); Cent. 1929, II 3077; C.A. 24, 982 (1930). (143) I.G., French 645,497, Oct. 26, 1928; Cent. 1929, II 234; C.A. 23, 2057 (1929). (144) Buxton (to Natl. Oil Prod. Co.), Brit. 535,014, March 24, 1941; Cent. 1942, II 2655; C.A. 36, 1442 (1942). (145) Matetskii, Rapoport, Garlinskaya, Tarnovskaya, Sherstyanoe Delo 19, No. 3/4, 14 (1940); Cent. 1940, II 2701; C.A. 37, 2583 (1943); C.A. 36, 5656 (1942). (146) Rapoport, Sherstyanoe Delo 18, No. 12, 20-22 (1939); Cent. 1940, II 1092; C.A. 36, 5656 (1942). (147) Frazier, Reid, Ind. Eng. Chem. 22, 604-608 (1930). (148) Zhebrovskii, Chistova, Org. Chem. Ind. (U.S.S.R.) 1, No. 1, 28-31 (1936); Cent. 1937, I 1290; C.A. 30, 4023 (1936). (149) Nemirovskaya, Sbornuk Dikhloretan 1939, 100-103; C.A. 36, 3974 (1942). (150) Papkov, Kargin, Rogovin, J. Phys. Chem. (U.S.S.R.) 10, 607-619 (1937); Cent. 1939, II 4206; C.A. 32, 5682 (1928).

(151) Rogovin, Kargin, Papkov, J. Phys. Chem. (U.S.S.R.) 10, 793-797 (1937); Cent. 1939, II 4206; C.A. 32, 8132 (1938). (152) Lindsay, U.S. 1,027,614, May 28, 1912; [C.A. 6, 1989 (1912)]. (153) Malm, Fisher (to Eastman Kodak Co.), U.S. 1,966,302, July 10, 1934; Cent. 1935, II 462; C.A. 28, :667 (1934). (154) Carroll (to Eastman Kodak Co.), U.S. 1,429,188, Sept. 12, 1922; Cent. 1922, IV 1183; C.A. 16, 3758 (1922). (155) Carroll (to Eastman Kodak Co.) U.S. 1,461,170, Aug. 7, 1923; Cent. 1923, IV 809; C.A. 17, 3253 (1923). (156) Goldberg, Abezguz, Margolis, Azerbaudzhanskoe Neftyanoe Khoz. 1935, No. 3, 74-81; Cent. 1935, II 3859; C.A. 29, 6411 (1935). (157) Standard Oil Development Co., French 790,852, Nov. 28, 1935; Cent. 1936, I 2672; C.A. 30, 3223 (1936). (158) Provorov, Caoutchouc and Rubber (U.S.S.R.) 1939, No. 11, 24-27; C.A. 34, 3133 (1940). (159) Coffex, A.G., Swiss 157,021, Nov. 16, 1932; Cent. 1933, I 2758; not in C.A. (160) Davenport (to Chicago Pneumatic Tool Co.), U.S. 1,803,098, April 28, 1931; Cent. 1932, I 1935; [C.A. 25, 3746 (1931)].

(161) Reid (to Eastman Kodak Co.), Ü.S. 2,053,532, Sept. 8, 1936; Cent. 1937, I 4427; C.A. 39, 7127 (1936). (162) Brounlee, U.S. 1,645,791-1,645,793, incl., Oct. 18, 1927; Cent. 1928, I 225; C.A. 22, 141 (1928). (163) Cathala, French 598,518, Dec. 18, 1925; Cent. 1926, I 2752; not in C.A. (164) Young, Perkins (to Carbide and Carbon Chem. Corp.), U.S. 1,948,777, Feb. 27, 1934; Cent. 1935, I 1807; [C.A. 28, 2723 (1934)]; Canadian 328,052, Nov. 29, 1932; Cent. 1935, I 1807; C.A. 27, 991 (1933). (165) Bright, Fisher (to Eastman Kodak Co.), U.S. 2,350,719, June 6, 1944; C.A. 38, 4960 (1944). (166) Fisher, Shearon (to Eastman Kodak Co.), U.S. 2,327,779, Aug. 24, 1943; C.A. 38, 665 (1944). (167) Fisher, Ind. Eng. Chem. 31, 942 (1939). (168) Martin, Patrick, Ind. Eng. Chem. 28, 1144-1149 (1936). (169) Patrick, Trans. Faraday Soc. 32, 347-358 (1936). (170) Patrick, U.S. 1,890,191, Dec. 6, 1932; Cent. 1933, I 1857; C.A. 27, 1724 (1933): French 719,212, June 27, 1931; C.A. 28, 3344 (1932).

(171) Shinkle, Brooks, Cady, Ind. Eng. Chem. 28, 275-280 (1936). (172) Shinkle (to U.S. Rubber Co.), U.S. 2,016,027, Oct. 1, 1935; Cent. 1936, II 3030; C.A. 29, 8176 (1935); U.S. 2,016,-026, Oct. 1, 1935; C.A. 29, 8175 (1935); French 43,916, Sept. 19, 1934; Cent. 1935, I 2100; not in C.A. (173) Rozenbaum, Sbornik Dikhloretan 1939, 109-119; C.A. 36, 2956 (1942). (174) Smyth, N. Y. State Med. J. 42, 1072-1079 (1942); C.A. 36, 4626 (1942). (175) McNally, Fostved T. Ind. Med. 19, 373-374 (1941); C.A. 36, 4627 (1942). (176) McCawley, Unr. Calif. Pub. Pharmacol. 2, 89-97 (1942); C.A. 36, 4911 (1942). (177) Wirtschaften, Schwartz, J. Ind. Hyg. Toxicol. 21, 128-131 (1939). (178) von Oettingen, J. Ind. Hyg. Toxicol. 19, 394-396 (1937). (179) Hueper, Smith, Am. J. Med. Sci. 189, 778-784 (1935); Cent. 1935, II 1059; not in C.A. (180) Barsoum, Saad, Quart. J. Pharm. Pharmacol. 7, 205-214 (1934); Cent. 1934, II 2550; C.A. 28, 6194 (1934).

(181) Tomb, Helmy, J. Trop. Med. Hyg. 36, 265-270 (1933); Cent. 1934, I 728; not in C.A. (182) Hall, Shillinger, J. Agr. Research 29, 313-332 (1924). (183) Gabbano, Z. Hyg. Infections-krankh. 109, 183-193, 194-200 (1928); Cent. 1928, II 2667-8; not in C.A. (184) Joachimoglu, Biochem. Z. 124, 130-136 (1921); Cent. 1922, I 363; C.A. 16, 946 (1922). (185) Plagge, Brochem. Z. 118, 129-143 (1921); Cent. 1922, I 52; C.A. 15, 2894 (1921). (186) Winteringham, J. Soc. Chem. Ind. 61, 190-192 (1942); C.A. 37, 1951. (187) Bogatkov, Zavodskaya Lab. 10, 319 (1941); Cent. 1942, II 1943; C.A. 35, 7318 (1941). (188) Van Winkle, Smith, J. Am. Chem. Soc. 42, 342 (1920). (189) Elkins, Hobby, Fuller, J. Ind. Hyg. Toxcool. 19, 474-485 (1937). (190)

Jones, Ind. Eng. Chem. 20, 367-370 (1928).

(191) Rauscher, Ind. Eng. Chem., Anal. Ed. 9, 296-299 (1937). (192) Winteringham, J. Soc. Chem. Ind. 61, 190-192 (1942); C.A. 37, 1951 (1943). (193) Mel'nikov, Senilov, Lab. Prakt. (U.S.S.R.), No. 9/10, 18-20 (1939); C.A. 34, 2286 (1940). (194) Rozenbaum, Sbornk Dikhloretan 1939, 109-119; C.A. 36, 2956 (1942). (195) Ginzburg, Zavodskaya Lab. 7, 1438 (1938); C.A. 33, 4909 (1939). (196) Guyot, Simon, Compt. rend. 170, 736 (1920). (197) Hanson, Ind. Eng. Chem., Anal. Ed. 13, 119-123 (1941). (198) Gettler, Siegel, Arch. Path. 19, 208-212 (1935); C.A. 29, 4786 (1935). (199) Crell's Chem. Ann. 2, 195-205, 310-316, 430-440 (1795). (200) Gayat. Ber. 76, 1115-1118 (1943).

(201) Conn, Kistiakowsky, Smith, J. Am. Chem. Soc. 60, 2764-2771 (1938). (202) Bahr, Zieler, Z. angev. Chem. 43, 233-236 (1930). (203) Sherman, Sun, J. Am. Chem. Soc. 56, 1096-1101 (1934). (204) Stewart, Smith, J. Am. Chem. Soc. 51, 3082-3095 (1929). (205) Schmitz, Schumacher, Jager, Z. physik. Chem. B-51, 281-305 (1942). (206) Kinumaki, et al., J. Chem. Soc. Japan 53, 398-403 (1932); 54, 142-150 (1933); 54, 150-152 (1933); C.A. 26, 4231 (1932); 27, 2369 (1933); 27, 2369 (1933), respt. (207) Kukushkin, Brodovich, Krasnovskaya, Coke and Chem. (U.S.S.R.) 1949, No. 4/5, 32-37; C.A. 37, 1245 (1943). (208) Golev, Sbornik Dikhloretan 1939, 18-20, 21-24; C.A. 36, 2523 (1942). (209) Rudenko, Sbornik Dikhloretan 1939, 14-17; C.A. 36, 2522 (1942). (210) Mamedaliev, Azerbaidzhanskoe Neftyanoe Khoz. 1935,

No. 3, 67-74; Cent. 1935, I 3915; C.A. 29, 6205 (1935).

(211) Dobryanskii, Gutner, Shchigel'skaya, Trans. State Inst. Applied Chem. (U.S.S.R.) 24, 21-31 (1935); C.A. 29, 7271 (1935); not in Cent. (212) Dobryanskii, Khomutin, Trans. State Inst. Applied Chem. (U.S.S.R.) 24, 32-47 (1935); C.A. 29, 7271 (1935); not in Cent. (213) Doroganevskaya, J. Chem. Ind. (Moscow) 8, 857-860 (1931); Cent. 1931, II 2385; C.A. 26, 79-80 (1932). (214) Smolenski, Przemysl Chem. 11, 146-182 (1927); Cent. 1927, II 1640; C.A. 23, 2930 (1929). (215) Groll, Hearne, LaFrance (to Shell Development Co.), U.S. 2,245,776, June 17, 1941; C.A. 35, 5913 (1941). (216) Ruys, Edwards (to Shell Dev. Co.), U.S. 2,099,231, Nov. 16, 1937; Cent. 1938, I 3387; C.A. 32, 190 (1938). (217) Reynhart (to Shell Dev. Co.), U.S. 2,043,932, June 9, 1936; C.A. 30, 5235 (1936); N.V. de Bataafsche Petroleum Maatschappij, Brit. 446,411, May 28, 1936; Cent. 1936, II 2611; C.A. 39, 6757 (1936). (218) Dow (Dow Chem. Co.), U.S. 1,841,279, Jan. 12, 1932; Cent. 1933, II 3046; C.A. 26, 1615 (1932). (219) Askensay, Heller, U.S. 1,851,970, April 5, 1932; Cent. 1932, II 1366; C.A. 26, 2989 (1932). (220) Curme, U.S. 1,315,545, Sept. 9, 1919; C.A. 13, 2883 (1919); not in Cent.

(221) Brooks, Smith, U.S. 1,231,123, June 26, 1917; C.A. 11, 2405 (1917). (222) Johannsen, Berger (to Röchlingsche Eisen u. Stahlwerke), Ger. 678,427, July 17, 1939; Cent. 1939, II 3487; C.A. 23, 7822 (1939). (223) Maier, Ger. 529,524, July 14, 1931; Cent. 1931, II 1921; C.A. 25, 5178 (1931): French 653,434, March 21, 1929; Cent. 1929, I 3141; C.A. 23, 3718 (1929). (224) Askenasy, Heller, Ger. 549,341, April 26, 1932; Cent. 1932, II 287; C.A. 26, 3807 (1932). (225) Engelhardt (to I.G.), Ger. 442,342, March 30, 1927; Cent. 1927, I 2685; not in C.A.: Brit. 177,362, April 20, 1922; Cent. 1923, II 476; C.A. 16, 3093 (1922): French 532,735, Feb. 10, 1922; Cent. 1923, IV 476; not in C.A. (226) Union Carbide Co., Ger. 437,000, Nov. 12, 1926; Cent. 1927, I 354; not in C.A.: Swiss 92,115, Dec. 16, 1921; Cent. 1923, II 475; not in C.A. (227) Wietzel, Dierksen (B.A.S.F.), Ger. 420,500, Oct. 24, 1925; Cent. 1926, I 2245; not in C.A. (228) Matter (to T. Goldschmidt A. G.), Ger. 298,931, Jan. 26, 1922; Cent. 1922, II 1170; not in C.A.: French

533,295, Feb. 27, 1922; Cent. 1922, II 1171; not in C.A. (229) I.G., French 770,943, Sept. 24, 1934; Cent. 1935, I 2255; C.A. 29, 817 (1935). (230) Maier, French 655,930, April 25, 1929; Cent. 1929, II 1347; C.A. 23, 3931 (1929).

(231) Damiens, de Loisy, Piette, French 535,210, April 11, 1922; Cent. 1923, II 741; not in C.A. (232) T. Goldschmidt, A. G., French 533,296, Feb. 27, 1922; Cent. 1922, IV 393; not in C.A.: Brit. 147,909, Nov. 3, 1921; Cent. 1922, IV 393-394; C.A. 15, 97 (1921). (233) Goldschmidt, Arnold, Brit. 158,836, March 10, 1921; Cent. 1921, II 1060; C.A. 15, 1953 (1921). (234) Marks, Brit. 136,489, July 2, 1919; C.A. 14, 1122 (1920), not in Cent. (235) Harding, Brit. 126,511, June 11, 1918; C.A. 13, 2375 (1919); not in Cent. (236) Gosudarstvennui Trest Rezinovoi Promuishlennosti & Matisen, Russian 24,877, Jan. 31, 1932; Cent. 1933, I 672; C.A. 30, 1808 (1936); also 26, 3513 (1932). (237) Gomberg, J. Am. Chem. Soc. 41, 1414-1431 (1919). (238) Shilov, Kanyaev, Domina, Ionina, J. Phys. Chem. (U.S.S.R.) 13, 1242-1248 (1939); C.A. 35, 371 (1941). (239) Shilov, Solodushenkov, Kurakin, J. Phys. Chem. (U.S.S.R.) 13, 759-766 (1939); C.A. 34, 7708 (1940). (240) Soc. Anon. Ind. Chim. Barzaghi, Italian 337,801, May 20, 1935; Cent. 1937, I 3548; not in C.A.

(241) Irvine, Haworth (to Carbide and Carbon Chem. Corp.), U.S. 1,496,675, June 3, 1924; Cent. 1924, II 1511; [C.A. 18, 2345 (1924)]. (242) Weber, Hennion, Vogt, J. Am. Chem. Soc. 61, 1457–1458 (1939). (243) Ernst, Wahl (to I. G.), Ger. 430,539, June 23, 1926; Cent. 1926, II 1189; not in C.A. (244) Vorhees, Skinner, J. Am. Chem. Soc. 47, 1127 (1925). (245) Coleman, Mullins, Pickering, J. Am. Chem. Soc. 50, 2739–2741 (1928). (246) Steinkopf, Kühnel, Ber. 75, 1323 (1942). (247) Wohler, Ann. Physik. 13, 297 (1825/9). (248) Moyer (to Solvay Process Co.), U.S. 2,152,357, March 28, 1939; Cent. 1939, II 1775; C.A. 33, 5001 (1939). (249) Gremli, Austrian 108,421, 108,424, Dec. 27, 1927, Cent. 1928, I 1229; not in C.A. (250) Bauer (to Rohm, Haas, A.G.), U.S. 1,540,748, June 9, 1925; Cent. 1925, II 1563; not in C.A.

(251) Reilly (to Dow Chem. Co.), U.S. 2,140,551, Dec. 20, 1938; Cent. 1939, I 3625; C.A. 33, 2540 (1939). (252) Mouneyrat, Bull. soc. chrm. (3) 19, 448-452 (1898). (253) Likhosherstov, Alekseev, J. Applied Chem. (U.S.S.R.) 7, 127-133 (1934); Cent. 1935, I 3915; C.A. 29, 452 (1935). (254) Besson, Fournier, Compt. rend. 150, 1120 (1910). (255) D'Ans, Kautzsch, J. prakt. Chem. (2) 80, 307-314 (1909). (256) Coleman, Noyes, J. Am. Chem. Soc. 43, 2214-2215 (1921). (257) Meyer, Muller, Ber. 24, 4249 (1891); J. prakt. Chem. (2) 46, 173-174 (1892). (258) Lossner, J. prakt. Chem. (2) 13, 421-423 (1876). (259) Friedel, Silva, Bull. soc. chim. (2) 17, 242 (1872). (260) Schorlemmer, J. Chem. Soc. 39, 143-144 (1881).

(261) Clark, Streight, Trans. Roy. Soc. Canada (3) 23, III 77-89 (1929). (262) Wurtz, Compt. rend. 45, 228 (1857); Ann. 104, 174-175 (1857); Ann. chim. (3) 55, 419-421 (1859). (263) Malinovskii, J. Gen. Chem. (U.S.S.R.) 9, 832-839 (1939); C.A. 34, 375 (1940). (264) Varvoglis, Praktika Akad. Athenon 13, 42-48 (1938); Cent. 1938, II 1394; C.A. 34, 5050 (1940). (265) Krassuski, J. Russ. Phys.-Chem. Soc. 34, 287-315 (1902); Cent. 1902, II 20. (266) Demole, Ber. 9, 560 (1876). (267) Levaillant, Compt. rend. 189, 466 (1929). (268) Suter, Evans, J. Am. Chem. Soc. 60, 536 (1938). (269) Levaillant, Compt. rend. 187, 732 (1928). (270) Caronna, Sansone, Atti congr. intern. chim. 10th Congr. Rome 1938 3, 77-81 (1939); Cent. 1939, II 3974; C.A. 34, 980 (1940).

(271) Ssolonina, J. Russ. Phys.-Chem. Soc. 30, 606-632 (1898); Cent. 1899, I 25. (272) Kilmer, du Vigneaud, J. Buol Chem. 154, 247-253 (1944). (273) I.G., Ger. 585,793, Oct. 9, 1933; Cent. 1934, I 124; C.A. 28, 1361 (1934). (274) Baxter, Edwards, Winter (to Imperial Chem. Ind., Ltd.), Brit. 363,009, Jan. 7, 1932; Cent. 1932, I 3497; [C.A. 27, 1365 (1933)]; French 721,808, Aug. 20, 1931; C.A. 26, 4067 (1932). (275) Boeseken, Bastet, Rec. trav. chim. 32, 187-188 (1913). (276) Biltz, Ber. 35, 3525 (1902). (277) Biltz, Kuppers, Ber. 37, 2398-2423 (1904). (278) Senderens, Compt. rend. 146, 1213 (1908); Bull. soc. chim. (4) 3, 828 (1908). (279) Reilly (to Dow Chem. Co.), U.S. 2,140,548, 2,140,549, Dec. 20, 1938; Cent. 1939, I 3625; C.A. 33, 2540 (1939). (280) Reilly (to Dow Chem. Co.), U.S. 1,947,491, Feb. 20, 1934; Cent. 1935, I 3345; C.A. 28, 2371 (1934).

(281) Compagnie des Prod. Chim. d'Alais, etc., French 804,491, Oct. 24, 1936; Cent. 1937, I 1545; C.A. 31, 3509 (1937). (282) Coleman, Moore (to Dow Chem. Co.), U.S. 2,174,737, Oct. 3, 1939; C.A. 34, 779 (1940). (283) Maier, Ger. 522,959, April 20, 1931; [Cent. 1931, I 3607; C.A. 25, 3670: French 655,930, April 25, 1929; Cent. 1929, II 1347; C.A. 23, 3931 (1929). (284) Jung, Zimmermann (to I. G.), Ger. 545,993, March 8, 1932; Cent. 1932, I 2893; C.A. 26, 3520 (1932). (285) Hamai, Bull. Chem. Soc. Japan 9, 542-548 (1934). (286) Kharasch, Brown, J. Am. Chem. Soc. 61, 2145 (1939). (287) Levine (to du Pont Co.), Can. 395,846, April 15, 1941; C.A. 35, 4782 (1941): Brit. 505,196, June 1, 1939; Cent. 1939, II 2712; C.A. 33, 7814 (1939). (288) Rodebush (to U.S. Ind. Alc. Co.), U.S. 1,402,318, Jan. 3, 1922; Cent. 1923, II 960; [C.A. 16, 935 (1922)]. (289) Tzyurikh, Trans. State Inst. Applied Chem. (U.S.S.R.) 24, 70-80 (1935);

C.A. 29, 7271 (1935); not in Cent. (290) Schrader, Havestadt (to T. Goldschmidt, A.G.), Ger. 712,999, Oct. 29, 1941; Cent. 1942, I 2064; C.A. 37, 4748 (1943).

(291) I.G., French 837,741, Feb. 20, 1939; Cent. 1939, II 228; [C.A. 33, 5865 (1939)]. (292) Young (to Carbide and Carbon Chem. Corp.), U.S. 1,752,049, March 25, 1930; Cent. 1930, II 1280; [C.A. 24, 2468 (1930)]. (293) Strosacker, Amstutz (to Dow Chem. Co.), U.S. 2,322,258, June 22, 1943, C.A. 38, 114 (1944). (294) I.G., French 694,575, Dec. 5, 1930; Cent. 1931, I 2112; C.A. 25, 1845 (1931). (295) Regnault, Ann. 14, 30, 37 Note (1835); Engel, Compt. rend. 164, 1621-1624 (1887). (296) Petrenko-Kritschenko, et al., Z. physik. Chem. 116, 317 (1925). (297) Petrenko-Kritschenko, Opotzky, Ber. 59, 2131-2140 (1926). (298) Tronov, Laduigina, J. Russ. Phys.-Chem. Soc. 62, 2165-2171 (1930); Cent. 1931, II 408; C.A. 25, 3957 (1931). (299) I.G., French 38,910, Aug. 10, 1931; Cent. 1932, I 1438; [C.A. 26, 1616 (1932)]; Brit. 341,074, Feb. 5, 1931; Cent. 1932, I 2994; [C.A. 25, 4891 (1931). (300) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994; [C.A. 26, 2747 (1932)].

(301) Bauer (to Rohm, Haas, A. G.), Ger. 574,064, April 8, 1933; Cent. 1933, I 3629; C.A. 27, 3486, 4546 (1933); French 629,204, Nov. 7, 1927; Cent. 1928, I 845; not in C.A. (302) Maier, French 656,651, May 11, 1929; Cent. 1929, II 649; C.A. 23, 4231 (1929). (303) Klebanskii, Dolgol'skii, J. Applied Chem. (U.S.S.R.) 7, 790-806 (1934); Cent. 1935, I 3915; C.A. 29, 2509 (1935): Russ. 42,071, March 31, 1935; Cent. 1936, I 435; C.A. 30, 8240 (1936). (304) Contardi, Ciocca, Ricerca sci. 16, II, 9-16 (1938); Cent. 1938, II 4310; C.A. 33, 9283 (1938). (305) Zeller, Hufner, J. prakt. Chem. (2) 11, 232 (1875). (306) Matter, Ger. 299,074, Feb. 24, 1920; Cent. 1920, IV 14; not in C.A.: Brit. 147,906, 147,907, Doc. 8, 1921; Cent. 1922, II 1079; C.A. 15, 97 (1921). (307) Rodebush (to U. S. Industrial Alc. Co.), U.S. 1,402,317, Jan. 3, 1922; Cent. 1923, II 960; C.A. 16, 934 (1922). (308) Ferrero, Vandendries, Congr. chem. and 15th Congr. Brussels (1935) 1936, 250-256; Cent. 1936, II 1896; C.A. 30, 5556 (1936). (309) Soc. Carbochim, Ger. 695,997, Aug. 8, 1940; [C.A. 35, 5914 (1941)]. French 774,186, Dec. 3, 1934, Cent. 1935, II 437; [C.A. 29, 4381 (1935)]. (310) Askenasy, Heller, U. S. 1,928,240, Sept. 26, 1933; Cent. 1934, I 463; C.A. 27, 5756 (1933).

(311) Brooks, Humphrey, J. Ind. Eng. Chem. 9, 750-751 (1917). (312) Jeltekow, Ber. 6, 558 (1873). (313) Hough, U.S. 1,206,222, Nov. 28, 1916; C.A. 11, 187 (1917). (314) Wada, Sato, J. Soc. Chem. Ind. Japan 38, Suppl. bindg. 497-500 (1935); Cent. 1936, I 1960, C.A. 38, 1028 (1936). (315) Tucker, Reid, J. Am. Chem. Soc. 55, 780 (1933). (316) Gomberg, J. Am. Chem. Soc. 41, 1430 (1919). (317) Davies, J. Chem. Soc. 117, 299 (1920). (318) Bouknight, Smith, J. Am. Chem. Soc. 61, 29 (1939). (319) Barron, "Modern Synthetic Rubbers," Van Nostrand Co., 2nd ed., 1943, pp. 272-289. (320) Baker, J. Chem. Education 20, 427 (1943).

(321) Golev, Sbornik Dıkhlaretan 1939, 11-13; C.A. 36, 2042 (1942). (322) Isskra, J. Chem. Ind. (Moscow) 12, 947-953 (1935); Cent. 1936, I 2823; not in C.A. (323) S.S. Drozdov, N.S. Drozdov, J. Chem. Ind. (Moscow), 1934, No. 2, 53-54; Cent. 1934, II 2745; C.A. 28, 3704 (1934). (324) Lenze, Metz, Z. ges. Schiess-u. Sprengstoffw. 27, 255-258, 293-296, 337-340, 373-376 (1932). (325) Kraus, White, J. Am. Chem. Soc. 45, 773 (1923). (326) Chablay, Compt. rend. 142, 93-94 (1906); Ann. chrm. (9) 1, 502-503 (1914). (327) Mouneyrat, Bull. soc. chim. (3) 19, 445-448 (1898). (328) Harlow, Ross (to Dow Chem. Co.), U.S. 1,891,415 Dec. 20, 1932, Cent. 1933, I 1683; C.A. 27, 1890 (1933). (329) Patterson, Robinson, J. Chem. Soc. 125, 1527 (1924). (330) I.G., French 701,505, March 17, 1931; Cent. 1931, II 1488; C.A. 25, 4012 (1931).

(331) Slator, J. Chem. Soc. 85, 1297 (1904). (332) Agruss, Ayers, Schindler, Ind. Eng. Chem., Anal. Ed. 13, 69-70 (1941). (333) Biesalski, Z. angev. Chem. 37, 317 (1924). (334) Ott (to Chem. Fabrik. Weiler-ter-Meer), Ger. 374,141, April 20, 1923; Cent. 1923, IV 720; C.A. 18, 2176 (1924). (335) Müller, Ehrmann, Ber. 69, 2207-2210 (1936). (336) Fargher, J. Chem. Soc. 117, 1351-1356 (1920). (337) Darzens, Congr. chim. ind. Nancy, 18, I 414-417 (1938); Cent. 1939, II 3060; not in C.A. (338) Kraut, Ann. 212, 251-256 (1882). (339) Hofmann, Ber. 23, 3297-3303; 3711-3718 (1890). (340) Mnookin, U.S. 2,049,467, Aug. 4, 1936; Cent. 1937, I 1792; C A. 30, 6389 (1936).

(341) Curme, Lommon (to Carbide and Carbon Chem. Corp.), U.S. 1,832,534, Nov. 17, 1931; Cent. 1932, I 581; C.A. 26, 999 (1932). (342) Barbieri, U.S. 2,078,555, April 27, 1937; Cent. 1937, II 857; C.A. 31, 4341 (1937). (343) Goodyear Tire and Rubber Co., French 739,317, Jan. 9, 1933; Cent. 1933, II 132; C.A. 27, 2159 (1933). (344) Krauss, J. Am. Chem. Soc. 39, 1512-1513 (1917). (345) Stähler, Ber. 47, 911-912 (1914). (346) von Braun, Dengel, Arnold, Ber. 70, 992 (1937). (347) Klebanskii, Mironenko, J. Applied Chem. (U.S.S.R.) 14, 618-631 (1941); C.A. 36, 3500 (1942). (348) Sisido, Kato, J. Soc. Chem. Ind. Japan 43, Suppl. bindg. 232-233 (1940); 44, 25-27 (1941); Cent. 1942, I 2199, 2200; C.A. 35, 1026, 4369 (1941). (349) Clark, Kuts (to General Electric Co.), U.S. 2,033,612, March 10, 1936; Cent. 1936, II 1036; C.A. 30, 2991 (1936). (350) B.A.S.F., Ger. 326,729, Sept. 29, 1920; Cent. 1921, II 51; not in C.A.

(351) Homer, J. Chem. Soc. 97, 1144-1145 (1910); Bodroux, Bull. soc. chim. (3) 25, 491-497 (1901). (352) Coleman, Hadler (to Dow Chem. Co.), U.S. 2,079,279, May 4, 1937; Cent. 1937, II 1267; C.A. 31, 4416 (1937). (353) Cope, J. Am. Chem. Soc. 57, 574 (1935). (354) Wohl, Berthold, Ber. 43, 2179 (1910). (355) Clemo, Perkin, J. Chem. Soc. 121, 644-646 (1922). (356) Ernst, Berndt (to I.G.), Ger. 525,188, May 20, 1931; Cent. 1931, II 1055; C.A. 25, 4284 (1931). (357) Coleman, Stratton (to Dow Chem. Co.), U.S. 2,130,990, Sept. 20, 1938; Cent. 1939, I 2295; C.A. 32, 9098 (1938). (358) Dreyfus, Brit. 166,767, Aug. 18, 1921; Cent. 1921, IV 1140; C.A. 16, 830 (1922). (359) I.G., French 805,563, Nov. 24, 1936; Cent. 1937, I 2258; [C.A. 31, 4345 (1937)]. (360) Wheeler (to Imperial Chem. Ind., Ltd.), Brit. 333,989, Sept. 18, 1930; Cent. 1930, II 3638; C.A. 25, 709 (1931).

(361) Meyer, Ger. 332,677, Feb. 7, 1921; Cent. 1921, II 646; not in C.A. (362) Rodebush (to U.S. Industrial Alc. Co.), U.S. 1,430,324, Sept. 26, 1922; Cent. 1924, II 1511; C.A. 16, 3903 (1922). (363) Coleman, Moore (to Dow Chem. Co.), U.S. 2,021,852, Nov. 19, 1935; Cent. 1936, I 1505; C.A. 30, 485 (1936). (364) Engelhardt (to Bayer and Co.), Ger. 404,999, Oct. 25, 1924; Cent. 1925, I 1530; not in C.A. (365) I.G., French 669,739, Nov. 20, 1929; Cent. 1930, I 3237; [C.A. 24, 1866 (1930)]. (366) N. V. de Bataafsche Petroleum Maatschappij, Brit. 496,290, Dec. 29, 1938; Cent. 1939, I 2294; C.A. 33, 2912 (1939). (367) Calingaert, Soroos, Hnizda, Shapiro, J. Am. Chem. Soc. 62, 1545-1547 (1940). Calingaert, Beatty, Neal, J. Am. Chem. Soc. 61, 2756 (1939). (368) Dougherty, J. Am. Chem. Soc. 51, 579-580 (1929). (369) Kharasch, Hannum, J. Am. Chem. Soc. 56, 714 (1934). (370) Lean, Lees, J. Chem. Soc. 71, 1062-1068 (1897).

(371) Perkin, J. Chem. Soc. 65, 578-589 (1893). (372) Bennett, J. Chem. Soc. 115, 577 (1919). (373) Schouten, Rec. trav chim. 56, 542-543 (1937). (374) Schouten, Rec. trav. chim. 56, 870-871 (1937). (375) Bodroux, Compt. rend. 208, 1023 (1939). (376) Frankel, Nussbaum, Biochem. Z. 182, 424-433 (1927); Cent. 1927, II 1340; not in C.A. (377) Davies, Evans, Hulbert, J. Chem. Soc. 1939, 416. (378) Tronov, J. Russ. Phys.-Chem. Soc. 58, 1278-1301 (1926); Cent. 1927, II 1145. (379) Weber, Chem. Ztg. 57, 836 (1933); Cent. 1933, II 3889; C.A. 28, 727 (1934). (380) Doughty, J. Am. Chem. Soc. 41, 1130-1131 (1919).

(381) Dahlen, Black, Foohey (to du Pont Co.), U.S. 1,979,144, Oct. 30, 1934; Cent. 1935, I 3051; [C.A. 29, 177 (1935)]. (382) Levy, Campbell, J. Chem. Soc. 1939, 1443. (383) Wanag, Ber. 75, 725 (1942). (384) Bistrzycki, Schmutz, Ann. 415, 22 (1918). (385) Gabriel, Ber. 20, 2226 (1887). (386) Gabriel, Ber. 21, 574 (1888). (387) Seitz, Ber. 24, 2626 (1891). (388) Wenker, J. Am. Chem. Soc. 59, 422 (1937). (389) Clemo, Walton, J. Chem. Soc. 1928, 728. (390) Heppel, Neal, Daft, Endicott, Orr, Porterfield, J. Ind. Hyg. Toxicol 27, 15-21 (1945).

(391) Lehman, Schmidt, Kehl, Arch. Hyg. Bakt. 116, 131-268 (1936), C.A. 31, 477 (1937) not in Cent. (392) Merritt, Levey, Cutter, J. Am. Chem. Soc. 61, 15-16 (1939).

3:5140 3,3-DICHLOROPROPENE-1
$$(1,1-Dichloropropene-2;$$
 allylidene (di)chloride; "acrolein dichloride") CH_2 — CH — CH — CH — CH — I_2 — I_2 — I_3 — I_4 — I_4 — I_5 — I_5 — I_5 — I_5 — I_5 — I_6 —

[See also 1,3-dichloropropene-1 (3:5280).]

85°

Note that C represents the synionic mesomer of 1,3-dichloropropene-1 (3:5280); reactions of either mesomer may under certain conditions lead to derivatives of the other: however, in practice the tendency appears to be strongly in the direction of 1.3-dichloropropene-1 (3:5280) so that most of the known reactions of C yield the same products as does the mesomer; the rate of reaction, however, is generally very much slower with C.

[For prepn. of C from acrolein (1:0115) with PCl₅ (16% yield C accompanied by 32% 1,3-dichloropropene-1 and some 1,1,3-trichloropropane (3:5660) (3)) (1) (4), or from 1.1.3-trichloropropane (3:5660) with alc. KOH (5) (other products are also formed), see indic. refs.]

[C with Cl2 adds 1 mole halogen giving (4) 1,1,2,3-tetrachloropropane (3:6035), b.p. 179-180° at 756.6 mm. (4).]

[C with conc. HCl in s.t. at 100° for 10 hrs. (4) isomerizes to 1,3-dichloropropene-1 (3:5280).]

[\bar{C} with NaOEt reacts much more slowly than its mesomer; however, after 15 hrs. refluxing with large excess NaOEt, \bar{C} gives 1-chloro-3-ethoxypropene [Beil. I-439], b.p. $126-127^{\circ}$, $D_{-}^{16}=1.018$, $n_{-}^{16}=1.438$ (3), i.e., the same product as from the mesomer.]

[\tilde{C} with Na phenolate in abs. alc. refluxed for 4 hrs. gives (3) ω -chloroallyl phenyl ether, the same prod. as correspondingly obtd. in $\frac{1}{2}$ hr. from the mesomer, q.v.]

[\bar{C} with Et₂NH in dry ether for 20 days gives (3) only a slight ppt. of diethylamine hydrochloride and but very small yield of N_iN -diethyl- γ -chloroallylamine (cf. the mesomer).

[C with NaOAc (3), CaBr₂ (3), CaI₂ (3) cf. (6), or C₆H₅MgBr (3) gives more slowly and in poor yields the same products as are formed readily from the mesomeric 1,3-dichloropropene-1 (3:5280), q.v.]

3:5140 (1) Hübner, Geuther, Ann. 114, 36-43 (1860). (2) Kirrmann, Grard, Compt. rend. 196, 876-878 (1930); Cent. 1930, II 29; C.A. 24, 3750 (1930); Bull. soc. chim. (4) 47, 834-847 (1930). (3) Kirrmann, Pacaud, Dosque, Bull. soc. chim. (5) 1, 860-871 (1934). (4) van Romburgh, Bull. soc. chim. (2) 36, 549-557 (1881). (5) van Romburgh, Bull. soc. chim. (2) 37, 98-103 (1882). (6) van Romburgh, Rec. trav. chim. 1, 234-237 (1882).

3:5150 1,2-DICHLOROPROPENE-1
$$CH_3$$
— $C=CH$ $C_3H_4Cl_2$ Beil. I - 199 (high-boilg. stereoisomer) I_1 — I_2 — I_3 — I_4

B.P. 84-86° (1)

[See also the lower-boilg. stereoisomer (3:5110).]

[For prepn. of \bar{C} from α,β,β -trichloro-n-butyric acid (3.0925) by soln. in aq. Na₂CO₃ and subsequent decompn. to \bar{C} (65% yield) by protracted boilg, see {1}.]

 \bar{C} with Cl_2 adds 1 mole halogen giving (1) 1,1,2,2-tetrachloropropane (3:5825), b.p. 153-154° (1).

3:5150 (1) Szenic, Taggesell, Ber. 28, 2667-2668 (1895).

3:5160
$$\alpha$$
-CHLOROPROPIONALDEHYDE H C_3H_5OCl Beil. I - 632 I_1 -(334) I_2 — Cl

B.P. 86° (1)
$$D_4^{15} = 1.182$$
 (1) $n_D^{17} = 1.431$ (1)

Oil, spar. sol. aq.; misc. with ether, AcOH, or C_6H_6 . — \bar{C} with aq. yields a hydrate, b.p. 80.5-81° (2).

C polymerizes in air to a white solid which upon htg. at 170-200° regenerates C (2).

[For prepn. from n-propyl alc. (1:6150) by actn. of Cl₂ at 45-50° in presence of catalysts such as AlCl₃, CrO₂Cl₂, or Mg turnings see (3); for formn. (together with other products) from propylene oxide (1:6115) + S₂Cl₂ see (4); for other modes of formn. see Beil. I-632 and I₁-(334).]

 \tilde{C} on oxidn. with excess alk. KMnO₄ yields acetic acid ac. (1:1010) (1) (2). — \tilde{C} reduces NH₄OH/AgNO₃ in the cold and Fehling's soln. on htg. — \tilde{C} gives positive fuchsin ald. test and yields a NaHSO₃ cpd. (1).

3:5160 (1) Brochet, Ann. chim. (7) 10, 341-344 (1897). (2) Oddo, Cusmano, Gazz. chim. ital. 41, II 232-234 (1911). (3) Bowman, Proc. S. Dakota Acad. Sci. 19, 112-114 (1939); C.A. 34, 2786 (1940). (4) Malinovski, J. Gen. Chem. (U.S.S.R.) 9, 832-839 (1939); C.A. 34, 375 (1940).

3:5170 1,1,2-TRICHLOROETHYLENE | HC==C-Cl | C₂HCl₃ | Beil. I - 187 | I₁-(78) | I₂-(159) |

B.P. F.P. 87.55° at 765 mm. (1) [-73° (14]]
$$D_4^{25} = 1.4597$$
 (9) $n_D^{25} = 1.4759$ (18) 88° at 760 mm. (2) $-83°$ (12) 1.4542 (5) 1.47488 (10) 87.0-87.3° at 753 mm. (3) $-86.4°$ (15) 1.4540 (17) 1.47458 (19) 87.0-87.2° at 760 mm. (4) $-86.9°$ (16) 1.454 (10) 1.4744 (8) 87.15° at 760 mm. (5) $-88°$ (9) 1.4742 (8) 86.95° at 760 mm. (6) (7) (15) $D_4^{20} = 1.4777$ (2) $n_D^{20} = 1.47820$ (20) 86.9° (3) 1.4679 (9) 1.47758 (4) 1.4775 (21) 86.60° at 758 mm. (10) 1.4649 (12) 86.0-87.5° at 760 mm. (11) 85.8-86.0° at 760 mm. (12) 85.9-86.0° (32) 83° at 680 mm. (13) 77.0° at 562 mm. (5) 65.0° at 385 mm. (5) 51.0° at 234 mm. (5) 45.0° at 183 mm. (5) 44.15° at 177 mm. (5) 38.20° at 139 mm. (5) 30.0° at 92 mm. (5) Note 2. For D_4^T over range 17.6°-75° see (5). 25.0° at 73 mm. (5)

Note 1. For vap. press. over range 0°-86.7° see (9).

Colorless mobile liquid with sweetish odor suggesting chloroform. — \bar{C} as such is not inflammable (see below).

MISCELLANEOUS PHYSICAL PROPERTIES

Various solubility relationships. \bar{C} is pract. insol. aq. and eas. volatile with steam: soly. of \bar{C} in aq. at $16^\circ = 0.081$ wt. % (23), at $18^\circ = 0.025$ wt. % (23), 0.18 ml. in 100 ml. aq. (24). — Soly. of aq. in \bar{C} at $-30^\circ = 0.0025$ wt. %, at $-20^\circ = 0.0050$ wt. %, at $-8^\circ = 0.0075$ wt. %, at $0^\circ = 0.0100$ wt. %, at $6^\circ = 0.0125$ wt. %, at $10^\circ = 0.0170$ wt. %, at $20^\circ = 0.0250$ wt. %, at $25^\circ = 0.0325$ wt. % (9).

[For data on soly. in \bar{C} of 248 org. cpds. see (25); for solv. actn. of \bar{C} on various dyes (in connection with use of \bar{C} as dry cleaning fluid) see (26) (see also below under uses of \bar{C}).] [For soly. of I_2 in \bar{C} over range 11-25° see (27); for use of such solns. in detn. of I_2 No. of oils and fats see (28). — For distrib. of I_2 between \bar{C} and aq. at 25° see (30) cf. (31).]

[For soly. in \tilde{C} at 20° of HCl or H₂S at 1 atm. see (32).]

[For absorption of vapors of C by kerosene see (33).]

Effect of \bar{C} on explosive range of various gases. Air satd. with \bar{C} at 14° conts. 5.7 vol. (?) % \bar{C} (34).

[Vapor of C does not form inflammable mixts. with air at ord. temp. and press.; below

25.5° $\bar{\rm C}$ has insufficient vap. press. to produce inflam. mixts. at total press. of 1 atm. or above even in mixts. contg. high concns. of O_2 . — At high temps. vapor of $\bar{\rm C}$ is inflammable in air, igniting at 463°; in oxygen at 419° (18). — Limits of inflammability of mixts. of $\bar{\rm C}$ with O_2 are 10.30–64.5 vol. % $\bar{\rm C}$ (35); for study of limits of inflam. of system $\bar{\rm C}/O_2/N_2$ see (18) (35).]

[For study of influence of vapors of \tilde{C} upon explosive regions of mixts. of air with hydrogen (36) (37), with acetylene (36), with methane (38) (39) (36) (40) (41) (42), or with carbon monoxide (34) (36) (43) see indic. refs.]

Adsorption of \tilde{C} by various materials. [For study of adsorption of \tilde{C} on charcoal at 20° (44) and use in detn. of \tilde{C} (45) see indic. refs.; on MnO₂ see (46); on dehydrated Al(OH)₃ gel at 10–40° and desorption at 90–150° as means of recovery of \tilde{C} see (47).]

Other physical properties. [For study of evapn. rate of \bar{C} see (48); for study of thermal conductivity of \bar{C} see (11).]

Binary systems contg. \tilde{C} (see also below under azeotropes). \tilde{C} + MeOH (1:6120): for diag. of b.p./vapor-liq. compn., D/compn., and n/compn. see (49). $-\tilde{C}$ + EtOH (1:6130): for diag. of b.p./vap.-liq. compn., D/compn., and n/compn. see (49). $-\tilde{C}$ + acetone (1:5400): for data on D_4^{25} /compn. and n_D^{25} /compn. see (10).

 \bar{C} + nicotine: for study of distrib. of nicotine between \bar{C} and aq. at 17° see (23).

 $\ddot{C} + CHCl_3$ (3:5050): for f.p./compn. diag., eutectic, f.p. -100.2° , contg. 68.6 wt. % \ddot{C} see (16). $-\ddot{C} + pentachloroethane$ (3:5880): for D_4^{25} /compn. data see (17) cf. (50).

Ternary systems contg. \tilde{C} (see also below under azeotropes). $\tilde{C}+MeOH$ (1:6120) + EtOH (1:6130): for D/compn. and n/compn. diags. see (49b). — $\tilde{C}+EtOH$ (1:6130) + H_2O : for soly./compn. diagram in wt. % at 25° and $n_D^{25}/compn$. diagram in wt. % see (8) cf. (51).

Azeotropic systems contg. \tilde{C} . Binary azeotropes. $\tilde{C} + H_2O$: gives a two-phase constbolig. mixt. (heteroazeotrope), b.p. 73°, contg. 65 mole % \tilde{C} (8).

C + MeOH (1:6120): forms a const.-boilg. mixt., b.p. 60.2° at 760 mm., $D_4^0 = 1.1643$ (52a) contg. 64 wt. % \bar{C} (52a) = 30 mole % \bar{C} (52a) = 51 vol. % \bar{C} (53). — \bar{C} + EtOH (1:6130): forms a const.-boilg. mixt., b.p. 70.9° at 760 mm., $D_4^0 = 1.212$, contg. 73 wt. % $\bar{C} = abt. 48.7 \text{ mole } \% \bar{C} (52b) \text{ cf. } (53) (54). - \bar{C} + n\text{-}propyl alc. } (1:6150): \text{ forms a const.-}$ boilg. mixt., b.p. 81.75° at 760 mm., $D_4^0 = 1.3283$, contg. 83 wt. % $\bar{C} = 69$ mole % \bar{C} (52c). $-\bar{C}$ + isopropyl alc. (1:6135): forms a const.-boilg. mixt., b.p. 75.5° (7), abt. 74° at 760 mm. (52d), $D_4^0 = 1.22$, contg. abt. 72 wt. $\% \bar{C}$ (70 wt. $\% \bar{C}$ (7)) = 54 mole $\% \bar{C}$ (52d). — $\bar{C} + n$ -butyl alc. (1:6180): gives a const.-boilg. mixt., b.p. 86.85° at 760 mm., contg. 97.5 wt. % \bar{C} (55). — \bar{C} + isobutyl alc. (1:6165): forms const.-boilg. mixt., b.p. 85.4° at 760 mm., $D_4^0 = 1.396$, contg. 91 wt. $\% \bar{C} = 86$ mole $\% \bar{C}$ (52e). $-\bar{C} + ter-butyl$ alc. (1:6140): forms const.-boilg. mixt., b.p. 75.8° (6), 75° (52f) at 760 mm., $D_4^0 = 1.326$ (52f), contg. 67 wt. % \bar{C} (6) (84 wt. % \bar{C} (52f) = 74 mole % \bar{C} (52f)). $-\bar{C}$ + ter-amyl alc. (1:6160): forms const.-boilg. mixt., b.p. 84.5° (6), 84° (52g), $D_4^0 = 1.372$ (52g), contg. 86 wt. % \bar{C} (6) (88 wt. % \bar{C} = 83 mole % \bar{C} (52g)). — \bar{C} + allyl alc. (1:6145): forms const. boilg. mixt., b.p. 80.95° at 760 mm., $D_4^0 = 1.335$, contg. 84 wt. $\% \bar{C} = 70$ mole $\% \bar{C}$ (52h). $\bar{C} + AcOH$ (1010): forms const.-boilg. mixt., b.p. 86.5° at 760 mm., contg. 96.2 wt. % Č (6).

 $\bar{C}+1,2$ -dichloroethane (ethylene dichloride) (3:5130); forms a const.-boilg. mixt., b.p. 82.9° at 760 mm., contg. abt. 18 wt. % \bar{C} (6).

Ternary azeotropes. $\ddot{C} + EtOH$ (1:6130) + H₂O: forms a ternary heteroazeotrope, b.p. 67.25° at 760 mm., contg. 38.4 mole % \ddot{C} + 41.2 mole % EtOH + 20.4 mole % H₂O (56a): note that this azeotrope conts. 69.4 vol. % \ddot{C} + 23.8 vol. % EtOH + 6.8 vol. % H₂O (53), and that upon condensation at 15° it separates into two layers, the upper having the composition 0.8 vol. % \ddot{C} + 7.2 vol. % EtOH + 5 vol. % H₂O (total upper layer = 13

vol. %), the lower having the composition 68.6 vol. % \overline{C} + 16.6 vol. % EtOH + 1.8 vol. % H₂O (total lower layer = 87%) (53). — For further discussion and data see also (8) (49).

 \ddot{C} + n-propyl alc. (1:6150) + H_2O : forms a ternary heteroazeotrope, b.p. 71.55° at 760 mm., contg. 51.1 mole % \ddot{C} + 16.6 mole % n-propyl alc. + 32.3 mole % H_2O (566).

 \ddot{C} + allyl alc. (1:6145) + H_2O : forms a ternary heteroazeotrope, b.p. 71.4° at 760 mm., contg. 49.2 mole % \ddot{C} + 17.3 mole % allyl alc. + 33.5 mole % H_2O (56c).

USES OF C

Most of the utility of \bar{C} in industry depends upon its physical properties especially as a solvent; these applications include the dehydration of alcohols and acids, degreasing of metal, wool, and leather, dry cleaning of fabrics, extracting of oils from seeds, etc.; dewaxing of mineral lubricating oils, use as fumigant and insecticide, refrigerant, etc. [For an excellent brief survey of these uses see (57) (58); for further and more recent examples see below.]

Use in dehydration of alcohols. [For use of \tilde{C} in dehydration of EtOH (or MeOH) by azeotropic distn. (Drawinol process) see (8) (49) (53) (59) (60) (61) (62); for patents on this method see (63). — For use of \tilde{C} in denaturing alc. see (64).]

Use in dehydration of acids. [For use of \bar{C} in concn. of AcOH (1:1010) see patents (65) (66). — For sepn. of AcOH (1:1010) from formic acid (1:1005) by distn. of mixt. with \bar{C} , the condensate sepg. into an upper layer of an azeotropic mixt. of \bar{C} + formic acid, the lower layer being \bar{C} see (67).]

Use of \bar{C} for degreasing of metal. [For patents on use as metal degreaser of mixts. of \bar{C} + an alc. + soap (68), \bar{C} + oleic acid (69), \bar{C} + ethylene dichloride (3:5130) (70) (71), or \bar{C} (72) (73) see indic. refs. — For use of \bar{C} + rosin + boiled linseed oil in cleaning and leaving coating preparatory to etching see (74). — Because of great toxicity of \bar{C} (see below) special attention (75) must be given to ventilation of degreasers using it.]

Use of \tilde{C} in dry cleaning of fabrics. Because of its solvent power supported by its low b.p. and non-inflammability \tilde{C} is widely used as dry cleaner's solvent [for general articles from this viewpoint see (76) (77) (78); for patent see (79); for solv. actn. of \tilde{C} on dyes see (26)].

Use of \bar{C} in extraction of fats and oils. [For use of \bar{C} as solv. for extraction see (81) (82) (83). — For use of \bar{C} for extraction of soybean oil (84) including n_D^{25} and D in g/cc. at 77°, 100°, and 122° F. (19) see indic. refs. — For study of losses of \bar{C} in extr. of fats see (85).]

[For use of \bar{C} in detn. of fats in foods (butter, margarine, etc.) see (86) (87).]

[For use of C in detn. of aq. in fats and oils see (88); cf. use of acetylene tetrachloride (3:5750) for this purpose.]

Use of C in dewaxing of mineral lubricating oils. [For articles including use of C for this purpose see (89) (90); for patents see (91).]

Use of \bar{C} as fumigant, insecticide, etc. [For comparative tests of \bar{C} see (92); for patents on such use of \bar{C} (93) or mixts. contg. \bar{C} (94) see indic. refs.]

Use of \bar{C} as component of refrigerating liquids. [For use of \bar{C} with dichloroethylene (3:5030) see (95) cf. (96); for use of \bar{C} or its mixts. in low-temp. cryostats see (16).]

Miscellaneous uses of \bar{C} . [For use of \bar{C} with MeBr (97) or with CCl₄ (98) as fire extinguishing compn. see indic. refs.; for use of \bar{C} as boiler or radiator cleaner (99) or as rust-retarder (100) see indic. refs.; for use of \bar{C} as weed-killer see (101); for addition to liq. HCN to diminish inflammability see (102); in prepn. of starch see (103); in recrystn. of T.N.T. see (104); for use as solv. in ebullioscopy (K = 44.3 per 100 g. solv.) see (105); to replace xylene in histological technique see (106) (107) (108).]

PHYSIOLOGICAL BEHAVIOR OF C

 \bar{C} is one of the more toxic of the group of chlorinated solvents; it is absorbable into the body not only by inhalation but also through the skin (109). — Although full detailed treatment of this aspect of \bar{C} is beyond the scope of this work, yet the following citations will be found useful as lead references for further information.

Toxicity of \tilde{C} . [For important surveys of physiological properties (110), toxicity (111), comparative toxicity of \tilde{C} and CCl_4 (112) see indic. refs.]

[For studies of liver injury by \bar{C} (113), of anemia from \bar{C} (114), of American cases since 1932 of industrial poisoning by \bar{C} (115), or role of impurities in toxicity of \bar{C} (116), of industrial hazards of \bar{C} (117) (118) (119), of relation between toxicity and b.p. (120) see indic. refs. — For other studies of toxicity or of poisoning by \bar{C} see (121)-(130), incl.]

 \bar{C} as narcotic, anesthetic, analgesic, etc. $[\bar{C}]$ has very important use in treatment of trigeminal neuralgia (131) (132) (133); for toxic effects of \bar{C} after long use as antineuralgic see (134); for chem. exam. of \bar{C} for medical use see (21).]

[For use of \bar{C} as an esthetic see (135) (136) (137); for use of \bar{C} in treatment of migraine see (138); for effect on pain threshold see (139); for neural depressing effect (140) and narcotic actn. of \bar{C} (141) (142) (143) (144) see indic. refs.]

[For studies of antiseptic and disinfectant actn. of C see (145) (146) (147) (148) (149) (150) (24).]

Miscellaneous related topics. [From dogs after inhalation anesthesia with \bar{C} from 5-8% of initial \bar{C} is excreted (151) as trichloroacetic acid (3:1150). — For study of anthelmintic actn. of \bar{C} see (152). — For actn. of \bar{C} on alc. fermentation see (153).]

DETERMINATION OF C

By physical methods. For detn. of \tilde{C} (as vapor) by use of the R + H "Tri-Per-Analyzer" (a recording ultra-violet photometer (154)) see (155); this instrument will measure \tilde{C} in conens. of 10–2000 p.p.m. and is insensitive to methyl chloride (3:7005), methylene (di)chloride (3:5020), CHCl₃ (3:5050), CCl₄ (3:5100), vinyl chloride (3:7010), ethylene (di)chloride (3:5130), acetylene tetrachloride (3:5750), and to many (but not all) common non-chlorinated solvents such as methyl, ethyl, and amyl alcohols, ethyl acetate, etc.; for details see (155). — For detn. of \tilde{C} in air by adsorption on charcoal see (45).

By chemical methods. Those involving decomposition of \bar{C} and subsequent detn. of resultant chloride ion. One class of these methods involves pyrolytic decomposition of \bar{C} by appropriate htg. (156) (157) cf. (158) (159) cf. (127); note that \bar{C} with air at 900–1000° gives exclusively $CO_2 + HCl$, provided that concn. of \bar{C} is not more than 12 mg. per liter; above this amt. from 2–20% of the total carbon and chlorine are converted to $CO + Cl_2$, but $COCl_2$ (3:5000) is not found up to concns. of 100 mg. \bar{C} per liter (159). — For variation of the pyrolytic method involving burning of \bar{C} (or solns. of \bar{C}) in a lamp see (160) (161) (162) (163) (164).

A second class involves decomposition of \bar{C} by chem. means, e.g., by use of Na + ethanolamine in dioxane (165) (166), or by complete hydrolysis of \bar{C} with excess aq. 25% KOH in s.t. at 150° for 1 hr. (167).

Note that C on oxidn. with CrO₃/H₂SO₄ as directed (168) gives quant. CO₂.

Detn. of \bar{C} by conversion to mercuric trichloroethylenide Hg (CCl = CCl₂)₂. \bar{C} with aq. KOH soln. of Hg(CN)₂ on shaking 24 hrs. at room temp. ppts. (169) Hg(CCl = CCl₂)₂ (for amplification see below under behavior of \bar{C} with inorganic reacts.). — For use of this method in detn. of \bar{C} even in pres. of methylene (di)chloride (3:5020), CHCl₃ (3:5050), CCl₄ (3:5100), 1,2-dichloroethylene (3:5030), or tetrachloroethylene (3:5460) see (169).

Detn. of \bar{C} colorimetrically by use of Fujiwara reaction with pyridine + alkali. \bar{C} with pyridine + aq. alk. gives on short warming a red coloration (similar to but recognizably different from the red-violet color obtd. with CHCl₃) which on further warming changes to orange; for use of this color in detn. of \bar{C} in air (accuracy $\pm 11\%$ except that at conciss of \bar{C} as low as 20 p.p.m. error may be as much as 50%) see (170) cf. (111) (127); for use in detn. of \bar{C} in animal tissue see (171); for table of sensitivity of this test under comparable conditions from \bar{C} as compared with CHCl₃ (3:5050), CCl₄ (3:5100), 1,1,2-trichloroethane (3:5320), 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750), and tetrachloroethylene (3:5460) see (151).

PREPARATION OF C

The principal method of preparation or manufacture of \bar{C} is from 1,1,2,2-tetrachloro-ethane (acetylene tetrachloride) (3:5750) by elimination of 1 HCl (see below), but it is formed as a by-product from various other reactions (see below). — [For general reviews of prepn. of \bar{C} and its relationships with other "chlorinated solvents" see (31) (172).]

From 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750). By pyrolytic loss of HCl (dehydrochlorination). [For prepn. of \tilde{C} from acetylene tetrachloride in s.t. at 300° for 15 hrs. (173), over pumice at 700° (174) or 400-500° (175), over pumice + cat. at 500° (176), over pumice contg. $Cu_3(PO_4)_2$ at 450-500° (177), over ThO_2 below 390° (178), over $BaCl_2$ at 300° (179), over bone char at 300-310° (180), over activated carbon at 200-300° (181), 260° (182), or 500° (176) see indic. refs. — Note claim (183) that forms. of \tilde{C} by dehydrochlorination of acetylene tetrachloride over charcoal at 250-300° is not effective and yield of \tilde{C} diminishes with increase of temp.]

By pyrolytic loss of HCl in pres. of an org. acceptor. [For prepn. of \bar{C} from acetylene tetrachloride (3:5750) or pentachloroethane (3:5880) or 1,1,1,2-tetrachloroethane (3:5555) with acetylene over cat. at 250° (181) cf. (184) or with MeOH over Al_2O_3 at 280° (185) see indic. refs.]

By loss of HCl in pres. of an inorganic acceptor. [For prepn. of \bar{C} from acetylene tetrachloride (3:5750) by htg. with aq. alk. or alk. carbonates (186) in pres. of tetraethylene glycol, etc., as promoter (187), or with aq. Ca(OH)₂ or alk. carbonates (186) (188) (192) (193) (for test of Ger. 171,900 (186) see (190) (191)), or with alc. KOH (194) (195) cf. (173), or with alc. NaOEt (194) see indic. refs.]

[For prepn. of \bar{C} from acetylene tetrachloride (3:5750) by elimination of 1 HCl with excess NH₃ gas in pres. of aq. at 60-70° (196), with conc. aq. NH₄OH at 160-170° (196) (191) (for test of Ger. 351,463 (196) see (191)), with liq. NH₃ at -40° (13) (197), or by refluxing with dry pyridine (198), or by action of C_6H_5MgBr (199) see indic. refs.]

Note on impurities in \bar{C} . Note that tech. \bar{C} obtained from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) by elimination of HCl often contains in its high-boilg. fractions ("Tri-Nachlauf" and "Tetra-Nachlauf") other chlorinated materials such as 1,1,2,3,4,4-hexachlorobutane (3:3155), 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), solid 1,2,3,4-tetrachlorobutadiene-1,3 (3:6150), and hexachloroethane (3:4835), (207). — [For use of these "Nachlaufe" as insecticides and weed-killers see (268).]

From other halogenated ethanes. [For formn. of C from 1,2-dichloroethane (ethylene dichloride) (3:5130) as by-product (29% yield) of action of Cl₂ in pres. of AlCl₃/NaCl/FeCl₃ at 400-480° (200), or as by-product of actn. of Cl₂ in u.v. light (201), see indic. refs.]

[For formn. of \bar{C} from 1-bromo-1,1,2-trichloroethane by elimination of HBr with hot alc. Na phenolate (60% yield) see (245).]

[For formn. of \bar{C} from pentachloroethane (3:5880) with acetylene over cat. at 250° (181), or with H_2 over Ni at 270° (22) (note that \bar{C} resists further hydrogenation; also

that pentachloroethane over NiCl₂ without H₂ yields (22) tetrachloroethylene (3:5460)), or by actn. of MeMgI (203) see indic. refs. — For formn. of \bar{C} from 1,1,2-trichloro-1,2-dibromoethane with H₂ over NI at 300° or without H₂ over BaCl₂ at 400° see (202).]

From miscellaneous sources. \bar{C} is formed as a by-product of actn. of acetylene with Cl₂ but no citations will be given here [for formn. of \bar{C} from chloral (3:5210) with P₂S₅ at 160-170° (204) or from di- or tri-thioparachloral on dry distn. (205), or from 2-(tri-chloroacryloyl)-3-sulfamidobenzoic acid by alk. hydrolytic cleavage (206), see indic. refs.].

CHEMICAL BEHAVIOR OF C

Pyrolysis of Č. [Č passed over pumice at 700° decomposes yielding (174) methylene (di)chloride (3:5020), CHCl₃ (3:5050), CCl₄ (3:5100), 1,1,1,2-tetrachloroethane (3:5555), pentachloroethane (3:5880), hexachloroethane (3:4835), 1,2-dichloroethylene (3:5030), tetrachloroethylene (3:5460), pentachlorobenzene (3:2290), hexachlorobenzene (3:4939), and other prods.]

Hydrogenation. [\bar{C} resists hydrogenation even with H₂ over Ni at 270° (22). — Note, however, that \bar{C} with HI in sunlight for 2 weeks in absence of air at room temp. is partially (25% (245)) reduced to 1,1,2-trichloroethane (3:5330).]

Oxidation. \tilde{C} on total oxidation with CrO_3/H_2SO_4 as directed (168) gives quant. CO_2 . — \tilde{C} over chlorinated CuO at 450° gives $CO_2 + H_2O$ accompanied (209) by some phosgene (3:5000).

[\tilde{C} with O_2 in ultra-violet light (210) (198) (211) or in pres. of cat. (e.g., Br₂, I₂, H₂SO₄, HNO₃, etc.) (212) (213) (214) yields dichloroacetyl chloride (3:5290). — Note that \tilde{C} in absence of O_2 is not decomposed either by direct or diffused sunlight (9).]

[For study of auto-oxidn. of \bar{C} see (215); for study of acidity developed from \bar{C} with air or oxygen over range -23° to 150° see (9).]

 $[\bar{C} \text{ with } O_3 \text{ gives (215) a very unstable ozonide which decomposes into phosgene (3:5000), CO, HCl, and oxides of chlorine.]$

Stabilization. Since in the presence of O_2 (air) \overline{C} has a definite tendency toward oxidation (see above), much study has been given to the problem of its stabilization by addn. of small amts. of other materials. — [For general study of the stability of \overline{C} under a wide variety of conditions see (9); for study of method of testing stability and the efficacy of various stabilizers see (216); for use of 2-3% of EtOH (1:6130) or of cyclohexane (1:8405) as stabilizers see (217).]

For stabilization of \tilde{C} a wide variety of compds. have been recommended in the patent literature [e.g., for use of 0.01% or less of hydroquinone monomethyl ether (1:1435) or hydroquinone monobenzyl ether (1:1539) see (218); for use of 0.1% or less of *p-ter*-butylphenol (1:1510) or *p-ter*-amylphenol (1:1495) see (219); for use of 0.001% *n*-hexylresorcinol (1:1465) see (220); for use of oil-sol. azo dyes contg. phenolic groups see (221); for use of various phenols, amines, and aminophenols see (222) (235); for use of very small amts. alc. NH₃ see (223); for use of trimethylamine (228) di-isopropylamine (224), triethylamine (225) (226), or other alkylamines (226), various nitrogenous cpds. such as dialkylated cyanamides, allylthiourea, hexamethylenetetramine, propionitrile, etc. (227), pyridine (228), caffeine (229), see indic. refs.].

[For stabilization of C with mercaptans, e.g., n-butyl mercaptan (230), with amylene (231) cf. (222), with gasoline (232), with alk. oleate (233), with fatty acids or soaps (234) see indic. refs.]

Polymerization. \bar{C} under certain conditions reacts with itself forming dimeric, trimeric, and prob. polymeric products [e.g., \bar{C} in glass, porcelain, or enameled vessels at 180-210° under press. (236) and in pres. of small amts. of various antioxidants (237) gives a dimer, a hexachlorobutene (b.p. 200° at 710 mm.) of undetermined structure, accompanied by

higher polymers and by hexachlorobenzene (3:4939); \tilde{C} at elev. temp. and press. or under reflux in pres. of peroxides (such as Bz_2O_2) gives (238) (239) mainly dimer, accompanied by some trimer and polymer; \tilde{C} with $AlCl_3$ gives on refluxing (240) a mixt. of resinous polymers suitable (especially in mixts. with trichlorobenzene) for use as electric-insulating material].

[For copolymerization of \bar{C} with various dienes (such as chloroprene (3:7080), etc.) see (241).]

Reaction with halogens. Behavior with fluorine. [\bar{C} with F_2 at 0° for 10 hrs. gives (242) by addition 1,2-diffuoro-1,2,2-trichloroethane, b.p. 72.3-72.6°, $D_4^{20} = 1.5555$, $n_D^{20} = 1.3967$, accompanied by other prods. such as 1-fluoro-1,2-dichloroethylene, and a hexachlorobutene (3:9050), m.p. 9.5-11.0°, b.p. 125.5° at 25 mm., $D_4^{20} = 1.6880$, $n_D^{20} = 1.5442$, which, however, is not 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), etc.]

Behavior with chlorine. \bar{C} under appropriate circumstances adds 1 mole Cl₂ giving pentachloroethane (3:5880) [e.g., for study of addn. of Cl₂ at 80°, 95°, and 115° in light of 4360 Å see (243), note, however, that reaction may go further and that \bar{C} with Cl₂ over activated charcoal at 60-70° either in light or in dark gives (98% yield (244)) hexachloroethane (3:4835)].

Behavior with bromine. \tilde{C} readily adds 1 mole Br₂ (245) (even when used as Br₂ aq. (202)) yielding 1,2-dibromo-1,1,2-trichloroethane, b.p. 204° dec. at 760 mm. (245), 125–126° at 85 mm. (202), 116.5° at 50 mm. (245), $n_D^{20} = 1.5710$ (245). [For study of rate of addn. to \tilde{C} of Br₂ in CCl₄ see (246).]

Behavior with iodine or thiocyanogen. C does not add I₂ (Wijs method) or (SCN)₂ (Kaufmann method) (167).

Behavior with halogen hydrides. Reactn. of \bar{C} with dry HCl. \bar{C} (1 mole) with dry HCl gas (1.57 moles) in pres. of anhydr. FeCl₃ (0.003 mole) in dark 6 days at room temp in abs. of air or peroxides, or \bar{C} (1 mole) with dry HCl gas (1.62 moles) in pres. of AlCl₃ (0.004 mole) in dark 3 days at 0° in abs. of air or peroxides gives exclusively (245) (yields: 49% and 22%, respectively) 1,1,1,2-tetrachloroethane (3:5555). [Note that \bar{C} with dry HCl in pres. of 5-10% AlCl₃ at 30-40° gives (86-88% (247)) 1,1,1,2-tetrachloroethane (3:5555), but that \bar{C} + AlCl₃ with dry HCl at 50° gives also (248) the sym.-1,1,2,2-tetrachloroethane (3:5750), two pentachlorobutadienes (cf. (249)), and hexachlorobenzene (3:4939).

Reaction of \bar{C} with dry HBr. \bar{C} in the pres. of an anti-oxidant does not react with HBr even after several days at 100° or after 30 days in sunlight (245).

However, \bar{C} in the pres. of suitable cat. adds HBr readily, but the mode of addn. differs according to conditions: e.g., \bar{C} + HBr in pres. of small amts. FeCl₃ or AlCl₃ gives exclusively in yields up to 81% (245) 1-bromo-1,1,2-trichloroethane, b.p. 152° at 760 mm., b.p. 54° at 20 mm., $n_D^{20} = 1.5217$ (245); but \bar{C} with HBr in pres. of air and/or peroxides gives exclusively in yields up to 91% 2-bromo-1,1,2-trichloroethane, b.p. 171° at 760 mm., b.p. 68.9° at 20 mm., $n_D^{20} = 1.5302$, $n_D^{14.5} = 1.5326$ (245).

Behavior of \tilde{C} with dry HI. \tilde{C} does not add HI even after 4 days at room temp. in dark and abs. of air; on exposure of the system for 2 weeks in sunlight 25% of \tilde{C} was reduced to 1,1,2-trichloroethane (3:5330) (245).

Behavior with oxygenated mineral acids. Reaction of \bar{C} with H_2SO_4 . $[\bar{C}$ with strong H_2SO_4 at elev. temp. undergoes reactns. leading ultimately (250) (189) to high yields of chloroacetic acid (3:1370). — For patents exemplifying various conditions see (251) (252) (253) (254) (255) (256). — Note also that the H_2SO_4 may be replaced by arom. sulfonic acids such as benzenesulfonic acid, etc. (257).]

[Č with fumg. H_2SO_4 (10% SO_3) shaken at 88° for $\frac{3}{4}$ hrs. gives (258) cf. (255) (259) α -chloro- α -sulfoacetic acid.]

Reaction of \bar{C} with HNO_3 . [\bar{C} with conc. HNO_3 (D=1.42, 4 vols.) refluxed 3 hrs. gives mainly (260) cf. (258) dichlorodinitromethane [Beil. I-78, I₁-(21), I₂-(44)], accompanied by some trichloronitromethane (chloropicrin); for behavior of \bar{C} with N_2O_5 in s.t. at 50° for 6 hrs. see (260).]

Behavior with alkali. \check{C} in either aq. susp. or alc. soln. does not neutralize N/10 aq. alk. (261) (for contrary earlier claim see (262)), but \check{C} with excess 2 N MeOH/KOH in s.t. at 100° for 30 min. uses alk. corresp. to 2 moles, i.e., apparent Sap. Eq. = M.W./2 = 65.8. $[\check{C}$ with aq. alk. or alk.-earth hydroxides at 175° under press. in pres. of copper salts is

claimed (263) to yield salts of glycolic acid (1:0430).]

[\bar{C} with ether passed as vapor with N₂ over solid KOH + CaO at 130° loses HCl giving (84–90% yield (264)) dichloroacetylene (3:5010) in the form of its mol. cpd. (1:1) with ether; for earlier work in which \bar{C} alone over solid granular KOH at 130° gives (65% yield (265)) dichloroacetylene (266) see indic. refs.]

[\bar{C} with EtOH/NaOEt at 60-75° condenses with elimination of NaCl giving (yields: 81% (267), 70% (268)) (269) (204) α,β -dichlorovinyl ethyl ether (3:5540). — Note that reaction of \bar{C} with alc. NaOEt has been accompanied by spontaneous explosions or ignition (270) (271) (272), presumably because of some formn. of either chloroacetylene (3:7000) or dichloroacetylene (3:5010) or both cf. (273).]

[For study of stability of \tilde{C} toward water under various conditions see (9); note that carefully purified \tilde{C} is more stable toward aq. than ord. tech. product (274).]

Behavior with metals. [For study of corrosive actn. of \bar{C} on soft steel, copper, brass, lead, aluminum, etc., at temps. 50-150° under various conditions see (9) (275) (276) (277) (278) (279) (280) (281). — For study of sensitivity to mechanical shock of \bar{C} with Li, Na, K, Ca, Sr, Ba see (282).]

Behavior with inorganic metal salts. With $AlCl_3$. [\bar{C} with $AlCl_3$ (4-5%) on refluxing several hours (249) or \bar{C} at 225-230° under press. in pres. of Fe cpds. (284) undergoes bimolecular condensation with elimination of HCl and forms. of pentachlorobutadienes; see also comments above on reaction of \bar{C} with HCl and remarks below on reaction of \bar{C} with other org. chlorine cpds.]

With AlBr₃. [C with AlBr₃ as directed (283) undergoes halogen interchange giving 1,1,2-tribromoethylene [Beil. I-191, I₁-(81), I₂-(164)], b.p. 163-164°.]

With FeCl₃. [C with anhydr. FeCl₃ in s.t. at 85° yields (215) pentachloroethane (3:5880), but various side reactions result also in some hexachloroethane (3:4835) and tetrachloroethylene (3:5460).]

Behavior with other miscellaneous inorganic reactants. [\bar{C} with excess Cl₂O in CCl₄ at -20° gives (285) pentachloroethane (3:5880), chloral (3:5210), and octachlorodiethyl ether (3:0738). — \bar{C} with nitryl chloride (ClNO₂) in s.t. at 100° for 3 hrs. gives (286) by addn. 1,1,1,2-tetrachloro-2-nitroethane, colorless oil, b.p. 76° at 18 mm. (286). — \bar{C} with S₂Cl₂ in s.t. at 140–150° for some hours (no reaction in open tube) gives mainly (287) pentachloroethane (3:5880).]

[For an attempt to react C with hydrazine hydrate in pres. of solid KOH see (288).]

BEHAVIOR OF C WITH ORGANIC REACTANTS

(See also above under C with alkali.)

Behavior with hydrocarbons. [\bar{C} with C_6H_6 in pres. of Al/Hg yields (289) both 1,1-diphenylethane [Beil. V-605, V₁-(285), V₂-(511)] and 1,1,2,2-tetraphenylethane [Beil. V-739, V₁-(371), V₂-(673)]. — \bar{C} (1 mole) with cyclopentadiene (2 moles) at 175-185° under press. yields (309) a Diels-Alder type adduct, b.p. 158-160° at 11 mm., which with phenyl azide gives (309) a hydrotriazole, m.p. 225-226°.]

Behavior with other halogenated hydrocarbons (for reaction of $\bar{\mathbf{C}}$ with itself see above under polymerization).

With CHCl₃ (3:5050). [C in the pres. of AlCl₃ at 20° adds CHCl₃ to its unsatd. linkage yielding (290) (291) 1,1,1,2,3,3-hexachloropropane (3:6460); note that at higher temp., e.g., 50-60°, yield is greatly diminished and several other prods. (290) are formed.]

With CCl₄ (3:5100). [Č in the pres. of AlCl₃ adds CCl₄ to its unsatd. linkage giving at 20-30° for 48 hrs. (49% yield (292)) (290) (291) 1,1,1,2,3,3,3-heptachloropropane (3:6860).] With 1,1,2-trichloroethane (3:5330). [Č in the pres. of AlCl₃ adds 1,1,2-trichloroethane to its unsatd. linkage, then loses HCl, giving after 7 days at 40° a small yield (293) of 1,1,1,4,4-pentachlorobutene-2 (3:9054) accompanied by much resin.]

With hexachloropropene (3:6370). $[\bar{C}\ (1\ mole)\ with\ AlCl₃ + hexachloropropene (1 mole) in CH₂Cl₂ (3:5020) or CHCl₃ (3:5050) at 30-37° gives (82% yield (294)) 1,1,2,3,3,-4,5,5,5-nonachloropentene-1, colorless liq. with cedar-like odor, b.p. 128° at 2-3 mm., 86° at 0.2 mm., <math>D_{20}^{20} = 1.812$, $n_{20}^{20} = 1.5703$ (294): $\bar{C}\ (2\ moles)\ with\ AlCl₃ + hexachloropropene (1 mole) as directed gives in 5 hrs. at 20° a mixt. of two dodecachloroheptenes (C₇H₂Cl₁₂), one m.p. 94-96°, the other m.p. 58-62° (294).]$

Behavior with paraformaldehyde (1:0080). [\bar{C} with paraformaldehyde in the pres. of conc. H₂SO₄at 20–25°, followed by treatment with aq., yields (295) O=(CH₂.CHCl.COOH)₂; note, however, that \bar{C} with paraformaldehyde + conc. H₂SO₄ + an alkyl hydrogen sulfate (296) or an alcohol (297) (to yield the alkyl hydrogen sulfate) gives the corresp. alkyl esters of α -chloroacrylic acid (3:1445).]

Behavior with organic OH or SH cpds. [\bar{C} with alc. NaOEt (see above under behavior of \bar{C} with alkali) at 60-75° gives (yields: 81% (267), 70% (268)) (269) (204) α,β -dichlorovinyl ethyl ether (3:5540).]

[Č (1 mole) with sodium salt of C_2H_5SH (1 mole) in abs. alc. refluxed 2 hrs. gives (298) both α,β -dichlorovinyl ethyl thioether, b.p. 77–80° at 30 mm., and $C_2H_5S.CH=C(SC_2H_5)_2$, b.p. 135–140° at 20 mm.]

[\tilde{C} (1 mole) with sodium salt of C_6H_5SH (either 1 mole or excess) in abs. alc. refluxed 24 hrs. gives α,β -dichlorovinyl phenyl thioether, b.p. 145–150° at 22 mm. (298).]

Behavior of Č with aromatic amines. With aniline. C (1 mole) with aniline (3 moles) + aq. 15% NaOH (3 moles) refluxed for 40 hrs., and any unreacted components then removed by steam distn., gives (crude yield 64% (288)) N-phenylglycine-(N,N-diphenylamidine), C₆H₅NH.CH₂.C (=N.C₆H₅).NHC₆H₅ [Beil. XII-557] (also known as "Sabanejev's base"), colorless cryst. from AcOEt or by rapid crystn. from hot alc., m.p. 189–190° (288). — [Note that this Sabanejev's base may be hydrolyzed in two distinct stages: e.g., on protracted refluxing with EtOH (288) it splits off 1 mole aniline leaving N-phenylglycine anilide = C₆H₅NH.CH₂.CO.NHC₆H₅ [Beil. XII-556], cryst. from dil. alc., m.p. 112-113° (288); on the other hand the Sabanejev's base (or the N-phenylglycine anilide) on more vigorous treatment, e.g. with boiling aq. Ca(OH)₂, etc., hydrolyzes further yielding N-phenylglycine (N-phenylaminoacetic acid) [Beil. XII-468, XII₁-(263)], m.p. 127-128° (an important starting point for prepn. of indigo). — For patents on the prepn. of N-phenylglycine from C by reactn. with aniline in the pres. of aq. Ca(OH)₂ at 170-180° under press. see (299) (300).]

[The reactn. of \bar{C} with aniline + aq. alk. to form Sabanejev's base (above) is also accompanied by various side reactions, including formn. (29% yield (301)) of 1,1,2-tri-(anilino)ethylene, m.p. 147° dec. (301); for further details on this and other by-products see (301) (302).]

With other aromatic amines. [For analogous behavior of \bar{C} with other aromatic prim. amines in the pres. of aq. alk., e.g., with p-toluidine (288) (302) (303) (note that o-toluidine behaves abnormally while m-toluidine does not react (288)), β -naphthylamine (302) cf.

(288), p-anisidine (288), p-phenetidine (288), p-aminobiphenyl (288), and many others (288) see indic. refs.

COLOR TESTS FOR C

- **P** Color test with α -naphthol (1:1500). \bar{C} with a few drops 2% alc. α -naphthol + conc. H_2SO_4 (2 ml.), shaken, diluted with aq. (1-2 ml.), gives red-peach color (304). [This test was devised especially for detection of \bar{C} in oils or melted fats (2-ml. samples); in olive oil \bar{C} can be detected in 1/2000, and can also be noted in presence of castor oil, grapeseed oil, raw linseed oil, lard, etc. Note, however, that test fails with oils which have been subjected to oxidn., e.g., boiled linseed oil, and its sensitivity is improved by the pres. of reducing agts., e.g., by a trace of Zn dust (304).]
- P Color test with cyclopentanol (1:6412). C (1 drop) with cyclopentanol (2 ml.) + trace solid NaOH, boiled 25 secs., cooled, acidified with AcOH or 85% H₂SO₄, stood 1 min., and shaken gives (305) green color. [Note that this same response is also shown by 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) but not by methylene dichloride (3:5020), CHCl₃ (3:5050), CCl₄ (3:5100), ethylene dichloride (3:5130), pentachloroethane (3.5880), cis (3:5042) or trans (3:5028)-1,2-dichloroethylene, or tetrachloroethylene (3.5460); for sensitivity for C see (305).]
- ② Color test with pyridine and aq. alk. (Fujiwara reaction). See above under detn. of
 C.
- Comment on behavior of C with NH₄OH/CuCl. Note that C with NH₄OH/CuCl does not give blue color within 5 min. (306) (diff. from pentachloroethane (3:5880) q.v.
- Mercury bis-(trichloroethylenide), Hg(—CCl=CCl₂)₂ (see also above under detn. of C̄). C̄ with aq. KOH soln. of Hg(CN)₂ on shaking 24 hrs. at room temp. (169), or C̄ with HgO + NaOEt + KCN in alc. shaken 1 hr. at 40-60° (not higher) (307) (308) cf. (273), gives (yields: 100% (169), 90% (307)) mercury bis-(trichloroethylenide), cryst. from ether or CHCl₃, m.p. 83° (169) (273), 82-83° (242) (note that after recrystn. from alc. a m.p. of 141° (307) has been reported). [For behavior of ordinary 1,2-dichloroethylene with aq. alk. Hg(CN)₂ solns. yielding mercury bis-(chloroactylide) Hg(—C≡CCl)₂, m.p. 185°, see text of that cpd. (3:5030).]
- 3:5170 (1) Veley, Proc. Roy Soc (London) 82-B, 219-220 (1910). (2) Mumford, Phillips, J. Chem. Soc. 1928, 159. (3) Bonino, Gazz. chim. ital. 55, 342 (1925). (4) Mathews, J. Am. Chem. Soc. 48, 569 (1926). (5) Herz, Rathmann, Chem. Zig. 36, 1417 (1912). (6) Lecat, Ann. soc. sci. Bruxelles 49, 110-111 (1929). (7) Lecat, Rec. trav. chim. 46, 242 (1927). (8) Colburn, Phillips, Trans. Am. Soc Chem. Engrs. 40, 333-359 (1944). (9) Carlisle, Levine, Ind. Eng. Chem. 24, 1164-1168 (1932). (10) Trew, Watkins, Trans. Faraday Soc 29, 1310-1318 (1933).
- (11) Bates, Hazzard, Palmer, Ind. Eng. Chem. 33, 375-376 (1941). (12) Erdmann, J. prakt. Chem. (2) 85, 78-89 (1912). (13) Mkryan, Sbornik Irudov Armyanskogo Filiala Akad. Nauk. 1940, No. 2, 36-41; C.A. 37, 5694 (1943). (14) Horz, Rathmann, Chem. Zig. 37, 621 (1913). (15) Timmermans, Bull. soc. chim Belg. 27, 334-343 (1913); Cent. 1914, I 618. (16) Kanolt, U.S. Bur. Standards, Sci. Paper 520; 20, 619-633 (1924/6). (17) Herz, Rathmann, Z. Elektrochem. 19, 589 (1913). (18) Jones, Scott, U.S. Bur. of Mines, Repts. Investigations 3666 (1942). (19) Johnstone, Spoor, Ind. Eng. Chem. 32, 832-835 (1940). (20) Eckart, Brennstoff-Chem. 4, 24-25 (1923); C.A. 17, 2356 (1923).
- (21) Tschentke, Ind. Eng. Chem., Anal. Ed. 6, 21-22 (1934). (22) Mailhe, Sabrou, Bull. soc. chim. (4) 47, 349-350 (1930). (23) Reilly, Kelly, O'Connor, J. Chem. Soc. 1941, 275-278. (24) Salkowski, Biochem. Z. 107, 191-201, 319 (1920); Cent. 1920, IV 515. (25) Gowing-Scopes, Analyst 39, 4-20 (1914). (26) Bird, J. Soc. Dyers Colourists 49, 379-380 (1933). (27) Margosches, Hinner, Friedmann, Z. anorg. allgem. Chem. 137, 81-90 (1924). (28) Margosches, Baru, J. prakt. Chem. (2) 103, 216-226 (1921/2). (29) Margosches, Hinner, Z. deut. Öl- u. Fett-Ind. 44, 97-100 (1924); Cent. 1924, I 2648; C.A. 18, 3731 (1924). (30) Herz, Rathmann, Z. Elektrochem. 19, 552-555 (1913).
- (31) Herrero, Ann. soc. españ. fís. quím. 31, 416-421 (1933); Cent. 1933, II 1132; not in C.A. (32) Bell, J. Chem. Soc. 1931, 1373, 1377. (33) Gross, Simmons, Trans. Am. Inst. Chem. Engrs.

(34) Langen van der Valk, Rec. trav. chim. 48, 206 (1929). (35) Huff, **49,** 121–141 (1944). U.S. Bur. Mines, Rept. Investigations 3745 (1944). (36) Jorissen, Meuwissen, Rec. trav. chim. 44, 132-140 (1925). (37) Jorissen, Ongkiehong, Rec. trav. chim. 44, 814-817 (1925). (38) Jorissen, Velisek, Rec. trav. chim. 43, 80-86 (1924). (39) Jorissen, Meuwissen, Rec. trav. chim. 43, 591-597 (1924). (40) Coward, Jones, Ind. Eng. Chem. 18, 970-974 (1926).

(41) Jorissen, Chem. Weekblad 23, 441-444 (1926); Cent. 1927, I 863. (42) Jorissen, Ind. Eng. Chem. 19, 430-431 (1927). (43) Jorissen, Langen van der Valk, Rec. trav. chim. 44, 812-813 (1925). (44) Alekseevski, Musin, J. Applied Chem. (U.S.S.R.) 12, 704-718 (1939); C.A. 34, 2652 (1940). (45) Cook, Coleman, J. Ind. Hyg. Toxicol. 18, 194-210 (1936). (46) Alekseevskii, Gol'braith, J. Gen. Chem. (U.S.S.R.) 4, 936-947 (1934); Cent. 1935, II 3750; C.A. 29, 3587 (1935). (47) Carlisle, Ward (to Roessler & Hasslacher Chem. Co.), U.S. 1,905,900, April 24, 1933; Cent. 1934, II 2870; C.A. 27, 3486 (1933). (48) Pasquill, Proc. Roy. Soc. (London), A-182, 75-95 (1943). (49) (a) Fritzweiler, Dietrich, Angew. Chem. 46, 241-243 (1933); (b) Beiheft. Z. Ver.

deut. Chem. No. 4 (1933). (50) Herz, Z. anorg. allgem. Chem. 104, 49 (1918).

(51) Mesamer, Sweeney, Proc. Iowa Acad. Sci. 47, 207-211 (1940); C.A. 35, 7254 (1941). (52) Lecat "L'Azeotropisme," 1918; (a) p. 82, No. 321; (b) p. 83, No. 355; (c) p. 85, No. 410; (d) p. 84, No. 380; (e) p. 86, No. 434; (f) p. 84, No. 389; (g) p. 85, No. 426; (h) p. 84, No. 396. (53) Fritzweiler, Dietrich, Angew. Chem. 45, 605-611 (1932).
 (54) Sastry, J. Soc. Chem. Ind.
 35, 450-452 (1916).
 (55) Lecat, Ann. soc. sci. Bruxelles, 47, I 152 (1928).
 (56) Lecat, "L'-Azeotropisme," 1918; (a) p. 186, No. 2251; (b) p. 186, No. 2266; (c) p. 186, No. 2260. (57) Thorpe "Dictionary of Applied Chemistry," 4th ed., 1937, I, 99-104. (58) Carlisle, Coyle, Chem. Markets 29, 243-248 (1931). (59) Dietrich, Z. Spiritusind. 57, 25-27 (1934); Cent. 1934, I 2051; C.A. 28, 3830 (1934). (60) Lithder, Z. Spiritusind. 57, 252 (1934); Cent. 1934, II 4031; C.A. 29, 3453 (1935).

(61) Fritzweiler, Dietrich, Intern. Sugar J. 35, 29-32, 71-74, 146 (1933); Cent. 1933, I 3254; C.A. 27, 5883 (1933). (62) Guinot, Compt. rend. 176, 1623-1626 (1923); C.A. 17, 2758 (1923). (63) Fritzweiler, Dietrich (to Reichsmonopolverwaltung für Branntwein), Ger. 585,065, Dec. 8. 1933; Cent. 1934, I 1123; [C.A. 28, 1464 (1934)]: French 742,666, March 14, 1933; Cent. 1933, II 147; C.A. 27, 3481 (1933). (64) Bozel-Maletra (Soc. ind. prod. Chim.), French 786,510, Sept. 5, 1935; Cent. 1936, II 714; C.A. 30, 810 (1936). (65) Clarke, Othmer (to Eastman Kodak Co.), U.S. 1,908,508, May 9, 1933; Cent. 1933, II 444; C.A. 27, 3723 (1933). (66) I.G., French 663,845, Aug. 26, 1929; Cent. 1929, II 2261; C.A. 24, 628 (1930). (67) I.G., Brit. 305,594, April 4, 1929; Cent. 1929, II 650; C.A. 23, 4711 (1929). (68) Hargreaves, Tudor, Hood (to Imperial Chem. Ind. Ltd.), Brit. 498,517, Feb. 9, 1939; Cent. 1939, I 3255; C.A. 33, 4575 (1939); French 838,993, March 21, 1939; Cent. 1939, I 4841; C.A. 33, 6790 (1939). (69) Levine (to du Pont Co.), U.S. 2,153,577, April 11, 1939; Cent. 1939, II 225; C.A. 33, 5353 (1939); du Pont Co., Brit. 471,756, Oct. 7, 1937; Cent. 1938, I 429; C.A. 32, 1238 (1938). (70) Reid (to Carbide and Carbon Chem. Corp.), U.S. 2,070,962, Feb. 16, 1937; Cent. 1937, I 4040; C.A. 31, 2716 (1937).

(71) Compagnie prod. chim. d'Alais, etc., French 785,864, Aug. 21, 1935; Cent. 1935, II 3859; C.A. 30, 629 (1936). (72) Gebruder Fessler, Ger. 480,389, Aug. 1, 1929; Cent. 1929, II 3184; C.A. 23, 4923 (1929). (73) Heller, Ger. 331,535, Jan. 11, 1921; Cent. 1921, II 644; not in C.A. (74) Swift (to United Carr Fastener Co.), U.S. 2,123,856, July 12, 1938; Cent. 1938, II 4126; C.A. 32, 7012 (1938). (75) Witheridge, Walworth, J. Ind. Hyg. Toxicol. 22, 175-187 (1940). (76) Brown, Bird, J. Soc. Dyers Colourists 50, 72-76 (1934). (77) Brown, J. Soc. Dyers Colourists 49. 42-45 (1933). (78) Brown, Dyer 68, 568-569 (1932); Cent. 1933, I 863: Dyer 68, 79-80 (1932); Cent. 1932, II 1547; C.A. 26, 5425 (1932): Dyer 67, 414-415, 463-465 (1932); Cent. 1932, II 943; C.A. 26, 3931 (1932); Chem. Age 27, 165-166 (1932). (79) Fluss, U.S. 1,947,522, Feb. 20, 1934; Cent. 1934, II 2318; C.A. 28, 2550 (1934). (80) Consortium für Elektrochem. Ind., Chem. Ztg. 31, 1095-1096 (1907); 32, 529-530 (1908).

(81) Hassel, Chem. Ztg. 49, 293-295 (1925). (82) Hassel, Seifensieder Ztg. 56, 370-372 (1929); Cent. 1929, II 3077; C.A. 24, 982 (1930). (83) Jahn, Brit. 413,041, Aug. 2, 1934; Cent. 1935. II 1989; C.A. 29, 630 (1935). (84) Measmer, Iowa State Coll. J. Sci. 17, 100-102 (1942); C.A. (85) Kiseleva, Kolodezhnaya, Myasnaya Ind. 1939, No. 11/12, 38-40; C.A. **37.** 3288 (1943). 36, 6027 (1942). (86) Sutthoff, Veltman, Z. Untersuch. Nahr. u. Genussm. 47, 146-147 (1924). (87) Grossfeld, Z. Untersuch. Nahr. u. Genussm. 44, 193-203 (1922): 45, 147-152 (1923); 46, 63-73 (1923): 47, 420-432 (1924): 49, 286-289 (1925); Chem. Zig. 51, 617-618 (1927); Rec. trav. chim. 43, 457-462 (1924). (88) Heiduschka, Chem. Ztg. 54, 271-272 (1930). (89) Backlund, J. Inst. Petroleum Tech. 19, 1-25 (1933). (90) (a) Poole, Ind. Eng. Chem. 21, 1098-1102 (1929); (b) Poole and collaborators, Ind. Eng. Chem. 23, 170-177 (1931); (c) Poole, Mangelsdorf, Ind. Eng. Chem. 24, 1215-1218 (1932).

(91) Stand. Oil Development Co., French 790,852, Nov. 28, 1935; Cent. 1936, I 2672; C.A. 30, 3223 (1936). (92) Hoyt, Ind. Eng. Chem. 20, 835-837 (1928). (93) Balzacs, Jugoslav 12,078, Feb. 1, 1936; Cent. 1936, I 4794. (94) Balzacs, Austrian 146,204, June 25, 1936; Cent. 1936, II 3351. (95) Anciens Estab. Brissoneau et Lotz, French 825,044, Feb. 22, 1938; Cent. 1938, II 903; C.A. 32, 5267 (1938). (96) Churchill, Chem. Markets 25, 592 (1929). (97) Malzac, French 789,462, Oct. 29, 1935; Cent. 1936, I 3878; C.A. 30, 1905 (1936). (98) Beythien (to Minimax, A.G.), Ger. 639,395, Dec. 4, 1936; Cent. 1937, I 1990; C.A. 31, 1534 (1937). (99) Bizzoni, Lent, U.S. 1,917,489, July 11, 1933; Cent. 1933, II 2342; C.A. 27, 4604 (1933). (100) Hampe, Ger. 369,968, Feb. 24, 1923; Cent. 1923, II,906; not in C.A.

(101) Ressler (to du Pont Co.), U.S. 2,110,842, March 8, 1938; Cent. 1938, I 4710; C.A. 32, 3546 (1938). (102) Kirschbaum (to Roessler & Hasslacher Chem. Co.), U.S. 1,591,842, July 6, 1926; Cent. 1926, II 2143; C.A. 20, 3213 (1926): Brit. 254,747, Sept. 8, 1925; Cent. 1926, II 3114; C.A. 21, 2763 (1927). (103) Bode (to Corn Products Refining Co.), Ger. 716,073, Jan. 13, 1942; Cent. 1942, I 2075; not in C.A. (104) Sprengstoff A. G. Carbonite, Ger. 299,015, May 22, 1920; Cent. 1920, IV 309; C.A. 14, 2989 (1920). (105) Walden, Ann. Acad. Sci. Fennicae A.29, No. 23 (Komppa Festschrift) (1927); Cent. 1928, I 166; C.A. 22, 1515 (1928). (106) Oltman, Stain Technol. 10, 23-24 (1935). (107) Saphier, Münch. med. Wochschr. 67, 133 (1920); Cent. 1920, II 579; not in C.A. (108) Bruch, Münch. med. Wochschr. 67, 1354-1355 (1920); Cent. 1921, II 155; not in C.A. (109) McCord, J. Am. Med. Assoc. 99, 409 (1932). (110) Taylor, J. Ind. Hyg. Toxicol. 18, 175-183 (1936).

(111) von Oettingen, J. Ind. Hyg. Toxicol. 19, 411-423 (1937). (112) Barrett, MacLean, Cunningham, J. Ind. Hyg. Toxicol. 20, 360-379 (1938). (113) Seifter, J. Ind. Hyg. Toxicol. 28, 250-253 (1944). (114) Browning, J. Ind. Hyg. Toxicol 25, 127 (1943). (115) Quadland, Ind. Med. 13, 45-50 (1944); C.A. 38, 4061 (1944). (116) Matruchot, Ber. 8 intern. Kongr. Unfallmed. u. Berufskrankh. 2, 910 (1939); C.A. 36, 3548 (1942). (117) Tupholine, Chem. Industries 39, 24-26 (1936). (118) Frietag, Rayon Textile Monthly 18, 543-545 (1937). (119) Lutz, Z. angew. Chem. 43, 805-808 (1930). (120) Ferguson, Nature 137, 361-362 (1936).

(121) Isenschm d, Schweiz. Arch. Neurol. 44, 288 (1939); C.A. 36, 3552 (1942). (122) Derville, Nun, Casts, Ber. 8 intern. Kongr. Unfallmed. u. Berufskrankh. 2, 903 (1939); C.A. 36, 3548 (1942). (123) Schwander, Arch. Gewerbepathol. Gewerbehyg. 7, 109-116 (1936); Cent. 1939, II 1331; not in C.A. (124) Jensenius, Samml. Vergitungsfüllen 9-A, 95-96 (1938); Cent. 1939, II 1717; not in C.A. (125) Jordi, Schweiz. med. Wochschr. 67, 1238-1240 (1937); Cent. 1938, I 1823; not in C.A. (126) Luce, Arch. Gewerbepathol. Gewerbehyg. 7, 437-451 (1936); Cent. 1937, I 1726; not in C.A. (127) Gasq, Bull. trav. soc. pharm. Bordeaux 75, 87-101 (1937); Cent. 1937, I 5006; C.A. 32, 3047 (1938). (128) Schütz, Arch. Gewerbepath. Gewerbehyg. 7, 452-467 (1936); Cent. 1937, I 1726; not in C.A. (129) Barsoum, Saad, Quart. J. Pharm. Pharmacol. 7, 205-214 (1934); Cent. 1934, II 2550; C.A. 28, 6194 (1934). (130) Lewin, Z. deut. Öl- u. Fett-Ind. 40, 421-425, 439-441 (1920); Cent. 1921, I 924; C.A. 14, 3163 (1920).

(131) Glasser, J. Am. Med Assoc. 96, 916-920 (1931). (132) Kramer, Berlin. klin. Wochschr. 58, 149-150 (1921); Cent. 1921, I 583; not in C.A. (133) Magunna, Klnn. Wochschr. 1, 618-619 (1922); Cent. 1922, I 1086; C.A. 17, 827 (1923). (134) Eichert, J. Am. Med. Assoc. 106, 1652-1654 (1936). (135) Hewer, Proc. Roy. Soc. Med. 35, 463-468 (1942); C.A. 38, 5594 (1944). (136) Hewer, Brit. Med. J. 1, 924-927 (1941). (137) Jackson, Anesthesia and Analgesia 13, 198-204 (1934); Cent. 1934, II 3404; C.A. 29, 1501 (1935). (138) Rubinstein, Arch. Neurol. Psychiatry 37, 638-640 (1937); Cent. 1937, I 4260; not in C.A. (139) Wolff, Hardy, Goodell, J. Clin. Investigation 29, 63-80 (1941); C.A. 35, 3713 (1941). (140) Rubinstein, Painter, Harne, J. Lab. Clin. Med. 24, 1238-1241 (1939); C.A. 33, 8819 (1939).

(141) Krantz, Carr, Musser, J. Am. Pharm. Assoc. 24, 754-756 (1935). (142) Lazarev, Arch. exptl. Pathol. Pharmakol. 141, 19-24 (1929); Cent. 1929, II 451; C.A. 25, 3074 (1931). (143) Joachimoglu, Biochem. Z. 120, 203-211 (1921); Cent. 1921, III 1212; C.A. 15, 3686 (1921). (144) Joachimoglu, Berlin. klin. Wochschr. 58, 147-149 (1921); Cent. 1921, I 583; not in C.A. (145) Trumper, Jones, Taylor, Lancet 231, 1390-1391 (1936); Cent. 1937, I 923; not in C.A. (146) Rimpau, Plochmann, Schneider, Arch. Hyg. 107, 268-276 (1932); Cent. 1937, II 389; C.A. 26, 4624 (1932). (147) Rimpau, Z. Hyg. Infektionskrankh. 112, 208-221 (1931); Cent. 1931, I 2900; C.A. 25, 3432 (1931). (148) Gabbano, Z. Hyg. Infektionskrankh. 109, 183-193, 194-200 (1928); Cent. 1928, II 2668; not in C.A. (149) Stoye, Z. Hyg. Infektionskrankh. 103, 97-105 (1922); Cent. 1924, II 1215; not in C.A. (150) Joachimoglu, Biochem. Z. 124, 130-136 (1921); Cent. 1922, I 363; C.A. 16, 946 (1922).

(151) Barrett, Cunningham, Johnston, J. Ind. Hyg. Toxicol. 21, 479-490 (1939). (152)
Wright, Schaffer, Am. J. Hyg. 16, 383-388 (1932). (153) Plagge, Biochem. Z. 118, 129-143 (1921); Cent. 1922, I 52; C.A. 15, 2894 (1921). (154) Hanson (to du Pont Co.), U.S. 2,286,985, June 16, 1942; C.A. 36, 6845 (1942). (155) Hanson, Ind. Eng. Chem., Anal. Ed. 13, 119-123 (1941). (156) Winteringham, J. Soc. Chem. Ind. 61, 190-192 (1942); C.A. 37, 1951 (1943). (157) Smyth, Ind. Eng. Chem., Anal. Ed. 8, 379 (1936). (158) Olsen, Smyth, Ferguson, Scheffan,

Ind. Eng. Chem., Anal. Ed. 8, 260-263 (1936). (159) Kohn-Abrest, Mafi, Ann. hyg. publ., ind. sociale 1937, 373-384; Cent. 1937, II 3446; C.A. 1937, II 3446; C.A. 31, 8441 (1937). (160)

Dargie, Analyst 62, 730 (1937).

(161) Elkins, Hobby, Fuller, J. Ind. Hyg. Toxicol. 19, 474-485 (1937). (162) Malisoff, Ind. Eng. Chem., Anal. Ed. 7, 428 (1935). (163) Wirth, Stross, Ind. Eng. Chem., Anal. Ed. 5, 85-87 (1933). (164) Kuz'mina, Sbornik Rabot Sanit.-Khim. Inst. Higney Truda i Profzabolevani Leningrad Gorzdravotdela 1940, 50-55; cf. Peregud, ibid. 41-49; C.A. 37, 5926 (1943). (165) Winteringham, J. Soc. Chem. Ind. 61, 186-187 (1942). (166) Rauscher, Ind. Eng. Chem., Anal. Ed. 9, 296-299 (1937). (167) Kelly, O'Connor, Relly, Analyst 66, 489-490 (1941). (168) Guyot, Simon, Compt. rend. 170, 734-736 (1920); Cent. 1920, II 792; C.A. 14, 2145 (1920). (169) Schmalfuss, Werner, Z. anal. Chem. 97, 314-317 (1934). (170) Barrett, J. Ind. Hyg. Toxicol. 18, 341-348 (1936).

(171) Bruning, Schnetka, Arch. Gewerbepath. Gewerbehyg. 4, 740-747 (1933); Cent. 1935, I 3961; C.A. 28, 991 (1941). (172) Converse, Chemistry & Industry 57, 1068-1072 (1938); Canadian Chem. Process Ind. 22, 361-364 (1938). (173) Berthelot, Jungfleisch, Ann. Suppl. 7, 254-255 (1870). (174) Nicodemus, J. prakt. Chem. (2) 83, 312-322 (1911). (175) Tompkins (to Clayton Anilline Co.), Ger. 222,622, June 2, 1910; Cent. 1910, II 121, C.A. 4, 2866 (1910): Brit. 23,780, Oct. 25, 1906; C.A. 1, 2520 (1907). (176) Consortium für Elektrochem. Ind., Brit. 302,321, Feb. 6, 1929; Cent. 1929; Cent. 1929, II 794; C.A. 23, 4231 (1929). (177) Schering-Kahlbaum, A. G., Brit. 374,949, July 14, 1932; Cent. 1932, II 2107; not in C.A. (178) Chem. Fabrik. Buckau, Ger. 274,782, May 27, 1914; Cent. 1914, II 95, C.A. 8, 3350 (1914). (179) Chem. Fabrik. Griesheim-Elektron, Ger. 263,457, Aug. 8, 1913; Cept. 1913, II 829; C.A. 7, 4048 (1913). (180) Körner, Suchy (to A. Wacker Soc. Elektrochem. Ind.), Ger. 464,320, Aug. 21, 1928; Cent. 1929, I 1044; C.A. 22, 4132 (1928).

(181) A. Wacker Soc. Elektrochem. Ind., Brit. 480,568, March 24, 1938; Cent. 1938, I 4236; C.A. 32, 5857 (1938). (182) Bozel-Maletra (to Soc. Ind. Prod. Chim.), French 715,421, Dec. 3, 1931; Cent. 1932, I 3345; C.A. 26, 1946 (1932). (183) Yamaguchi, J. Chem. Soc. Japan 55, 1227-1231; 1232-1235 (1934); C.A. 29, 4326 (1935). (184) Wiegand (to Chem. Fabrik von Heyden), Ger. 566,034, Dec. 14, 1932; Cent. 1933, I 1351; [C.A. 27, 1012 (1933)]. (185) Andrusov (to I.G.), Ger. 634,549, Aug. 29, 1936; Cent. 1936, II 4048; C.A. 31, 419 (1937). French 805,563, Nov. 24, 1936; Cent. 1937, I 2258, C.A. 31, 4345 (1937). (186) Consortum für Elektrochem. Ind., Ger. 171,900, June 18, 1906; Cent. 1906, II 571; not in C.A: Ger. 208,834, April 8, 1909; Cent. 1909, I 1785; C.A. 3, 2210 (1909). (187) Strosacker, Amstutz (to Dow Chem. Co.), U.S. 2,322,258, June 22, 1943; C.A. 38, 114 (1944). (188) MacMillan (to Niagara Alkali Co.), U.S. 1,397,134, Nov. 15, 1921; Cent. 1922, IV 941; C.A. 16, 565 (1922). (189) Klebanskii, Gosudarst vennyl Inst. Prikladnoi, Khim., Sbornik Statei 1919-1939, 359-383 (1939); C.A. 36, 2521 (1942). (190) Shagalov, Dobromil'skaya, Trans. State Inst. Applied Chem. (U.S.S.R.) 24, 67-77 (1935); C.A. 29, 7272 (1935).

(191) Valyashko, Kosenko, Ukrain Khem. Zhur. 7, No. 1, Sci Pt. 12-35 (1932); Cent. 1933, 13554; C.A. 27, 1611 (1933). (192) Igi, J. Chem. Ind. Japan 23, 1217-1237 (1920); C.A. 15, 2273 (1921). (193) Miloslavski, Postovski, J. Chem. Ind. (U.S.R.) 7, 1414-1419 (1930); Cent. 1931, I 1164; [C.A. 25, 5391 (1931)]. (194) Sastry, J. Soc. Chem. Ind. 35, 450-452 (1916); Cent. 1916, II 306; C.A. 10, 1942 (1916). (195) Langguth, Chume & industrie, 25, 22-25 (1931). (196) Guyot, U.S. 1,343,716, June 15, 1920; C.A. 14, 2344 (1920); Comp. Prod. Chim. d'Alais, Ger. 351,463, April 7, 1922; Cent. 1922, IV 154; not in C.A.: Brit. 132,755, May 14, 1919; C.A. 14, 285 (1920). (197) Pogosyan, Mkryan, Russ. 50,533, Feb. 28, 1937; Cent. 1938, II 412; C.A. 31, 8549 (1937). (198) Müller, Ehrmann, Ber. 69, 2207-2210 (1936). (199) Swarts, Bull. soc. chim. (4) 25, 169 (1919). (200) Reilly (to Dow Chem. Co.), U.S. 2,140,548, Dec. 20, 1938; Cent. 1939, I 3625; C.A. 33, 2540 (1939).

(201) Rodebush (to U.S. Ind. Alc. Co.), U.S. 1,402,318, Jan. 3, 1922; Cent. 1923, II 960; [C.A. 16, 935 (1922)]. (202) Mailhe, Bull. soc. chim. (4) 29, 538-539 (1921). (203) Rebek, Mandrino, Oesterr. Chem. Ztg. 41, 363-364 (1938); Cent. 1939, I 919; C.A. 33, 1266 (1939). (204) Paterno, Oglialoro, Ber. 7, 81 (1874). (205) Chattaway, Kellett, J. Chem. Soc. 1939, 2914. (206) Zincke, Ann. 416, 69, 71, 81 (1918). (207) Müller, Hüther, Ber. 61, 589-600 (1931). (208) Kaufler, Schwaebel (to A. Wacker Soc. Elektrochem. Ind.), Ger. 465,178, Sept. 8, 1928; Cent. 1929, I 1044; not in C.A. (209) Biesalski, Z. angew. Chem. 37, 317 (1924). (210) Müller, Schumacher, Z. physik. Chem. B-37, 365-373 (1937).

(211) Kirkbride (to Imperial Chem. Ind., Ltd.), U.S. 2,292,129, Aug. 4, 1942; C.A. 37, 656 (1943): Brit. 523,555, July 17, 1940; C.A. 35, 6267 (1941): Belg. 438,987, Aug. 23, 1941; Cent. 1942, I 928. (212) Mugdan, Wimmer (to Consortium für Elektrochem. Ind.), French 706,320, June 23, 1931; Cent. 1931, II 1489; C.A. 26, 1302 (1932); Ger. 531,579, Dec. 8, 1929; C.A. 26, 1302 (1932); not in Cent. (213) Deutsch (to Consortium für Elektrochem. Ind.), Ger. 391,674.

March 10, 1924; Cent. 1924, II 888; not in C.A. (214) Consortium für Elektrochem. Ind., Ger. 340,872, Sept. 19, 1921; Cent. 1921, IV 1101; C.A. 16, 2867 (1922). (215) Erdmann, J. prakt. Chem. (2) 85, 78-89 (1912); cf. Staudinger, ibid. 330-333 (1912). (216) Dietrich, Lohrengel, Angew. Chem. 47, 830-832 (1934). (217) Taketomi, Waseda Applied Chem. Soc. Bull. 17, No. 3, 95-99 (1940); C.A. 35, 4731 (1941); not in Cent. (218) Pitman (to Westvaco Chlorine Prods. Co.), U.S. 2,319,261, May 18, 1943; C.A. 37, 6372 (1943). (219) Levine, Cass (to du Pont Co.), U.S. 2,155,723, April 25, 1939; Cent. 1939, II 946; C.A. 33, 5869 (1939). (220) Pitman (to Westvaco Chlorine Prod. Co.), U.S. 1,910,962, May 23, 1933; Cent. 1933, II 1927; C.A. 27, 3951 (1933).

(221) Zuckermandel (to Bow Chem. Co.), U.S. 1,891,585, Aug. 18, 1931; Cent. 1931, II 2657; C.A. 25, 5678 (1931). (222) Roessler & Hasslacher Chem. Co., French 732,569, Sept. 22, 1932; Cent. 1932, II 3785, C.A. 27, 304 (1933); Ger. 573,105; March 3, 1932; [C.A. 27, 2961 (1933)]; not in Cent. (223) Dietrich, Lohrengel (to Reichsmonopolverwaltung fur Branntwein), Ger. 649,118, Sept. 13, 1937, Cent. 1937, II 4102; C.A. 32, 951 (1938). (224) Levine, Cass (to du Pont Co.), Can. 396,353, May 6, 1941, Cent. 1942, II 1180; not in C.A. (225) Pitman (to du Pont Co.), U.S. 1,925,602, Sept. 5, 1933, Cent. 1933, II 3192; C.A. 27, 5445 (1933). (226) Imperial Chem. Ind. Ltd., French 744,128, April 12, 1933; Cent. 1933, II 605; C.A. 27, 3941 (1933). (227) Missbach (to Stauffer Chem. Co.), U.S. 2,043,257-2,043,260, incl., June 9, 1936; Cent. 1936, II 3845, C.A. 30, 5240 (1936). (228) Consortium fur Elektrochem. Ind., French 726,362, May 27, 1932; Cent. 1932, II 1363, CA. 26, 4829 (1932). (229) Calisle (to du Pont Co.), U.S. 1,996,717, April 2, 1935; Cent. 1935, II 920; C.A. 29, 3353 (1935). (230) Stewart, DePree (to Dow Chem. Co.), U.S. 1,917,073, July 4, 1933; C.A. 27, 4539 (1933).

(231) Roessler & Hasslacher Chem. Co., Ger. 562,820, March 3, 1932; C.A. 27, 992 (1933). (232) Dangelmajer (to Roessler & Hasslacher Chem. Co.), U.S. 1,816,895, Aug. 4, 1931; Cent. 1931, II 2656; C.A. 25, 5436 (1931). Can. 303,663, Sept. 2, 1930; C.A. 24, 5309 (1930). (233) Levine (Can. Ind., Ltd.), Can. 343,747, Aug. 7, 1934, Cent. 1936, I 176; C.A. 28, 7383 (1934). (234) Savage, Pitter (to Imperial Chem. Ind., Ltd.), Brit. 378,084, Sept. 1, 1932; Cent. 1932, II 3013; C.A. 27, 3941 (1933). (235) Carlsle, Harris (to Can. Ind., Ltd.), Can. 341,792, May 22, 1934; C.A. 28, 5076 (1934). (236) Consortum für Elektrochem. Ind., French 814,423, June 23, 1937; Cent. 1937, II 3953, C.A. 32, 957 (1938): French 51,288, Feb. 18, 1942; Cent. 1942, II 1180: Ger. 721,380, April 30, 1942, [C.A. 37, 4748 (1943)]. (237) Mugdan, Wimmer (Consortum für Elektrochem. Ind.), U.S. 2,338,297, Jan. 4, 1944; C.A. 38, 3668 (1944); Ger. 736,232, April 29, 1943; C.A. 38, 2972 (1944). (238) Consortium für Elektrochem. Ind., Ger. 718,057, Feb. 28, 1942; Cent. 1942, II 99, C.A. 38, 2343 (1944). (239) Rohm, Haas, A. G., French 841,728, May 25, 1939; Cent. 1939, II 4376; C.A. 34, 4395 (1940): Brit. 517,213, Jan. 23, 1940; [C.A. 35, 6599 (1941)]. (240) Clark, Kutz (to Gen. Flec. Co.), U.S. 1,998,309, April 16, 1935; Cent. 1935, II 1619; C.A. 29, 3751 (1935).

(241) Hopff, Rautenstrauch (to I G.), Ger. 719,914, April 21, 1942; Cent. 1942, II 721; C.A. 37, 2104 (1943). (242) Miller, J. Am. Chem. Soc. 62, 342-343 (1940). (243) Muller, Schumacher, Z. physik. Chem. B-35, 458-462 (1937); Z. Elektrochem. 43, 807-808 (1937). (244) Mkryan, Babayan, Sbornik Trudov Armyanskogo Fılıala Akad. Nauk. 1940, No 2, 51-58; C.A. 37, 5694 (1943). (245) Kharasch, Norton, Mayo, J. Ory Chem. 3, 48-54 (1938). (246) Hofmann, Kirmreuther, Ber. 42, 4484-4485 (1909) (247) Prins, Rec. trav. chim. 45, 80-81 (1926). (248) Muller, Hönn, J. prakt. Chem. (2) 133, 289-290 (1932). (249) Kaufler, Ann. 433, 48-51 (1923). (250) Simon, Chavanne, Compt. rend. 176, 309-311 (1923), Bull. soc. chim. Belg. 32, 285-287 (1923); Cent. 1923, III 1212; C.A. 18, 1112 (1924).

(251) Simon, Chavanne, U.S. 1,304,108, May 20, 1919; C.A. 13, 2039 (1919): Brit. 129,301, May 21, 1917; C.A. 13, 2878 (1919): French 22,304, June 30, 1921; Cent. 1922, II 1172. (252) Comp. Prod. Chim. d'Alais, etc., Ger. 359,910, Sept. 28, 1922; Cent. 1923, II 404; not in C.A. (253) Comp. Prod. Chim. d'Alais, etc., Ger. 377,524, June 21, 1923; Cent. 1923, IV 536; not in C.A. (254) Comp. Prod. Chim. d'Alais, etc., Ger. 383,029, Oct. 9, 1923; [Cent. 1924, I 1712]; not in C.A.: Austrian 88,199, Aug. 10, 1932, Cent. 1923, IV 591; not in C.A. (255) Comp. Prod. Chim. d'Alais, French 602,395, March 17, 1926; Cent. 1928, I 1710; not in C.A. (256) A. Wacker Soc. Elektrochem. Ind., French 705,905, June 16, 1931; Ger. 531,580, March 1, 1930; Cent. 1931, II 1489; C.A. 26, 154 (1932). (257) Comp. Prod. Chim. d'Alais, etc., Ger. 377,411, June 19, 1923; [Cent. 1923, IV 591]; not in C.A.: French 519,813, June 16, 1921; Cent. 1921, IV 653; not in C.A. (258) Böeseken, Rec. trav. chim. 32, 15-22 (1913). (259) Gunther, Hetzer (to I.G), U.S. 2,037,229, April 14, 1936; Cent. 1936, II 3382; C.A. 30, 3836 (1936). (260) Burrows, Hunter, J. Chem. Soc. 1932, 1357-1360.

(261) Hershberg, Ph.D. Thesis, M.I.T. (262) Ward, J. Chem. Soc. 1930, 2146. (263) Consortium für Elektrochem. Ind., Ger. 257,878, March 22, 1913; Cent. 1913, I 1373; C.A. 7, 2836 (1913). (264) Ott, Ber. 75, 1517-1522 (1942). (265) Ott, Ottemeyer, Packendorff, Ber. 63, 1941-1944 (1931). (266) Mets, J. prakt. Chem. (2) 135, 142-144 (1932). (267) Stephens,

J. Soc. Chem. Ind. 43, 314-315 (T) (1924). (268) Crompton, Vanderstichele, J. Chem. Soc. 117, 691-692 (1920). (269) Imbert (to Consortium für Elektrochem. Ind.), Ger. 216,940, Dec. 13, 1909; Cent. 1910, I 308; C.A. 4, 1087 (1910). (270) Thron, Chem. Ztg. 48, 142 (1924).

(271) Fritz, Chem. Zig. 48, 293 (1924). (272) Welwart, Sevensieder Zig. 56, 26 (1929); Cent. 1929, I 1523; C.A. 23, 3361 (1929). (273) Hofmann, Kirmreuther, Ber. 41, 315-317 (1908). (274) Consortium für Elektrochem. Ind., Ger. 345,868, Dec. 19, 1921; Cent. 1922, II 807; not in C.A. (275) Gowing-Scopes, Analyst 39, 6-7 (1914). (276) Sastry, J. Soc. Chem. Ind. 35, 94-95 (1916). (277) Crudes, Industria y quim. 13, 265-266 (1916); C.A. 11, 544 (1917); not in Cent. (278) Griesheim-Elektron A.G., Chem. Zig. 35, 256 (1911). (279) Elsner, Chem. Zig. 41, 901-902 (1917). (280) Formanek, Chem. Obzor 5, 57-59 (1930); Cent. 1930, II 976; C.A. 24, 4492 (1930).

(281) Imperial Chem. Industries, Chem. Trade J. 93, 227-229 (1933); Cent. 1933, II 3612. (282) Lenze, Metz, Z. ges. Schiess- u. Sprengstoffw. 27, 294 (1932). (283) Harlow, Ross (to Dow Chem. Co.), U.S. 1,891,415, Dec. 20, 1932; Cent. 1933, I 1683; C.A. 27, 1890 (1933). (284) Consortium für Elektrochem. Ind., Swiss 215,655, Oct. 1, 1941; Cent. 1942, I 2064; not in C.A.: Italian 377,536, Oct. 2, 1939; Cent. 1942, I 2195; not in C.A. (285) Goldschmidt, Schüssler, Ber. 58, 566-570 (1925). (286) Steinkopf, Kühnel, Ber. 75, 1327 (1942). (287) Pope, Smith, J. Chem. Soc. 119, 396 (1921). (288) Ruggli, Marszak, Helv. Chim. Acta 11, 180-196 (1928), (289) Böeseken, Bastet, Rec. trav. chim. 32, 203-205 (1913). (290) Prins, J. prakt. Chem. (2) 89, 415, 417, 421 (1914).

(291) Prins, Ger. 261,689, July 2, 1913; Cent. 1913, II 294; C.A. 7, 3641 (1913). (292) Henne, Ladd, J. Am. Chem. Soc. 66, 2494-2495 (1938). (293) Prins, Rec. trav. chim. 56, 120, 123 (1937). (294) Prins, Rec. trav. chim. 57, 659-666 (1938). (295) Prins, Rec. trav. chim. 51, 469-474 (1932). (296) Mead (to Imperial Chem. Ind., Ltd.), Brit. 550,853, Jan. 27, 1943; C.A. 38, 1751 (1944). (297) Roberts (to Imperial Chem. Ind., Ltd.), Brit. 550,854, Jan. 27, 1943; C.A. 38, 1751 (1944). (298) Cusa, McCombie, J. Chem. Soc. 1937, 769-770. (299) Levinstein, Imbert (to British Dyestuffs Corpn.), Brit. 173,540, Feb. 2, 1922; Cent. 1922, IV 760; C.A. 16, 1435 (1922): Ger. 436,620, Nov. 5, 1926; [Cent. 1927, I 181]; not in C.A.: French 527,554, Oct. 27, 1921; Swiss 93,576, March 16, 1922; Cent. 1922, IV 761]; not in C.A. (300) Wyler (to British Dyestuffs Corpn.), Brit. 188,933, Dec. 14, 1922; Cent. 1923, IV 663; C.A. 17, 1646 (1923): Ger. 437,409, Nov. 16, 1926; [Cent. 1927, I 3228]; not in C.A.

(301) Shibata, Tech. Repts. Tohoku Imp. Univ. 8, 21-25, 491-495 (1929); Cent. 1930, I 1291; C.A. 24, 834 (1930). (302) Shibata, Nishi, J. Soc. Chem. Ind. Japan 36, Suppl. bindg. 625-630 (1933); Cent. 1934, I 1039; C.A. 28, 748 (1934). (303) Shibata, Nishi, J. Soc. Chem. Ind. Japan 36, Suppl. bindg. 538-540 (1933); Cent. 1934, I 382; [C.A. 28, 475 (1934)]. (304) Testoni, Ann. chim. applicata 27, 497-499 (1937); Cent. 1938, I 4734; C.A. 32, 6178 (1938). (305) Weber, Chem. Ztg. 57, 836 (1933); Cent. 1933, II 3889; C.A. 28, 727 (1934). (306) Doughty, J. Am. Chem. Soc. 41, 1130-1131 (1919). (307) Fitzgibbon, J. Chem. Soc. 1938, 1218-1222. (308) Parker (to Imperial Chem. Ind., Ltd.), Brit. 427,979, May 30, 1935; Cent. 1936, I 642; C.A. 29, 6608 (1935). (309) Diels, Rickert, Ann. 543, 27 (1940).

3:5180 DICHLOROACETALDEHYDE Cl $C_2H_2OCl_2$ Beil. I - 613 I_1 -(328) I_2 -(677)

Anhydrous Č is strongly lachrymatory liq.; in s.t. Č can be kept but in open containers it gradually changes to an amorphous polymer, insol. alc. but from which Č can be regenerated at 120° (2) cf. (6).

[For prepn. of \bar{C} from dichloroacetaldehyde diethylacetal (3:6110) by distn. with conc. H_2SO_4 (1) (2) (7) or with benzoic anhydride (1:0595) + a little conc. H_2SO_4 (3) (yield: 81% (5), 78% (8)) see indic. refs.; for prepn. of \bar{C} from chloral hydrate (3:1270) with Al/Hg see (9); for manufacture of \bar{C} from chloroform + formaldehyde with SO_2Cl_2 at 300° (10) or with heat, pressure, and cat. (11) see indic. refs.]

[For formn. of \tilde{C} from α,β,β -trichloroethyl ethyl ether (1), β,β -dichlorovinyl methyl (12) or ethyl (1) ethers on htg. with acids; from β,β,β -trichlorolactic acid or its sodium salt by htg. in CO_2 (13) or warming aq. soln. (14) (22), or from its acetate with ethereal Et₂N followed by warming with aq. (13) (15); from ethyl α -ethoxy- β,β -dichloroacrylate on warming with aq. (16); from dichloropyruvic acid by htg. with aq. (15) see indic. refs.]

[For form. of \bar{C} from acetylene with HOCl (17) or from chloroacetylene (3:7000) with NaOCl (18) see indic. refs.]

 \bar{C} in pres. of conc. H_2SO_4 polymerizes (19) to a cryst. tri (?) mer paradichloroacetaldehyde, m.p. $129-130^\circ$ (19), and eas. sol. alc.; this prod. on htg. in a s.t. at $240-245^\circ$ or with conc. H_2SO_4 at $120-130^\circ$ regenerates \bar{C} . [For use of \bar{C} and this polymer as insecticides see (20).]

Č with 1 mole aq. and cooling yields (1) dichloroacetaldehyde hydrate (3:1085), m.p. 56°.

Č with abs. EtOH yields (1) dichloroacetaldehyde monoethylacetal (dichloroacetaldehyde ethyl alcoholate) (3:5310). [For dichloroacetaldehyde diethylacetal, b.p. 184° see 3:6110.]

 \bar{C} reduces NH₄OH/AgNO₃. — \bar{C} on oxidn. with fumg. HNO₃ yields (21) dichloroacetic acid (3:6208).

[Č with PCl₅ yields (22) 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) (which if much HCl is present may be accompanied by $\alpha,\beta,\beta,\alpha',\beta',\beta'$ -hexachlorodiethyl ether (22)).]

 \bar{C} with 1 mole NH₂OH.HCl in aq. soln. yields (23) a liquid oxime, b.p. 67-69° at 17 mm., 40-44° at 2-3 mm. dec.; however, with excess NH₂OH.HCl + Na₂CO₃ \bar{C} yields (14) (16) glyoxal dioxime [Beil. I-761, I₁-(394), I₂-(818), m.p. 177-178° (16), 173° (14).

Č with excess phenylhydrazine yields (24) (25) glyoxal bis-phenylosazone, pale yel. pl. from boilg. alc., m.p. 169-171° (25), 170° (24).

 \bar{C} with 1 mole semicarbazide in alc. yields (26) dichloroacetaldehyde semicarbazone, m.p. 155-156° (26); \bar{C} with 2 moles semicarbazide in aq. soln. gives on boilg. (26) glyoxal bis-semicarbazone, insol. in usual solvents and not melting below 270° (27).

- 3:5180 (1) Oddo, Mameli, Gazz. chim. ital. 33, II 388-412 (1903). (2) Paterno, Zeit. für Chemie 1868, 667. (3) Wohl, Roth, Ber. 40, 217 (1907). (4) Cheng, Z. physik. Chem. B-26, 295 (1934). (5) van der Walle, Bull. soc. chim. Belg. 28, 308-309 (1914/1919). (6) Friedrich, Ann. 206, 252 (1880). (7) Grimaux, Adam, Bull. soc. chim. (2) 34, 29 (1880). (8) Boeseken, Tellegen, Plusje, Rec. trav. chim. 57, 75 (1938). (9) Deodhar, J. Indian Chem. Soc. 11, 84-85 (1934). (10) Standard Oil Development Co., Ger. 629,897, May 26, 1936; Cent. 1936, II 2448; C.A. 30, 6006 (1936).
- (11) Frolich, Wiezevich (to Standard Oil Development Co.), U.S. 2,042,303, May 26, 1936; Cent. 1936, II 3193; C.A. 30, 4871 (1936). (12) Denaro, Gazz. chim. ital. 14, 119 (1884). (13) Koetz, J. prakt. Chem. (2) 90, 312-314 (1914). (14) Reisse, Ann. 257, 331-333 (1890). (15) Koetz, Otto, J. prakt. Chem. (2) 88, 551-552 (1913). (16) Koetz, J. prakt. Chem. (2) 103, 235 (1921/22). (17) Wittorf, J. Russ Phys.-Chem. Soc. 32, 88-117 (1900); Cent. 1900, II 29. (18) Ingold, J. Chem. Soc. 125, 1536-1537 (1924). (19) Jacobsen, Ber. 8, 87-88 (1875). (20) Ger. 528,194, June 26, 1931; Cent. 1931, II 1910.
- Paterno, Zeil. für Chemie 1869, 394. (22) Paterno, Pisati, Gazz. chim. ital 1, 463 (1871).
 Routala, Neovius, Ber. 57, 252-254 (1924). (24) Oddo, Cusmano, Gazz chim. ital. 41, II
 (25) (1911). (25) Chattaway, Farinholt, J. Chem. Soc. 1830, 96. (26) Kling, Bull. soc. chim.
 (4) 5, 414-415 (1909). (27) Harries, Temme, Ber. 40, 171 (1907).

3:5190 2,3-DICHLOROPROPENE-1 Cl Cl C₃H₄Cl₂ Beil. I - 199 (
$$\beta$$
-Chloroallyl chloride) $CH_2 = C$ CH_2 $I_1 - I_2 - C$

B.P. 94-94.5° (1) (6)
$$D_{25}^{25} = 1.204$$
 (3) $n_{D}^{21} = 1.4600$ (5) 94° (2) (3) 92.5° (4)

Colorless oil, insol. aq., sol. alc., ether.

[For prepn. of \tilde{C} from 1,2,3-trichloropropane (3:5840) + aq. alk. (yield 80% (5), 87% (4), 70% (1)) or alc. alk. (4) see indic. refs.; for other misc. methods of forms. see Beil. I-199.]

C shaken with 6-7 pts. conc. H₂SO₄, poured into aq., and distd. yields (7) chloroacetone (3:5425), b.p. 118°.

C adds Br₂ giving (3) 2,3-dichloro-1,2-dibromopropane [Beil. I-112], b.p. 205° (3).

Č htd. with fumg. HCl in s.t. at 100° yields (3) 1,2,2-trichloropropane (3:5475), b.p. 123°. [For study of addn. of HF see (4).]

[For use of C in prepn. of cellulose ethers with unsatd. linkages see (8).]

3:5190 (1) Bon, Uchenye Zapiski Leningrad. Gosudarst. Univ, Ser. Khim. Nauk 3, 3-37 (1938); Cent. 1939, II 366. (2) Kirmann, Bull. soc. chim. (5) 6, 846 (1939). (3) Friedel, Silva, Jahresber. 1871, 404; 1872, 322-323. (4) Henne, Haeckl, J. Am Chem. Soc 63, 2692-2694 (1941). (5) Hurd, Webb, J. Am. Chem. Soc. 58, 2191 (1936). (6) Claus, Ann. 170, 126 (1874). (7) Henry, Ber. 5, 190-191 (1872). (8) du Pont Co., Brit. 429,949, July 11, 1935, Cent. 1936, I 4098.

B.P.
$$96.8^{\circ}$$
 at 760 mm. (1) (2) $D_{4}^{20} = 1.1545$ (6) $n_{D}^{20} = 1.4388$ (9) $96.4^{\circ} = 1.60$ mm. (6) $95.2^{\circ} = 1.4388$ (9) $D_{4}^{20} = 1.1545$ (6) $D_{4}^{20} = 1.4388$ (9) $D_{4}^{20} = 1.4388$

Colorless oil. — For b.p.'s at various pressures from 33-847 mm. see (6) (10). — Almost insol. in aq.; for precise data see (3) (4) (5). — [For use as technical solvent see (11); for use in conen. of AcOH by forms, with aq. of const.-boilg. mixt., b.p. 96° see (12).]

[For prepn. of \bar{C} from corresp. alc., propanediol-1,2 (propylene glycol) (1:6455), with PCl₃ + ZnCl₂ (13% yield {13}), or PCl₅ + ZnCl₂ (11% yield {13}), or SOCl₂ (15% yield {13}), or SOCl₂ + pyridine (28% yield {13}), see {13}; for prepn. of \bar{C} from propylene by addn. of Cl₂ (88% yield (9)) see {9} {14} (30); for formn. of \bar{C} (35.6% {15}) together with other products by chlorination of propane (15) (16) (17) see indic. refs.; for formn. of \bar{C} (60% (18)) together with 1,3-dichloropropane (3:5450) (40% {18}) from 1-chloropropane (3:7040) with SO₂Cl₂ see {18}; for other misc. methods see Beil. I-105.]

[For study of limits of inflammability (3.4%-14.5%) by volume) of \bar{C} in air see (19); for study of thermal conductivity of \bar{C} see (20); for adsorption of \bar{C} by activated carbon at various temps, see (31).]

Č on further chlorination with SO₂Cl₂ yields (18) cf. (32) 48% 1,2,2-trichloropropane (3:5475), 37% 1,2,3-trichloropropane (3:5840) cf. (21), and 15% 1,1,2-trichloropropane (3:5630).

[For reactn. of \tilde{C} with salts of lower aliphatic acids yielding esters of d,l-propylene glycol (1:6455) see (24); with conc. aq. NH₄OH at 78-80° giving (92% yield (25)) propylenediamine dihydrochloride and other products (26) see indic. refs.]

 \bar{C} htd. with aq. + PbO in s.t. at 150° is said [Beil. I-105] to yield d,l-propylene glycol (1:6455), but \bar{C} htd. with 20 vols. aq. in s.t. at 210-220° yields (2) from the glycol a mixt. of propionaldehyde (1:0110) and acetone (1:5400). — [For behavior of \bar{C} with boilg. aq. + trace of NaHCO₃, or with boilg. aq. + Fe, see (15).]

- 1,2-Diphenoxypropane: m.p. 32°, b.p. 175-178° at 12 mm. (27). [From 1-bromo-2-phenoxypropane with 25% alc. NaOC₆H₅ (27); it has not, however, been reported direct from C.]
- ---- 1,2-Di(α -naphthoxy)propane: unrecorded.
- 3:5200 (1) Hass, McBee, Weber, Ind. Eng. Chem. 28, 338 (1936). (2) Linnemann, Ann. 161, 62-64 (1872). (3) Gross, Physik. Z. 32, 589 (1931). (4) Gross, Z. physik. Chem. B-6, 215-220 (1929). (5) Gross, J. Am. Chem. Soc. 51, 2362-2366 (1929). (6) Nelson, Young, J. Am. Chem. Soc. 55, 2429-2433 (1933). (7) Kahovec, Wagner, Z. physik. Chem. B-47, 52 (1940). (8) Kohlrausch, Ypsilanti, Z. physik. Chem. B-32, 416 (1936). (9) Goudet, Schenker, Helv. Chim. Acta 10, 132-137 (1927). (10) Kireev, Nikiforova, J. Gen. Chem. (U.S.S.R.) 6, 75-77 (1936); Cent. 1937, I 4219, C.A. 30, 7427 (1936).
- (11) Durrans, "Solvents," 4th ed., London, 1938, p. 182. (12) Othmer (to Eastman Kodak Co.), U.S. 2,021,852, Nov. 19, 1935; Cent. 1936, I 1505. (13) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929). (14) Union Carbide Co., Ger. Pat. 363,269, Nov. 6, 1922; Cent. 1923, II 475-476. (15) McBee, Hass, Chao, Welch, Thomas, Ind. Eng. Chem. 33, 176-181 (1941). (16) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,073, June 4, 1935; Cent. 1936, I 1500. (17) Hass, McBee (to Purdue Research Foundation), U.S. 2,105,733, Jan. 18, 1938; Cent. 1938, I 4533. (18) Kharasch, Brown, J. Am. Chem. Soc. 61, 2142-2149 (1939). (19) Jones, Miller, Seaman, Ind. Eng. Chem., 25, 771-773 (1933). (20) Bates, Hazzard, Palmer, Ind. Eng. Chem. 33, 375-376 (1941).
- (21) Klebanskii, Vol'kenshtein, J. Applied Chem. (U.S.S.R.) 8, 106-116 (1935); Cent. 1935, II 3298. (22) Essex, Ward, U.S. 1,477,047, Dec. 11, 1923; C.A. 18, 537 (1924). (23) Young (to Carbide and Carbon Chem. Corp.), U.S. 1,752,049, March 25, 1930; Cent. 1936, II 1280. (24) Coleman, Moore (to Dow Chem. Co), U.S. 2,021,852, Nov. 19, 1935; Cent. 1936, I 1505. (25) Darzens, Compt. rend. 208, 1503-1504 (1939); C.A. 33, 6243 (1939). (26) Mnookin, U.S. 2,049,467, August 4, 1936, Cent. 1937, I 1792. (27) Gilta, Bull. soc. chim. Belg. 31, 249 (1922) (28) Reboul, Ann. chim. (5) 14, 462-464 (1878). (29) Dahlen, Black, Foohey (to du Pont Co.), U.S. 1,979,144; Oct. 30, 1934; Cent. 1935 I 3051; [C.A. 29, 177 (1935)]. (30) Gavat, Ber. 76, 1115-1118 (1943).
- (31) Pearce, Eversole, J. Phys. Chem. 38, 383-393 (1934). (32) Zellner (to Tide Water Associated Oil Co.), U.S. 2,370,342, Feb. 27, 1945; C.A. 39 3534 (1945).

:5210	TRICHLOROACI (Chloral)	ETALDEHYDE	Cl ₈ C.CHO	C ₂ HOCl ₈	Beil. I - 616 I ₁ -(328) I ₂ -(677)
B.P.		F.P.			(,
97.8-9	98.1°	(1) -57.5° (9)	$D_4^{25} = 1.50$	060 (1) cf. (19)
97.75	at 760 mm.)49 (15) (19	
97.73	at 760 mm.	(3)	1.50	030 (9) cf. (19)
97.7°		(4)	1.47	30 (5)	
97.4-8	7.6° at 768 mm.	(5) (19)	$D_4^{21.4} = 1.50$	$059 (16) n_1^2$	$\frac{21.4}{16} = 1.45412 (16)$
97.2°	cor. at 760 mm.	(6)	-		- v
			$D_4^{20} = 1.51$	21 (10) n	$_{\rm D}^{20} = 1.4568 $ (17)
97.2°	at 731.3 mm	. (7)			1.4559 (14)
97°	at 747 mm.	(8)	1.50	66 (14)	1.45572 (10)
97°	at 740 mm.	(9)	See also Note	e 2.	
96-97	° at 750 mm.	(10)		n_1^2	$\frac{10}{10} = 1.4548 (16)$
96.5-9	6.9°	(11)		_	
96.5°		(12) (13)	Note 1. For	vapor press	of C between 0°
96.4°	at 749 mm.	(14)		30° see (18).	
See also Note 1.			Note 2. For D_4^t over range 25-85° see (15).		

[See also chloral hydrate (3:1270) and chloral ethylalcoholate (3:0860).]

Important note: The chemistry of anhydrous chloral on one hand and that of chloral hydrate on the other is so closely interwoven that the division of material between them in this book is necessarily arbitrary. For instance, there are many reactions actually employing chloral hydrate as the starting point, which by virtue of the simultaneous use of conc. H_2SO_4 are undoubtedly in effect reactions of anhydrous chloral In such cases the allocation of text between the two entries has been influenced by the nature and magnitude of the context. Although cross references have been liberally employed, the texts of both anhydrous chloral and of chloral hydrate should be compared.

MISCELLANEOUS PHYSICAL PROPERTIES

Binary systems contg. \tilde{C} . \tilde{C} with H_2O combines to give chloral hydrate (3:1270) q.v. (for use in this reaction of \tilde{C} in effecting drying of halogen compounds used in fire extinguishers see (20)); for extensive study of system \tilde{C} + aq. see (9).

Č with EtOH (1:6130) combines to give chloral ethylalcoholate (3:0860) q.v.— For analogous reactions of Č with other alcs. see below under chemical behavior of Č.

Azeotropic mixtures containing $\bar{\mathbb{C}}$. A few such systems are known including the following: $\bar{\mathbb{C}}$ with methylcyclohexane (hexahydrotoluene) (1:8410) gives a const.-boilg. mixt., b.p. 94.45° at 760 mm., contg. 57% $\bar{\mathbb{C}}$ (2); $\bar{\mathbb{C}}$ with isobutyl formate (1:3065) gives a const.-boilg. mixt., b.p. 100.1° at 760 mm., contg. 60% $\bar{\mathbb{C}}$ (21); $\bar{\mathbb{C}}$ with *n*-propyl acetate (1:3075) gives a const.-boilg. mixt., b.p. 102.55° at 760 mm., contg. 50.5% $\bar{\mathbb{C}}$ (21); $\bar{\mathbb{C}}$ with nitromethane gives a const -boilg. mixt., b.p. 93° at 760 mm., contg. 65% $\bar{\mathbb{C}}$ (20).

PREPARATION OF C

FROM HALOGEN-FREE STARTING POINTS

From ethyl alcohol. [\bar{C} was first prepared (22) from EtOH (1:6130) by action of Cl₂; for discussion of mechanism of reaction see (23) (24); note that various by-products (25) (26) such as 1,1-dichloroethane (3:5035), 1,2-dichloroethane (3:5130), 1,1,2-trichloroethane (3:5330), β,β,β -trichloroethanol (3:5775), ethyl dichloroacetate (3:5850), and chloroform

(3:5050) have been detected; for patents on prepn. of \tilde{C} (or its hydrate) from EtOH with Cl₂ see (27) (28); for use of Cl₂ in pres. of FeCl₃ see (29).]

From acetaldehyde. [For prepn. of C from acetaldehyde (1:0100) with Cl₂ see (30) (31).]

From other non-halogenated materials. [For formation of \tilde{C} from ethyl formate (1:3000) with SO_2Cl_2 in s.t. at 170° (32) or from starch or sucrose by distn. with $MnO_2 + HCl$ (33) see indic. refs.]

From Halogenated Starting Materials

From chloro-unsaturates. [For formn. of \bar{C} from 1,1,2-trichloroethylene (3:5170) with large excess Cl₂O in CCl₄ at -20° (34) or on oxidn. in pres. of FeCl₃, AlCl₃, TiCl₄, or SbCl₃ as directed (35) see indic. refs.; from chloroacetylene (3:7000) with aq. 30% NaOCl + H₃BO₃ see (36).]

From carbon tetrachloride. [For prepn. of \tilde{C} from CCl₄ (3:5100) with formaldehyde + SO₂Cl₂ + cat. at high temp. (200-500°) and high press. (20-200 atm.) see (404).]

From various chloral derivatives. [For prepn. of \tilde{C} from chloral hydrate (3:1270) by dehydration with conc. H_2SO_4 (note that \tilde{C} is appreciably soluble in conc. H_2SO_4 (9)) or with CaC_2 slowly in cold but rapidly at 100° (37); from chloral ethylalcoholate (3:0860) (or other chloral alcoholates) with conc. H_2SO_4 ; from chloral polymers such as "metachloral" by htg. at 180-200° (38); from trichloroacetaldehyde diethylacetal ("trichloroacetal") (3:6317) above 200° (39) or on distn. with conc. H_2SO_4 (39) (40); from dichloroacetaldehyde diethylacetal ("dichloroacetal") (3:6110) with Cl_2 at 60-70° (41) see indic. refs.]

CHEMICAL BEHAVIOR OF C WITH INORGANIC REACTANTS

GENERAL

[For review of chemistry of \bar{C} and its hydrate (3:1270) see (42).]

REDUCTION OF C

According to the nature of the reagent and the conditions, \bar{C} (or its hydrate) may undergo reduction either at its —CCl₃ group or at its —CHO group.

Reduction at —CCl₃ group [\bar{C} with H₂ + Pd in alc. KOH (43) or with H₂ + Ni + aq. alk. (44) splits off all its halogen as HCl. — \bar{C} with Zn + AcOH (45) (46), with Al + AcOH (75), with Zn + strong HCl (47) (48), with Zn + dil. H₂SO₄ (49) (50), reduces to acetaldehyde (1:0100); because of easy volatility of this product the reaction may be used for the identification and detection of \bar{C} (47) (49) (50), or for detection of \bar{C} in presence of CHCl₃ (3:5050) or of α,α,β -trichloro-n-butyraldehyde ("butyrchloral") (3:5910) (49). — Note that \bar{C} with aq. Zn or Fe powder especially on warming gives (51) CH₄ + MeCl (3:7005) + CH₂Cl₂ (3:5020).]

[$\ddot{\mathbf{C}}$ in aq. with Al/Hg gives (52) dichloroacetaldehyde hydrate (3:1085), while C (as hydrate) on electrolytic reduction (53) gives dichloroacetaldehyde (3:5180) + chloroacetaldehyde (3:7212) + acetaldehyde (1:0100).]

Reduction at —CHO group. [Č with Al(OEt)₃ in abs. EtOH gives (yields: 85% (54), 84% (55), 80% (56)) (57) (58) (59) cf. (60) 2,2,2-trichloroethanol-1 (3:5775); for reduction of Č to this same product using Al isopropylate in isopropyl alc. (61) in pres. of acetaldehyde (yield 72–87% (62)), C₂H₅OMgBr (63), (CH₃)₂CHOMgBr (63), or other metallic isopropylates (64), ZnEt₂ (65) (66), AlEt₃ compd. with ether (88.5% yield (67)) (note, however, that SnEt₄ is not effective (67)), or fermenting yeast (68) (69), see indic. refs.—For formn. of 2,2,2-trichloroethanol-1 (3:5775) during reaction of Č with various RMgX compounds see below under behavior of Č with RMgX cpds.]

OXIDATION OF C

Č or its hydrate (3:1270) on oxidation under appropriate conditions gives trichloroacetic acid (3:1150); under some circumstances extensive decompn. also occurs (see below).

[$\bar{\mathbf{C}}$ on oxidn. with fumg. HNO₃ (70) cf. (71), with HNO₂ (72), with NO₂ at 40-60° (70% yield (73)) or with aq. chlorates + cat. (74) gives trichloroacetic acid (3:1150); for formn. of latter as by-product of action of $\bar{\mathbf{C}}$ with O₂ including comments on inhibitors, etc., see (38) (75).]

[Chloral hydrate (3:1270) on oxidn. with fumg. HNO₃ (63% yield (76)) cf. (72), with KMnO₄ (77) (80), with KClO₃ (78), with aq. chlorates + cat. (74), or with Ca(OCl)₂ (79) gives trichloroacetic acid (3:1150).]

Chloral hydrate (3:1270) reduces NH₄OH/AgNO₃ (81) or Fehling's soln. (for study of sensitivity of this reaction see (82) [for oxidn. of chloral hydrate by HgO, KMnO₄, or CrO₃ see (83); for reduction by chloral hydrate of AgCl, AgBr, AgI, or AgSCN to metallic silver (84) or of alkaline solns. of Au, Ag, Bi, and Cu salts (85) see indic. refs.].

[C in dry C₆H₆ is but slowly attached by silver oxide (86).]

REACTIONS INVOLVING DECOMPOSITION OF C

(See also below under behavior of C with alkalies.)

[\bar{C} with aq. HIO₃ at 100° decomposes yielding (87) CHCl₃ (3:5050) + CO₂ + ICl₃ + I₂. $-\bar{C}$ on chlorine-sensitized (88) or bromine-sensitized (12) photochemical oxidn. with O₂ at 70-90° decomposes yielding (88) (12) COCl₂ (3:5000) + CO + HCl.]

[\overline{C} on thermal decompn. at about 440°C. especially if catalyzed by I_2 (89) or NO (89) (90) gives CHCl₃ (3:5050) + CO.]

[Č with AlCl₃ on htg. gives various products according to conditions; these include tetrachloroethylene (3:5460) (91) (92), pentachloroethane (3:5880) (93), $\alpha,\alpha,\beta,\beta,\gamma,\gamma,\gamma$ heptachloro-n-butyraldehyde ("perchlorobutanal") (94), chloral polymers (especially metachloral (91) (92) (95)), chloralide (3:3510) (92) (94), and others.]

BEHAVIOR OF C WITH HALOGENS

With chlorine. [\bar{C} with Cl_2 in sunlight decomposes giving (96) CCl_4 (3:5100) + CCl_2 (3:5000) + CCl_2 (3:5000) + CCl_2 at 70-90° giving CCl_4 (3:5100) + CCl_2 + CCl_2 + CCl_2 with Cl_2 at 70-90° giving CCl_4 (3:5100) + CCl_2 + CCl_2 + CCl_2 + CCl_2 with Cl_2 , CCl_2 (3:5100) + CCl_2 + CCl_2 with CCl_2 + CCl_2 (3:5100) + CCl_2 + CCl_2 with CCl_2 + CCl_2 with CCl_2 + CCl_2 (3:5100) + CCl_2 + CCl_2 with CCl_2 with CCl_2 + CCl_2 with CCl_2 with CCl_2 + CCl_2 +

With bromine. [\ddot{C} with Br₂ at 150° gives (99) trichloroacetyl bromide + bromotrichloromethane + CO + HBr; for extensive study of photochem. reaction of \ddot{C} with Br₂ at 70-90° giving bromotrichloromethane, CHCl₃ (3:5050), COBr₂, CO + HBr see (13).]

BEHAVIOR OF C WITH INORGANIC ACIDS

Č with inorganic acids reacts in various ways according to circumstances; e.g., by formn. of addn. products, by decomposition, by formation of chloralide, by polymerization (see also its own heading below), or by combinations of these reactions.

With HCl. [\bar{C} with HCl gas at -15 to -75° yields (100) (113) an addn. product \bar{C} .HCl commonly designated as chloral hydrochloride; this crystn. product with aq. dissociates giving \bar{C} (as hydrate) + HCl; note that little, if any, polymerization occurs (100).]

With HBr. [C with HBr gas at -15° yields (100) an addn. prod.; C.HBr, similar in behavior to that of the preceding HCl addn. product.]

With HNO₃. [Č with HNO₃ at 20° yields (101) an addition prod., C.HNO₃.]

With H_2SO_4 . [\bar{C} with fumg. H_2SO_4 contg. 2% SO_3 gives on warming substantially 100% yields (102) of chloralide (3:3510); note, however, that \bar{C} with fumg. H_2SO_4 contg.

10% SO₂ gives at 0° an addn. prod. of the type C_m .(SO₃)_n.(H₂O)_p which on warming dec. giving $COCl_2$ (3:5000) + SO₂Cl₂ + SO₂ + CO₂ + CO + HCl (102); for other (older) refs. on conversion of \bar{C} with fumg. H₂SO₄ to chloralide (3:3510) see (61) (81) (103) (104); for conversion of chloral hydrate (3:1270) with fumg. H₂SO₄ to chloralide (3:3510) (yields: 61% (105), 44-51% (106)) see indic. refs. — Note, however, that within a narrow range of strength (best about 79.8%) H₂SO₄ appears to give with \bar{C} or its hydrate certain unstable addition products of type $CCl_3.CH(OH).SO_2OH.H_2O$ (148).]

With CISO₃H. [\bar{C} with chlorosulfonic acid at 50° for several days gives (65% yield (107)) bis- $(\alpha,\beta,\beta,\beta$ -tetrachloroethyl) ether (3:0738); note that even at -50° for 10–12 hrs. yield of this prod. may be as high as 50%; also that various other products including chloralide (3:3510) are also formed; and finally that \bar{C} with FSO₃H behaves similarly (107).]

POLYMERIZATION OF C

 \bar{C} is known to give at least three polymers; the oldest and most common polymer is that designated as "metachloral"; in addition two isomeric α - and β -"parachlorals" (possibly comprising a pair of cis-trans stereomers) have also been reported (108).

Metachloral. [\bar{C} in presence of H₂SO₄ below 0° (108) (sometimes suddenly cf. (109)), fumg. H₂SO₄ (18), pyridine (18), or AlCl₃ as directed (18) (92) (110) gives metachloral [Beil. I-618, I₁-(329), I₂-(680)], a white amorphous polymer of unknown mol. wt. or structure. This polymer is insol. aq., alc., ether, or acids but dissolves in aq. Na₂CO₃ forming chloral hydrate (3:1270), on distn. at 180° regenerates \bar{C} , oxidizes with HNO₃ to trichloroacetic acid, with alkalies behaves like \bar{C} (see also below), and with ClSO₃H at 50° gives (107) bis-(α,β,β,β -tetrachloroethyl) ether (3:0738).]

Parachloral. [\bar{C} with a large excess conc. H_2SO_4 at 15–20°, carefully dissolved and stood 3 days at 15–20°, gives in addn. to metachloral (above) and chloralide (3:3510) small amts. of two isomeric trimers, viz., α -parachloral, rhombs from hot alc., m.p. 116°, b.p. 223° at 760 mm., and β -parachloral, pr. from alc., m.p. 152°, b.p. 250°. Note that yield of parachloral is only about 1% of original \bar{C} , that both are more sol. in hot alc. than the main prod. metachloral, that neither form is convertible to the other or to metachloral, and that both on distn. at ord. press. dissociate to \bar{C} .]

Mixed polymers. [\bar{C} (1 mole) with acetaldehyde (3 moles) + HCl gas at 0° for 15-20 hrs. gives (78% yield (111)) 2,4-dimethyl-6-(trichloromethyl)-1,3,5-trioxane, b.p. 97° at 13 mm., $D_4^{16} = 1.3915$, $n_D^{16} = 1.4708$. Similar mixed polymers (presumably analogous to the preceding case) are similarly formed (112) from \bar{C} with trimethylacetaldehyde (1:0133), \bar{C} with propionaldehyde (1:0110), and \bar{C} with isobutyraldehyde (1:0120).]

Behavior of \tilde{C} with alkalies. \tilde{C} with conc. aq. alkalies (even in cold (22)), or \tilde{C} on distn. with aq. alkalies or alk. earths (22) (114) (115), undergoes cleavage into CHCl₃ (3:5050) + the corresp. salt of formic acid (1:1005); this cleavage is claimed to occur also even with conc. NH₄OH (114) or aq. amines (114) and may also produce some CO (114) and chloride ion. — [For extensive studies of kinetics of this cleavage see (116) (117) (118) (119) (120) (121) (122) (126).]

Note that \tilde{C} is very stable toward hydrolysis by aq. (126) (even in s.t. at 190-200° for 2 hrs. (118)) or by dilute acid (even in s.t. at 150° (118)); however, \tilde{C} with aq. in sunlight is claimed (123) to give formaldehyde (1:0145) + CO_2 + HCl (presumably by formn. and decompn. of OCH.C(OH)₃), and C with aq. is claimed (124) to undergo slight formn. of dichloroacetic acid (3:6208) + HCl.

 \overline{C} with alc. KOH gives (125) CHCl₃ (3:5050) + ethyl formate (1:3000).

[Note that chloral deuterate, $CCl_2CH(OD)_2$ (from $\tilde{C}+D_2O$), with NaOD (17) or Ca-(OD)₂ (127) in D₂O gives deuteriochloroform, CDCl₃, b.p. 0.5° higher than ord. CHCl₃

(3:5050), m.p. -64.69 to -64.15° , $D_4^{20} = 1.5004$ (higher than 1.4888 for CHCl₃), $n_D^{20} = 1.4450$ (same as CHCl₃) (17).]

BEHAVIOR OF C WITH AMMONIA, HYDROXYLAMINE, HYDRAZINE, ETC.

With NH₃. [C̄ with dry NH₃ gas (81) (48) in dry CHCl₃ (128) (129) or chloral hydrate (3:1270) with NH₃ in dry ether (129) gives a white solid, m.p. 72-74° (129), 62-64° (128), originally (81) (48) (128) regarded as chloralammonia CCl₃.CH(OH).NH₂ but later (on discovery of double the expected mol. wt. (129) cf. (130)) thought to have structure CCl₃.CH(OH).NH.CH(NH₂).CCl₃.H₂O. — The prod. with KCN in conc. aq. NH₄OH gives (93% yield (131)) dichloroacetamide, m.p. 98.5-99.0° (131).]

[Note that chloral hydrate (3:1270) with NH₄OAc at 100° gives (132) a prod., cryst. from alc., m.p. 97°, regarded as a dimeric form [Beil. XXIII-15] of chloralimide, CCl₅—CH=NH; this dimer is also accompanied (132) cf. (133) by two stereoisomeric trimers [Beil. XXVI-9-10] of chloralimide.]

With hydroxylamine. The behavior of C with hydroxylamine differs according to the circumstances employed.

[Č as chloral hydrate (3:1270) with large excess NH₂OH.HCl (4 moles) in a little aq. (134) or with NH₂OH.HCl (1 mole) in pres. of conc. aq. CaCl₂ (2 moles) at 50-60° (135) gives trichloroacetaldoxime, m.p. 56° (135), 39-40° (134), b.p. 85° at 20 mm. (135).]

[C as chloral hydrate (3:1270) with NH₂OH.HCl (3 moles) in aq. Na₂CO₃/aq. NaOH as directed (136) (137) gives (yields: 50% (137), 40% (136) (138)) the alkali-stable form of chloro-oximino-acetaldehyde oxime ("chloroamphiglyoxime") [Beil. III-605, III₁-(216), III₂-(393)], ndls. of monohydrate from boilg. aq., m.p. 114° (136) (138) cf. (137); note that this prod. in dry ether with HCl gas (136) or with fumg. HCl (138) isomerizes to the acid-stable form ("chloroantiglyoxime") [Beil. III-606, III₁-(216), III₂-(393)], m.p. 161° (138), 161° dec. (136).]

[Note, however, that chloral hydrate (3:1270) (1 mole) with NH₂OH.HCl (2 moles) powdered with dry Na₂CO₃ (1 mole), allowed to stand in a desiccator some hours, then dissolved in aq. and extracted with ether gives (139) an addition product, cryst. from ether, CHCl₃, or C₆H₆, m.p. 98°, regarded as chloralhydroxylamine, CCl₃.CH(OH).NH.OH.]

[For behavior of \tilde{C} with NH₂OH.HCl + aniline giving isatin see below under reaction of \tilde{C} with primary aromatic amines.]

WITH HYDRAZINE

[C as chloral hydrate (3:1270) with hydrazine hydrate in aq. (140), ether (141), or AcOH (142), or merely fused with hydrazine hydrochloride or sulfate (143), appears to give first the expected addition product, viz., chloralhydrazine, CCl₃.CH(OH).NH.NH₂, ndls. from alc., m.p. 100° (141), 85° dec. (140); note, however, that this structure is not certain and that the material readily changes to a compound C₄H₂ON₂Cl₅, m.p. 187° cf. (140) (141) (142) (143).]

BEHAVIOR OF C WITH MISCELLANEOUS INORGANIC REACTANTS

With various compounds of phosphorus. [Č with PCl₅ in acetone gives a product regarded (144) cf. (145) as CCl₃.CH OPCl₃, b.p. 238-242°, accompanied by tetrachloroethylene (3:5460) and pentachloroethane (3:5880).]

[Č with PCl₃Br₂ is claimed (146) to give 1,1-dibromo-2,2,2-trichloroethane [Beil. I-93, I_{2} -(65)], b.p. 93-95° at 14-15 mm., $D_{4}^{19.5} = 2.295$, $D_{5}^{26.7} = 1.52991$ (146).]

[\tilde{C} with P_2S_5 in s.t. at 160-170° gives (147) a complicated reaction mixture from which only trichloroethylene (3:5170) has been identified.]

With various salts of inorganic acids (for KCN see further below).

With alkali bisulfites (or sulfites). [C or its hydrate (3:1270) with aq. alk. bisulfites (81) (149) reacts readily; for discussion of products see (81) (150) (151).]

With hydrogen peroxide. [\bar{C} with H_2O_2 in ether (151), or \bar{C} with $K_2S_2O_8 + H_2SO_4$ at ord. temp., gives (152) "dichloral peroxide hydrate," viz., CCl₃.CH(OH)—O.O.CH(OH).-CCl₃, cryst. from C_6H_6 or CHCl₃, m.p. 122° dec.]

CHEMICAL BEHAVIOR OF C WITH ORGANIC REACTANTS

BEHAVIOR OF C WITH HYDROCARBONS

With alkanes. [C with aliphatic hydrocarbons in presence of AlCl₃ reacts violently, but no definite products have been isolated (153).]

With aromatic hydrocarbons. \bar{C} with aromatic hydrocarbons in presence of H_2SO_4 or other condensing agent (note that, when H_2SO_4 is present in large excess, chloral hydrate (3:1270) is frequently substituted for \bar{C}) reacts in either or both of two modes: \bar{C} with 1 mole of hydrocarbon giving trichloromethyl-aryl-carbinols, \bar{C} with 2 moles of hydrocarbon giving 1,1,1-trichloro-2,2-diarylethanes. Although reaction of \bar{C} with hydrocarbons cannot here be summarized for all possible cases, yet the following examples will exemplify both modes of reaction.

[C with C_6H_6 + AlCl₃ (154) (156) or chloral hydrate (3:1270) with C_6H_6 + AlCl₃ (153) cf. (158) (162) or with C_6H_6 + conc. H_2SO_4 (155) gives trichloromethyl-phenyl-carbinol [Beil. VI-476, VI₁-(237)], m.p. 37° (155), b.p. 145° at 15 mm. (155) (corresp. acetate, m.p. 87.5° (155); corresp. benzoate, m.p. 97.5° (155); corresp. p-nitrobenzoate, m.p. 109° (156)) accompanied (155) by 1,1,1-trichloro-2,2-diphenylethane (3:1420), the latter also obtainable from $C + C_6H_6$ with conc. H_2SO_4 (157) or with AlCl₃ in CS_2 (80% yield (162)).]

[\bar{C} with toluene + AlCl₃ (154) or chloral hydrate (3:1270) (3 moles) with toluene (1 mole) + conc. H₂SO₄ (155) gives trichloromethyl-p-tolylcarbinol [Beil. VI-508, VI₁-(255)], m.p. 63-64° (154), 63° (155), 61.5-62.5° (159), 58-59° (160); b.p. 155° at 13.5 mm. (155), 154-156° at 13.5 mm. (154) (corresp. acetate, m.p. 107.5° (155), 105-106° (160); corresp. benzoate, m.p. 100.5° (155), 94-95° (160)). — On the other hand \bar{C} with toluene (2 moles) in pres. of H₂SO₄ (161), or AlCl₃ (153) in CS₂ at 0° (162) gives (80% yield (162)) 1,1,1-trichloro-2,2-b1s-(p-tolyl)ethane [Beil. V-619, V₁-(292), V₂-(522)], m.p. 89° (161) (162) (155), also obtained as by-product of the above carbinol (155); for study of loss of HCl with alc. KOH yielding 1,1-dichloro-2,2-di-(p-tolyl)ethylene [Beil. V-648, V₂-(559)], m.p. 92° (161), 85° (162) see (161) (162) (163).]

[For generally analogous behavior of \bar{C} with other aromatic hydrocarbons such as terbutylbenzene (405), m-xylene (153) (163), ethylbenzene (155), naphthalene (164), anthracene (164), or phenanthrene (164) in presence of condensing agents see indic. refs.]

BEHAVIOR OF C WITH ARYL HALIDES

With chlorobenzene. [That \ddot{C} with chlorobenzene (3:7903) (1 mole) + conc. H₂SO₄ gives the expected trichloromethyl-p-chlorophenyl-carbinol, b.p. 187-188° at 26 mm. (165) (corresp. acetate, m.p. 120-121° (165); corresp. benzoate, m.p. 128-129° (165)), has never been reported, this prod. having been obtd. only by condensation of p-chlorobenzaldehyde (3:0765) with CHCl₃ (3:5050) in pres. of KOH (23.5% yield (165)).

However, C or chloral hydrate with chlorobenzene (2 moles) + conc. H₂SO₄ gives the

extremely important 1,1,1-trichloro-2,2-bis-(p-chlorophenyl)ethane ("DDT") (3:3298) whose text should be consulted for further details.

With bromobenzene. [That \bar{C} with bromobenzene (1 mole) + conc. H_2SO_4 gives the expected trichloromethyl-p-bromophenyl-carbinol, b.p. 183-187° at 18 mm. (166) (corresp. acetate, m.p. 145-147° (166)), has never been reported, this product having been obtd. (29% yield (166)) only by reaction of \bar{C} with p-Br.C₆H₄.MgCl.]

[However, \bar{C} or chloral hydrate (3:1270) with bromobenzene (2 moles) + conc. H₂SO₄ + fumg. H₂SO₄ gives (167) (168) 1,1,1-trichloro-2,2-bis-(p-bromophenyl)ethane, m.p. 144° (167), 139-141° (168); note that this prod. with alc. KOH loses HCl, giving (82% yield (167) (168)) 1,1-dichloro-2,2-bis-(p-bromophenyl)ethylene, m.p. 123.5° (167), 119-120° (168).]

With iodobenzene. [The carbinol to be expected from \bar{C} with iodobenzene (1 mole) + conc. H₂SO₄ has not been reported.]

[However, \tilde{C} with iodobenzene (2 moles) + conc. H₂SO₄ gives (155) 1,1,1-trichloro-2,2-bis-(p-iodophenyl)ethane, m.p. 172° (155).]

BEHAVIOR OF C WITH ORGANIC HYDROXY COMPOUNDS

With Alcohols

General. Since \bar{C} is an aldehyde, it may be expected (at least with the assistance of a condensing agent such as dry HCl) to react with 1 mole of an alcohol to yield the corresponding hemiacetal, CCl₃.CH(OH)R, with 2 moles of an alcohol to give the corresponding acetal, CCl₃.CH(OR)₂, particularly since both these types of products are well known.

However, the special influence of the —CCl₃ group becomes apparent in this reaction and only the first type (hemiacetals) are usually obtained by direct condensation, the latter (acetals) being obtained indirectly. Moreover, members of the first group (hemiacetals) are formed with extreme ease (even in absence of condensing agents) so that, by analogy to the combination of chloral with water to give chloral hydrate (3:1270), they are generically designated as chloral alcoholates; e.g., chloral methylalcoholate, chloral ethylalcoholate, etc. Corresponding reaction of several molecules of chloral with multihydric alcohols can also occur as illustrated below.

The formation of these chloralalcoholates is profoundly influenced by conditions (especially the solvent (169)); furthermore, they readily dissociate into their original components on heating and, therefore, on heating in other alcohols (170) (171) or orthoformate esters of other alcohols (170) suffer reactions involving redistribution of the various alkyl radicals.

With monohydric alcohols. Although reaction of \bar{C} with all possible monohydric alcohols obviously cannot be included here, the following examples will serve to exemplify the reaction.

With methyl alcohol. [C with MeOH (1:6120) (1 mole) gives (171) (172) (173) (174), trichloroacetaldehyde monomethylacetal (chloral methylalcoholate), hygroscopic ndls., m.p. abt. 50° (172), 38° (171), b.p. 116° (173), 106° (172), 98° (174) (corresp. carbamate, m.p. 121° (175)). — Note that trichloroacetaldehyde dimethylacetal, CCl₃.CH(OCH₃)₂ [Beil. I-621, I₂-(681)], b.p. 183.2° cor. (176), 68-69° at 10 mm. (177), is obtd. by indirect means; note incidentally that this acetal is isomeric with butyrchloral hydrate (3:1905) and with chloral ethylalcoholate (3:0860).]

With ethyl alcohol. [Č with EtOH (1:6130) gives trichloroacetaldehyde monoethylacetal (chloral ethylalcoholate) (3:0860), q.v. for details. For the corresp. acetal, viz., trichloroacetaldehyde diethylacetal, CCl₃.CH(OC₂H₅)₂, b.p. 204°, see its own text as 3:6317.

With n-propyl alcohol. [\bar{C} with n-PrOH (1:6150) (178) (171) (170), or with NaO-n-Pr (179) or chloral hydrate (3:1270) with n-PrOH (1:6150) (170) gives (yields: 90% (178), 77-90% (170)) trichloroacetaldehyde n-propylhemiacetal (chloral n-propylalcoholate), liquid, b.p. 119-121° at 742.4 mm. (170), 120-122° (178), $D_4^{25.7} = 1.2996$ (170), $D_5^{25} = 1.4622$. (Note that the corresp. trichloroacetaldehyde di-n-propylacetal is unreported.)]

With isopropyl alcohol. [C with iso-PrOH (1:6135) (178) (171) gives trichloroacetaldehyde isopropylhemiacetal (chloral isopropylalcoholate), m.p. 47° (178), 45° (171); b.p. 108° (178) (note that the corresp. trichloroacetaldehyde di-isopropylacetal is unreported).]

With n-butyl alcohol. [C with n-BuOH (1:6180) gives (171) (179) (170) trichloro-acetaldehyde n-butylhemiacetal (chloroal n-butylalcoholate) (3:0843), m.p. 49-50° (180), 49° (171) (170); b.p. 129-130° at 742 mm. (170) (note that corresp. trichloroacetaldehyde di-n-butylacetal is unreported).]

With isobutyl alcohol. [C with iso-BuOH (1:6165) gives (180) trichloroacetaldehyde isobutylhemiacetal (chloral isobutylalcoholate), liquid, b.p. 122° without decompn. (180); note that trichloroacetaldehyde df-isobutylacetal, b.p. 241.8° at 760 mm. (181), has been prepared indirectly).]

With sec-butyl alcohol. [Č with butanol-2 (1:6155) gives (180) (171) trichloroacetaldehyde sec-butylhemiacetal (chloral sec-butylalcoholate), m.p. 12° (171), b.p. 120-121° (180); note that the corresp. trichloroacetaldehyde di-sec-butylacetal is unreported.]

With ter-butyl alcohol. [C with ter-butyl alc. (1:6140) gives (171) trichloroacetaldehyde ter-butylhemiacetal (chloral ter-butylalcoholate), m.p. 43° (171) (note that the corresp. trichloroacetaldehyde di-ter-butylacetal is unreported).]

With other monohydric alcohols. [For analogous forms, of hemiacetals from \bar{C} with isoamyl alc. (1:6200) (180), with ter-AmOH (1:6160) (171), with allyl alc. (1:6145) (99), with n-octyl alc. (1:6255) (171), with benzyl alc. (1:6480) (171), with cinnamyl alc. (1:5920) (171), with methyl-neopentyl-carbinol (182), or with β,β,β -trichloro-ter-butyl alcohol ("Chloretone") (3:2662) (183) see indic. refs.]

With dihydric alcohols. With ethylene glycol. [\bar{C} (1 mole) with ethylene glycol (1:6465) (1 mole) at 0° for 2 weeks gives (184) cf. (185) trichloroacetaldehyde (β -hydroxyethyl)-hemiacetal ("chloral ethyleneglycolate"), m.p. 50–51° (184), 42° (185); note that this product with conc. H₂SO₄ on stdg. or htg. loses 1 H₂O with ring closure to the cyclic acetal, 2-(trichloromethyl)-1,3-dioxolane, m.p. 40° (184). — However, \bar{C} (2 moles) with ethylene glycol (1:6465) (1 mole) gives (186) cf. (185) ethylene glycol 1,2-bis-(β , β , β -trichloro-methyl)-1,3-dioxolane, m.p. 42° (186).]

With polyhydric alcohols. With glycerol. [For behavior of \bar{C} with glycerol (1:6540) see (186) (184).]

With erythritol. [For behavior of C with erythritol (1:5825) see (186).]

With various carbohydrates. C combines with various polyhydroxy compounds of the carbohydrate type to give products collectively designated as chloraloses. Such combinations can be effected with pentoses or hexoses, with various stereoisomers within any such group, and more than one molecule of chloral per mole of carbohydrate is sometimes involved. In the light of modern work these chloraloses are probably cyclic acetals. Although space cannot here be taken for an extensive record, the following comments will serve as starting points for further exploration.

The most important chloralose is that derived from d-glucose and often indexed as glucochloralose. Two forms of this compound are known, viz., α -glucochloralose and β -glucochloralose; for important studies of their structures see (187) (188). For study of β -xylochloralose see (189).

For important (but older) factual data on chloraloses see (190) (191) (192).

Although the biochemical and physiological aspects of the chloraloses cannot be treated here, attention is called to several recent papers (193) (194) (195) (196) relative to their detection and determination, especially in body fluids.

WITH PHENOLS

Because in phenois there is involved not only the H of the OH group but also reactive H of the aromatic nucleus, their condensation with Č may lead to various products according to circumstances.

With monohydric phenols. With phenol. [\bar{C} (1 mole) with phenol (1:1420) (1 mole) + small amt. dry K_2CO_3 in CHCl₃ gives (7.5% yield (148)) trichloroacetaldehyde phenylhemiacetal, m.p. 15-18°, and rather unstable (148); note that the corresp. trichloroacetaldehyde diphenylacetal is unreported. — However, \bar{C} with phenol + dry K_2CO_3 as directed (197) (198), or chloral hydrate (3:1270) with phenol + dry K_2CO_3 on fusion and long stdg. (199), gives trichloromethyl-(p-hydroxyphenyl)-carbinol (corresp. diacetate, m.p. 155° (198), corresp. dibenzoate, m.p. 132° (198)).]

[Č (1 mole) with phenol (1:1420) (2 moles) in AcOH/H₂SO₄ (200) cf. (199) or in pres. of AlCl₃ (153), or chloral hydrate (3:1270) (1 mole) with phenol (1:1420) (2 moles) + conc. H₂SO₄ (201) (202), gives (80% yield (201)) 1,1,1-trichloro-2,2-bis-(p-hydroxyphenyl)-cthane [Beil. VI-1006, VI₁-(491)], m.p. 212° (153), 202° (201) (199), 202° dec. (200), 199–200° (202).]

[For different behavior of \tilde{C} in large excess with phenol (1:1420) + conc. H₂SO₄ see (207).]

With p-cresol. [\bar{C} (1 mole) with p-cresol (1:1410) (1 mole) + dry K₂CO₃ in CHCl₃ gives (35% yield (148)) cf. (203) trichloroacetaldehyde p-tolyhemiacetal, m.p. 52-56° (203), 46-47° (48); note, however, that the corresp. trichloroacetaldehyde di-p-tolylacetal is unreported. — However, \bar{C} (1 mole) with p-cresol (1:1410) (1 mole) + dry K₂CO₃ as directed (197) (198) (199), or chloral hydrate (3:1270) + p-cresol + dry HCl (148), gives trichloromethyl-(2-hydroxy-5-methylphenyl)-carbinol, m.p. 147-148° (197) (199) (148) (corresp. diacetate, m.p. 106° (198) 104.5° (148); corresp. dibenzoate, m.p. 139° (198)).]

[Note that chloral hydrate (3:1270) with o-cresol (1:1400) or with m-cresol (1:1730) + conc. H₂SO₄ gives (202) products presumably to be regarded respectively as 1,1,1-trichloro-2,2-bis-(4-hydroxy-3-methylphenyl)ethane, m.p. 121-122°, and as 1,1,1-trichloro-2,2-bis-(4-hydroxy-2-methylphenyl)ethane, m.p. 162-163°, although no other record of these compounds is reported.]

With other monohydric phenols. [For hemiacetal formn. in pres. of K_2CO_3 or $N_{a_2}CO_3$ from \tilde{C} + other phenols, such as o-methoxyphenol (guaiacol) (1:1405) (197) (198) (199) o-ethoxyphenol (1:1745) (204), 2,6-dimethoxyphenol (205) (206), o-chlorophenol (3:5980) (197), p-chlorophenol (3:0475) (197), see indic. refs.]

With polyhydric phenols: [For hemiacetal formns. in pres. of K_2CO_3 from \bar{C} with polyhydric phenols, such as pyrocatechol (1:1520) (198) (199), resorcinol (1:1530) (198) (199), see indic. refs.]

BEHAVIOR OF C WITH ORGANIC SH COMPOUNDS (MERCAPTANS AND THIOPHENOLS)

 \ddot{C} with RSH compds. in pres. of dry HCl combines mole for mole yielding monothiohemiacetals of the type CCl₈.CH(OH).SR. [e.g., for behavior of \ddot{C} in dry C₆H₆ + dry HCl with ethyl, *n*-butyl, and benzyl mercaptans, or with thiophenol, *p*-chlorothiophenol or *p*-thiocresol, see (8); for study of vapor-phase reaction of \ddot{C} + mercaptans see (208).]

BEHAVIOR OF C WITH PHENOL ETHERS

With Ethers of Monohydric Phenols

With phenyl methyl ether (anisole). [\bar{C} with 2 moles anisole (1:7445) + conc. H₂SO₄ or AlCl₈ (153) (162) or chloral hydrate (3:1270) with 2 moles anisole (1:7445) in AcOH/H₂SO₄ (201) gives (yields: 94% (162), 90% (201)) 1,1,1-trichloro-2,2-bis-(p-methoxyphenyl)ethane [Beil. VI-1007, VI₁-(491)], m.p. 94° (162), 92° (201), 89° (209), 78° (153). — Note that neither trichloroacetaldehyde p-methoxyphenylhemiacetal nor trichloroacetaldehyde di-(p-methoxyphenyl)acetal is reported.]

With phenyl ethyl ether (phenetole). [\bar{C} with 2 moles phenetole (1:7485) + conc. H₂SO₄ or AlCl₃ (153) (162) or chloral hydrate (3:1270) with 2 moles phenetole (1:7485) in AcOH/H₂SO₄ (209) gives (91% yield (162)) 1,1,1-trichloro-2,2-bis-(p-ethoxyphenyl)-ethane [Beil. VI-1007, VI₁-(491)], m.p. 105.3° (162), 105° (209). — Note that neither trichloroacetaldehyde p-ethoxyphenylhemiacetal nor trichloroacetaldehyde di-(p-ethoxyphenyl)acetal is reported.]

With ethers of other monohydric phenols. [For analogous prepn. of other 1,1,1-trichloro-2,2-di(alkoxyaryl)ethanes from \bar{C} with p-cresol methyl ether (1:7495) (162), p-cresol ethyl ether (1:7535) (162), ethyl α -naphthyl ether (1:7635) (201), and ethyl β -naphthyl ether (1:7135) (201) see indic. refs.]

With Ethers of Dihydric Phenols

With pyrocatechol dimethyl ether (veratrole). [For behavior of chloral hydrate (3:1270) with veratrole (1:7560) + conc. H₂SO₄ yielding (210) 1,1,1-trichloro-2,2-bis-(3,4-dimethoxyphenyl)ethane [Beil. VI-1172], m.p. 116-119° (211), see indic. refs.]

With hydroquinone dimethyl ether. [Č with hydroquinone dimethyl ether (1:7160) in AcOH/H₂SO₄ gives (212) 1,1,1-trichloro-2,2-bis-(2,5-dimethoxyphenyl)ethane [Beil. VI-1172], m.p. 123° (212).]

BEHAVIOR OF C WITH ALDEHYDES

With Formaldehyde

[Chloral hydrate (3:1270) (2 parts) with 40% aq. formaldehyde (formalin) (1:0145) (1 part) + conc. H₂SO₄ as directed (213) gives both 2,4-bis-(trichloromethyl)-1,3,5-trioxane ("hexachlorodimethyltrioxin") [Beil. XIX-384], m.p. 129°, and 2,6-bis-(trichloromethyl)-tetramethylenetetroxide-1,3,5,7 ("hexachlorodimethyltetroxan") [Beil. XIX-434], m.p. 189°.]

BEHAVIOR WITH KETONES

[C with acetone (1:5400) in AcOH in s.t. at 100-150° for 15 hrs. (398) (399) cf. (400) (401) gives by addition the corresp. carbinol, viz., trichloromethyl-acetonyl-carbinol ("chloralacetone") [Beil. I-831, I₂-(872)], cryst. from lgr., m.p. 75-76° (398) (399) (401) (corresp. oxime, m.p. 104-106° (399), 95-105° (402)).]

[C with methyl phenyl ketone (acetophenone) (1:5515) in AcOH refluxed 20 hrs. (398) (402) or at 135° (399) gives (45% yield (400)) by addition the corresp. carbinol, viz., trichloromethyl-phenacyl-carbinol ("chloralacetophenone") [Beil. VIII-116], m.p. 76-77° (398), 76° (399), 68-70° (400) (corresp. oxime, m.p. 135-137° (402), 131-132° (399)).]

[For behavior of chloral hydrate (3:1270) with acetophenone (1:5515) or benzophenone (1:5150) in pres. of AlCl₃ see (153).]

BEHAVIOR WITH KETENES

[For reaction of C with diphenylketene in s.t. at 130° for 12 hrs. see (214).]

BEHAVIOR WITH ORGANIC ACIDS

With Acids Containing No Other Functional Group

[For behavior of \bar{C} with AcOH in pres. of AlCl₃ see (153); with Hg(OAc)₂ + ethylene in alc. soln. giving a prod. possibly having the structure CCl₃.CH(OC₂H₅) (OCH₂CH₂-HgOAc) see (215).]

[Note that \tilde{C} is able to add to its carbonyl group a reactive H atom derived from certain acids [e.g., \tilde{C} with malonic acid (1:0480) in AcOH at 100° for 40 hrs. (216) cf. (217), or in pyridine at 100° for 2 hrs. (67.5% yield (218)) cf. (219), or chloral hydrate (3:1270) + malonic acid (1:0480) + pyridine at 100° (220) gives (note loss of CO_2) γ,γ,γ -trichloro- β -hydroxy-n-butyric acid [Beil. III-310, III₁-(117), III₂-(221)], m.p. 118-119° (217) (218), 118.5° (216) (note hydrate, m.p. 52-54° (218)); note also that by further elimination of H₂O (e.g., with Ac₂O + NaOAc (217)) this prod. yields γ,γ,γ -trichlorocrotonic acid [Beil. II-418, II₁-(190), II₂-(397)], m.p. 113-114° (217).]

[Similarly, \bar{C} adds one of the α H atoms from succinic acid (1:0530): e.g., \bar{C} with disodium succinate + Ac₂O yields an intangible intermediate which suffers two types of further change, on one hand losing H₂O to give trichloromethylparaconic acid (β -carboxy- γ -trichloromethyl- γ -butyrolactone) [Beil. XVIII-372], and on the other suffering hydrolysis of its —CCl₃ group to give isocitric acid (α -hydroxypropane- α , β , γ -tricarboxylic acid) [Beil. III-555, III₂-(359)]; for details of execution of these reactions see (221).]

With a-Hydroxy Acids

Condensation of \bar{C} (or its hydrate) with acids containing an α -hydroxy group leads to the formation of products generically designated as "chloralides"; these are ether-esters comprising position-5 substitution products of the true parent 2-(trichloromethyl)-1,3-dioxolanone-4 (from α -hydroxyacetic acid) and are not to be confused with the specific compound "chloralide" (3:3510) obtd. from \bar{C} with H₂SO₄. With true chloralides above the initial parent, two geometrically isomeric forms are possible.

With α -hydroxyacetic acid. [\bar{C} with glycolic acid (1:0430) in s.t. at 120–130° for 2 days gives (224) 2-(trichloromethyl)-1,3-dioxolanone-4 ("glycolic acid chloralide") [Beil. XIX-103], m.p. 41–42°.]

With lactic acid. [\overline{C} with anhydrous lactic acid (1:0400) in s.t. at 150-160° (225) (224) or better chloral hydrate (3:1270) with lactic acid (1:0400) + conc. H₂SO₄ (226) (227) (228) (229) gives 2-(trichloromethyl)-5-methyl-1,3-dioxolanone-4 ("lactic acid chloralide") [Beil. XIX-105], m.p. 45° (226) (227), b.p. 222-224° (224) (225), 218-220° at 714 mm. (226); note, however, that two geom. isomers, cis, m.p. 56°, and trans, b.p. 210-212°, are claimed (229).]

With malic acid. [\bar{C} with l-malic acid (1:0450) at 120-130° for 20 hrs. (224), or chloral hydrate (3:1270) with l-malic acid (1:0450) + conc. H_2SO_4 (230) (228), gives 2-(trichloromethyl)-5-(carboxymethyl)-1,3-dioxolanone-4 ("1-malic acid chloralide"), m.p. 141° (230), 139-140° (224) (228): note, however, that chloral hydrate (3:1270) + d,l-malic acid + conc. H_2SO_4 at room temperature overnight gives (59% yield (231)), m.p. 180-181°.]

With citric acid. [Chloral hydrate (3:1270) with citric acid (1:0455) + conc. H_2SO_4 gives (228) (231) 2-(trichloromethyl)-5,5-bis-(carboxymethyl)1,3-dioxolanone-4 ($C_8H_8O_7$ - Cl_8), m.p. 164° (231), 161° (228).]

With mandelic acid. [\bar{C} with d,l-mandelic acid (1:0465) at 120° (224) cf. (227), or chloral hydrate (3:1270) with d,l-mandelic acid (1:0465) + conc. H₂SO₄ (228) (231), gives 2-(trichloromethyl)-5-phenyl-1,3-dioxolanone-4 [Beil. XIX-129], m.p. 82-83° (224)

(228), 70-71° (231), 59-60° (227); note that this disagreement of m.p.'s may be due to mixtures of possible cis-trans stereoisomers.]

With benzilic acid. [\bar{C} with benzilic acid (1:0770) in s.t. at 160-165° for 5 hrs. gives (231) 2-(trichloromethyl)-5,5-diphenyl-1,3-dioxolanone-4 ("benzilic acid chloralide"), m.p. 70°. Note that an analogous prod. has been reported (232) from chloral hydrate (3:1270) with thiobenzilic acid, (C_6H_6)₂C(SH)COOH in AcOH + HCl gas.]

With tartaric acid. [Since this acid is twice an α -hydroxy acid it reacts with 2 moles of \bar{C} forming a dichloralide of compn. $C_8H_4O_6Cl_6$: e.g., \bar{C} with d-tartaric acid (1:0525) at 150° (224), or chloral hydrate (3:1270) with d-tartaric acid (1:0525) (227) (228) (230) (231) or d,l-tartaric acid (1:0550) (227) (228) gives "tartaric acid dichloralide" [Beil. XIX-449], m.p. 213-215° (229); 164-166° (227), 161-162° (231), 161° (229), 160° (228), 159-161° (227); 128-130° (228), 122-124° (224), 116-118° (227). Note that this product should exist in three stereoisomeric forms (230), and the three groups of m.p.'s above given may represent this expectation.]

With mucic acid. This acid combines with 3 moles of chloral hydrate to give a prod. commonly called a "trichloralide"; note, however, that it is undoubtedly a dichloralide which has further condensed at its two free OH groups with a third molecule of chloral [e.g., chloral hydrate (3:1270) with mucic acid (1:0845) + H₂SO₄ gives (228) (229) a "trichloralide," m.p. 200-201° (228), 198° (229), 174-175° (229); doubtless these represent at least two stereoisomeric forms].

With Phenolic Acids (or Their Ethers)

In condensation of \bar{C} (or its hydrate) with phenolic acids, the latter behave like carboxy-substituted phenols; two series of products result according to whether *one* or *two* moles of carboxy-phenol are involved per mole of chloral. To assist in recognizing this analogy, the several products are here named as substituted carbinols or ethanes just as was done above in the behavior of \bar{C} with phenols (q.v.). Since the methyl ethers of these phenolic acids in general behave similarly, they are associated below with the corresponding phenolic acids.

With o-phenolic acids. With o-hydroxybenzoic acid. [Chloral hydrate (3:1270) with salicylic acid (1:0780) + conc. H₂SO₄ gives (233) cf. (234) some 1,1,1-trichloromethyl-(4-hydroxy-3-carboxyphenyl)-carbinol, m.p. 180–182° (233), but main prod. is 1,1,1-trichloro-2,2-bis-(4-hydroxy-3-carboxyphenyl)ethane, m.p. 290–292° (corresp. diacetate, m.p. 207–209° (233)).]

With o-methoxybenzoic acid. [Chloral hydrate (3:1270) with o-methoxybenzoic acid (1:0685) + conc. H₂SO₄ gives (yields: 45% (234), 25% (235)) 1,1,1-trichloro-(4-methoxy-3-carboxyphenyl)-carbinol, m.p. 224° (234), 216° (235), some sulfonation also occurring (235).]

With 2-hydroxy-3-methylbenzoic acid. [Chloral hydrate (3:1270) with o-cresotic acid [Beil. X-220, X_1 -(96)] + conc. H_2 SO₄ gives (236) 1,1,1-trichloro-2,2-bis-(4-hydroxy-3-methyl-5-carboxyphenyl)ethane, m.p. $283-285^{\circ}$ (236): note that the corresp. carbinol to be expected from chloral hydrate + 1 mole o-cresotic acid is unreported.]

With 2-hydroxy-4-methylbenzoic acid. [Chloral hydrate (3:1270) with m-cresotic acid [Beil. X-233, X₁-(100)] is complex and disputed; for discussion see (236) (237) (238) (239). — For behavior of $\ddot{\mathbf{C}}$ with 2-methoxy-4-methylbenzoic acid see also (241).

With 2-hydroxy-5-methylbenzoic acid. [Chloral hydrate (3:1270) with p-cresotic acid [Beil. X-227, X_1 -(98)] + conc. H_2SO_4 gives (236) a prod. of compn. $C_{12}H_8O_4Cl_6$ (2,4-bis-(trichloromethyl)-6-methyl-1,3-benzdioxin-8-carboxylic acid), m.p. 285-286° dec., derived from 2 moles chloral hydrate + 1 mole p-cresotic acid.]

With 2-hydroxy-3-naphthoic acid. [For behavior of chloral hydrate (3:1270) with 2-hydroxy-3-naphthoic acid (1:0850) + conc. H_2SO_4 see (242).]

With m-phenolic acids (or their ethers). Condensation of $\bar{\mathbf{C}}$ or its hydrate with m-phenolic acids leads generally to substituted phthalides.

With m-hydroxybenzoic acid. [Chloral hydrate (3:1270) with m-hydroxybenzoic acid (1:0825) + conc. H₂SO₄ gives (243) (244) 3-(trichloromethyl)-6-hydroxyphthalide [Beil. XVIII-20], m.p. 199-200° (244), 197-198° (243). — Note that chloral hydrate (3:1270) with ethyl m-methoxybenzoate (1:4131) + conc. H₂SO₄ gives (243) (245) 3-(trichloromethyl)-6-methoxyphthalide [Beil. XVIII-20], m.p. 135° (243) (245), which by alk. hydrol. of the —CCl₃ group gives (243) (245) 6-methoxyphthalide-3-carboxylic acid [Beil. XVIII-525], m.p. 170° (245), 169-170° (243).]

With 2-chloro-3-hydroxybenzoic acid. [Chloral hydrate (3:1270) with 2-chloro-3-hydroxybenzoic acid (3:4395) + conc. H₂SO₄ gives (246) 3-(trichloromethyl)-7-chloro-6-hydroxyphthalide, m.p. 195.5-196°.]

With 4-methyl-3-hydroxybenzoic acid. [Chloral hydrate (3:1270) with 4-methyl-3-hydroxybenzoic acid [Beil. X-237] + conc. H₂SO₄ gives (247) 3-(trichloromethyl)-5-methyl-6-hydroxyphthalide, m.p. 232° (247). — Similarly, chloral hydrate (3:1270) with 4-methyl-3-methoxybenzoic acid + conc. H₂SO₄ gives (247) 3-(trichloromethyl)-5-methyl-6-methoxyphthalide, m.p. 132° (247).]

With 3,4,5-trihydroxybenzoic acid. [Chloral hydrate (3:1270) with gallic acid (1:0875) + conc. H₂SO₄ gives (236) according to conditions three different products: with excess of gallic acid prod. is 3-(trichloromethyl)-4,5,6-trihydroxyphthalide, m.p. 210-212° (236), for further reactions of which see (236) (248); with excess chloral, however, the reaction gives two other materials (236). — Note that chloral hydrate (3:1270) with 3,4,5-trimethoxybenzoic acid (gallic acid trimethyl ether) [Beil. X-481, X₁-(240)] + conc. H₂SO₄ (249) (250) (251), or with methyl 3,4,5-trimethoxybenzoate (methyl gallate trimethyl) ether) [Beil. X-484, X₁-(242)] (252), gives (56% yield (249)) 3-(trichloromethyl)-4,5,6-trimethoxyphthalide [Beil. XVIII₁-(389)], m.p. 76-77° (249), 71-72° (250), 70-71° (252) (note also that during condensation some demethylation may occur (253), avoided by (251)); this prod. by hydrolysis of the trichloromethyl group yields 4,5,6-trimethoxyphthalide-3-carboxylic acid [Beil. XVIII₁-(544)], m.p. 147-149° (249), 147-148° (250), 147° (251), 146-149° (254), 142-143° (252).]

With p-phenolic acids (or their ethers). With p-hydroxybenzoic acid. [Chloral hydrate (3:1270) (3 moles) with p-hydroxybenzoic acid (1:0840) (1 mole) + conc. H₂SO₄ at room temp. for 3 days condenses giving (31% yield on the acid (255)) 2,4-bis-(trichloromethyl)benzodioxin-1,3-carboxylic acid-6, m.p. 225.5-226.5° (255); for further related reactions of this prod. see (256); for further generally similar work in benzodioxin series see (257) (258); note that neither the substituted carbinol nor the substituted ethane corresp. to the behavior of o-hydroxybenzoic acid (see above) under similar conditions is reported.]

With p-methoxybenzoic acid. [Chloral hydrate (3:1270) with p-anisic acid (1:0805) + conc. H₂SO₄ reacts in a 1:1 ratio (note difference from 2:1 ratio in preceding paragraph) giving (259) cf. (235) trichloromethyl-(2-methoxy-5-carboxyphenyl)-carbinol, m.p. 198-199° (259); note that the earlier product (235) was impure.]

With 4-hydroxy-3,5-dimethoxybenzoic acid. [Chloral hydrate (3:1270) with syringic acid (1:0830) + conc. H₂SO₄ gives (86% yield (253)) 3-(trichloromethyl)-5-hydroxy-4,6-dimethoxyphthalide, m.p. 172-173° (253).]

With keto acids (see also below under behavior with esters of organic acids).

With levulinic acid. [\ddot{C} (1 mole) with β -acetopropionic acid (levulinic acid) (1:0405)

in pres. of NaOAc refluxed 4 hrs. gives (30% yield (271)) α -(trichloroethylidene)- β -aceto-propionic acid, m.p. 113.5° (271).]

BEHAVIOR WITH ESTERS OF ORGANIC ACIDS

[Note that \bar{C} does not (170) react with orthoformates (difference from chloral hydrate (3:1270) q.v. — Note that \bar{C} with esters of α -ketoacids on htg. gives (260) 5-substituted-2-(trichloro)-1,3-dioxolanone-4's, such esters reacting in their enolic forms as esters of α -hydroxy unsaturated acids; for such products from ethyl acetopyruvate [Beil. III-747, III₁-(261), III₂-(465)] (261) or from ethyl benzoylpyruvate [Beil. X-815, X₁-(395)] see (260). — \bar{C} with ethyl acetoacetate (1:1710) in pyridine at 25–30° for 5 days gives (262) by addn. the corresp. carbinol, viz., ethyl α -(2,2,2-trichloro-1-hydroxyethyl)acetoacetate.]

BEHAVIOR WITH ACID CHLORIDES

(See also behavior with anhydrides below.)

[\ddot{C} with acetyl chloride (3:7065) (263) (264) in pres. of conc. H₂SO₄ (265), or chloral hydrate (3:1270) with acetyl chloride (3:7065) (263) gives α,β,β,β -tetrachloroethyl acetate ("chloral-acetyl chloride"), b.p. 193° (264), 185° (263).]

[For analogous behavior of \bar{C} with propionyl chloride (3:7170) (265), with *n*-butyryl chloride (3:7370) (265), with acetyl bromide (266), or with acetyl iodide (266) see indic. refs.]

[For behavior of \bar{C} with carbonyl chloride (3:5000) in pres. of tertiary amines (except pyridine) giving α,β,β,β -tetrachloroethyl chloroformate [Beil. III-12] or bis-(α,β,β,β -tetrachloroethyl)carbonate [Beil. III-8] see (267).]

BEHAVIOR WITH ACID ANHYDRIDES

[\bar{C} with acetic anhydride (1:1015) at 150° (263) or in pres. of H_2SO_4 at 5° (268) or chloral hydrate (3:1270) with Ac_2O (1:1015) + H_2SO_4 (269) gives trichloroethylidene diacetate, $CCl_3.CH(OAc)_2$ [Beil. II-153, II₁-(71), II₂-(167)], b.p. 221-222° (263), 221° at 751 mm. (269), 111-113° at 10 mm. (268): for study of pyrolysis of this prod. see (270).]

Behavior involving Condensation of C with Reactive C-H of various Organic Compounds

(See also above under acids.)

With various alkylated pyridines. With 2-methylpyridine. [\bar{C} with 2-methylpyridine (α-picoline) [Beil. XX-234, XX₁-(82)] in iso-AmOAc refluxed 10-12 hrs. (272) (273) (274) (275) (276) (277) (278), or without solvent at 100° for 10 hrs. (279) or 112° for 36-40 hrs. (280), gives (yields: 67% (280), 47% (278), 40-47% (276)) trichloromethyl-α-picolyl-carbinol = 1-(trichloromethyl)-2-(α-picolyl)ethanol [Beil. XXI-46], m.p. 86-87° (272) (273) (279), 86° (278), 85-86° (280), 82° (277) (corresp. B.HCl, m.p. 201-202° (272), 199-200° (274); corresp. B.PkOH, m.p. 167° (274)). — For studies on dehydrative hydrolysis of this prod. to β-(α-pyridyl)acrylic acid [Beil. XXII-55], m.p. 202-203° (272), 200° dec. (274) (corresp. hydrochloride, m.p. 220° dec. (273)), see (280) (275) (273) (274) (272); for studies on its reduction see (281) (275) (274).]

With 4-methylpyridine. [C with 4-methylpyridine (γ -picoline) [Beil. XX-240, XX₁-(85)] at 100° for 15 hrs. (282), or in pres. of ZnCl₂ in s.t. at 85-90° (283) (284) or at 34° for 24 hrs. then at 100° for 2 hrs. (285) (286), gives (yields: 42% (286), 16-18% (285), 8-9% (284)) trichloromethyl- γ -picolyl-carbinol = 1-(trichloromethyl)-2-(γ -picolyl)-ethanol [Beil. XXI-57, XXI₁-(204)], m.p. 168° cor. (286), 166-167° cor. (285), 166° cor. (283), 160° (282). — For studies on dehydrative hydrolysis (yields: 73% (285), 70% (283))

of this prod. to β -(γ -pyridyl)acrylic acid [Beil. XXII₁-(505)], m.p. 296° cor. dec. (283), 293–295° cor. (285), see indic. refs.]

With other alkylated pyridines. [For corresp. condensations of \bar{C} with 3-ethyl-4-methylpyridine (" β -collidine") [Beil. XX-250, XX₁-(87)] (287) (288), with 5-ethyl-2-methylpyridine [Beil. XX-248, XX₁-(86)] (290), with 2,4,6-trimethylpyridine ("collidine") [Beil. XX-250, XX₁-(87)] (289) (291) see indic. refs.]

With various alkylated quinolines. [For corresp. condensations of \bar{C} with 2-methyl-quinoline (quinaldine) [Beil. XX-387, XX₁-(148)] (285) (292) (293) (294) (295), or with 4-methylquinoline ("lepidine") [Beil. XX-395, XX₁-(150)] (296) (297) (295), see indic. refs.]

With nitroparaffins. C in aq. mildly alk. soln. also adds 1 reactive hydrogen atom from nitroalkanes yielding the corresp. substituted alcohols.

With nitromethane. [Chloral hydrate (3:1270) (1 mole) with nitromethane (1 mole) in aq. Na₂SO₃ at 70° gives (100% yield (298)) the corresp. carbinol, viz., 1,1,1-trichloro-3-nitropropanol-2 [Beil. I-366], m.p. 48-49° (299), 45-46° (298), 42-43° (300); b.p. 119° at 3 mm. (298) (corresp. acetate, m.p. 61-62°, b.p. 160° at 25 mm., 148° at 16 mm. (298)); note that other mildly alk. salts such as K₂CO₃ (298) (300), NaOAc (298), or Na₂B₄O₇ (298) may be used although Na₂SO₃ is best (298); note also that this prod. does not (298) react further with chloral. — For studies of the behavior of this prod. or its esters with diazonium salts (299) (301), with various amines (302) (303), or reducing agents (304) see indic. refs.]

With nitroethane. [Chloral hydrate (3:1270) with nitroethane in aq. Na₂SO₃ + K₂CO₃ gives (80% yield (305)) the corresp. carbinol, viz., 1,1,1-truchloro-3-nitrobutanol-2, oil, b.p. 115° at 2 mm. (corresp. acetate, b.p. 125° at 2 mm., 98° at 0.05 mm. (305)).]

With phenyl-nitromethane. [Chloral hydrate (3:1270) with phenyl-nitromethane in aq. K₂CO₃ at 80° gives (305) 1,1,1-trichloro-3-phenyl-3-nitropropanol-2, m.p. 109° (corresp. acetate, m.p. 98° (305)).]

BEHAVIOR WITH GRIGNARD REAGENTS

Č with RMgX reagents may react in either or both of two modes: on the one hand normal addition may occur leading to the corresp. carbinols; on the other, reduction at the expense of the RMgX cpd. may occur leading to formn. of 2,2,2-trichloroethanol-1 (3:5775). Of these two types the former occurs when the RMgX cpd. is not easily dehydrogenated.

With aliphatic RMgX compounds. With MeMgX. [C with MeMgBr (306) (307) cf. (308) or MeMgI (307) (166) cf. (308) in ether gives (yields: 40% (306) (307)) 1,1,1-trichloropropanol-2 (3:0846); note, however, that yield is profoundly influenced by press of certain metal salts (306), that some reduction of C to 2,2,2-trichloroethanol-1 (3:5775) probably occurs, and that this latter is favored by use of EtOMgBr, etc. (see 3:5775).]

With EtMgX. [C with EtMgBr (309) (310) (311) or with EtMgI (166) gives both addition and reduction leading respectively to 1,1,1-trichlorobutanol-2 (3:5955) q.v. and 2,2,2-trichloroethanol-1 (3:5775) q.v.]

With n-PrMgX. [\bar{C} with n-PrMgBr in ether gives (21-23% yield (310)) the carbinol from addition, viz., 1,1,1-trichloropentanol-2 [Beil. I₂-419], b.p. 115° at 686 mm. (310), $D_{20}^{20} = 1.481$ (310) (corresp. acetate, b.p. 168-169° at 686 mm., corresp. benzoate, b.p. 197-198° at 686 mm. (310)) but whether the material still unaccounted for represents 2,2,2-trichloroethanol (3:5775) from reduction of \bar{C} has not been reported.]

With iso-PrMgX. [C with iso-PrMgBr in ether gives (31-33% yield (312)) the carbinol from addition, viz., 1,1,1-trichloro-3-methylbutanol-2 [Beil. I-392, I₂-(425)], b.p. 105° at

674 mm., $D_{20}^{20} = 1.402$ (312) (corresp. acetate, b.p. 156-157° at 685 mm.; corresp. benzoate b.p. 180-181° at 685 mm. (312)), but whether the material still unaccounted for represents 2,2,2-trichloroethanol-1 (3:5775) from reduction of $\bar{\mathbf{C}}$ has not been reported.]

With n-BuMgX. [\bar{C} with n-BuMgBr in ether gives (34-36% yield (312)) the carbinol from addition, viz., 1,1,1-trichlorohexanol-2 [Beil. I₂-(438)], b.p. 108° at 673 mm., $D_{20}=1.327$ (312) (corresp. acetate, b.p. 157-158° at 684 mm.; corresp. benzoate, b.p. 182-183° at 684 mm. (312)), but whether the material still unaccounted for represents 2,2,2-trichloroethanol-1 (3:5775) from reduction of \bar{C} has never been reported.]

With higher alkyl MgX cpds. [Č with n-AmMgBr (313) or with n-HexMgBr (313) in ether gives (yields respectively 50-61% and 56-69%) the reduction product, 2,2,2-tri-chloroethanol-1 (3:5775); the corresponding carbinols to be expected by addition are unreported.]

With aromatic RMgX compounds. With C_6H_5MgX . [\bar{C} with C_6H_5MgBr in ether gives (70% yield (314)) (315) the expected truchloromethyl-phenyl-carbinol [Beil. VI-476, VI₁-(237)], m.p. 37° (155), b.p. 145° at 15 mm. (155) (corresp. acetate, m.p. 87.5° (155); corresp. benzoate, m.p. 97.5° (155); corresp. p-nitrobenzoate, m.p. 109° (156)).]

With alkaryl MgX compounds. With $C_6H_5CH_2MgX$ cpds. [C with $C_6H_5CH_2MgCl$ (309) (310) or $C_6H_5CH_2MgBr$ (166) gives both addition (309) (310) (166) and reduction (309) yielding from the former trichloromethyl-benzyl-carbinol, b.p. 158-160° at 18 mm. (166) (corresp. acetate, m.p. 110-111° (166), 109-110° (309)), together with a very small amount (309) of 2,2,2-trichloroethanol-1 (3:5775).]

With cyclohexyl MgX cpds. [\bar{C} with cyclohexyl MgBr (314) (316) in ether is claimed to give (30% yield (316)) trichloromethyl-cyclohexyl-carbinol, b.p. 119-121° at 15 mm., $D_{20}^{20} = 1.2839$, $n_{20}^{25} = 1.4820$ (corresp. acetate, b.p. 173° at 680 mm.; corresp. benzoate, b.p. 210° at 683.3 mm.), and also (42% yield (314)) 2,2,2-trichloroethanol-1 (3:5775).]

With various other cases. [For behavior of \tilde{C} with the RMgX cpds. from β -phenylethyl bromide, γ -phenylpropyl bromide, and δ -phenylbutyl bromide where the reaction appears to be mainly reduction of \tilde{C} see (317).]

BEHAVIOR WITH HCN (OR ITS SALTS)

Behavior with HCN. [\bar{C} with strong aq. HCN refluxed several days (318) or chloral hydrate (3:1270) with aq. 10-12% HCN (319) (320) or with aq. 15% HCN in s.t. at 100° for 4 hrs. (321) cf. (322) gives (71% yield (321)) β,β,β -trichloro- α -hydroxypropionitrile = trichlorolactonitrile = chloral cyanohydrin [Beil. III-288, III₁-(111), III₂-(210)], m.p. 60-61° (318), 58-61° (321) (corresp. benzoate, m.p. 40-41° (323)); this prod. upon partial hydrolysis in AcOH/H₂SO₄ gives (324) trichlorolactamide [Beil. III-288, III₁-(111), III₂-(210)], m.p. 95-96° (324), or on complete hydrolysis with conc. HCl (321) (318) (320) gives trichlorolactic acid [Beil. III-286, III₁-(111), III₂-(210)], very sol. aq., but cryst. from ether, m.p. 118-119° (321).]

Behavior with KCN. [C with MeOH/KCN gives within 1 min. (84% yield (131)) methyl dichloroacetate (3:5655); C with EtOH/KCN similarly gives (88% yield (131)) ethyl dichloroacetate (3:5850); C with n-propyl alc./KCN similarly gives (70% yield (131)) n-propyl dichloroacetate (3:6000); for extensive discussion of this reaction see (131) (325) (329).]

[For discussion of behavior of chloral hydrate (3:1270) with KCN in C₆H₆ see (326): note that chloral hydrate (3:1270) with NaCN + CaCO₃ as directed (328) is an important method of prepn. (88-92% yield) of dichloroacetic acid (3:6208) q.v.: note also that chloral hydrate (3:1270) + NH₄OH + KCN in ether as directed (329) gives (65-78% yield) dichloroacetamide (see under the acid (3:6208).]

BEHAVIOR WITH DIAZOMETHANE

[Č (309) (330) (331) or chloral hydrate (3:1270) (332) gives (yields: 64% (330), 48% (309), 47.5% (332)) 3,3,3-trichloro-1,2-epoxypropane (3:5760) q.v.]

BEHAVIOR WITH AMINES

With primary aromatic amines. With aniline. [\bar{C} with aniline (333) (334), or chloral hydrate (3:1270) with aniline in aq. (334), gives 1,1,1-trichloro-2,2-dianilinoethane (θ,θ,β -trichloroethylidene)di-aniline [Beil. XII-187, XII₁-(168)], pr. from ether/alc., m.p. 107-108° (335), 107.5° (334), 100-101° (333). — Note that the addition product to be expected from 1 mole \bar{C} with 1 mole aniline has not itself been isolated (except as a molecular compound with chloral hydrate (336)) since it appears to react immediately with a second mole of aniline to give the above-indicated prod.]

With aniline + hydroxylamine. [Chloral hydrate (3:1270) (1 mole) with aniline (1 mole) + NH₂OH.HCl (3 moles) + HCl + Na₂SO₄ in aq. soln. as directed gives (80-91%) yield (337) cf. (338) (339) isonitrosoacetanilide [Beil. XII₁-(275)], m p. 175° dec. (337) (338) (339). — Note that this product with conc. H₂SO₄ (337) (340) gives (71-78%) yield (337)) indigo; for extension of the method to use of other amines (and ultimately substituted indigos) see (338) (341) (345).]

With other primary aromatic amines. The condensation of \bar{C} or of chloral hydrate (3:1270) with many other primary aromatic amines and diamines has been studied but cannot be detailed here [for extensive review and discussion see (336) (334) (335) (342) (343) (344) (403)].

With secondary aromatic amines. With N-alkylanilines. [Chloral hydrate (3:1270) with N-methylaniline on warming gives (346) trichloromethyl-(p-methylaminophenyl)-carbinol [Beil. XIII-628], m.p. 112° dec.; sımılarly, chloral hydrate (3:1270) with N-ethylaniline on warming gives (346) trichloromethyl-(p-ethylaminophenyl)-carbinol [Beil. XIII-628], m.p. 98°.]

With N-alkyl-o-toluidines. [Chloral hydrate (3:1270) with N-methyl-o-toluidine + ZnCl₂ gives (347) trichloromethyl-(4-methylamino-3-methylphenyl)-carbinol, m.p. 104-105°; similarly, chloral hydrate (3:1270) with N-ethyl-o-toluidine + ZnCl₂ gives (349) trichloromethyl-(4-ethylamino-3-methylphenyl)-carbinol, m.p. 107° (for studies of nitration (348) and bromination (349) of these two products see indic. refs.).]

With tertiary aromatic amines. With N,N-dralkylanthnes. [C with N,N-dimethylaniline in phenol at room temp. (350) or chloral hydrate with N,N-dimethylaniline + ZnCl₂ on stdg. (351) (352) gives trichloromethyl-(p-dimethylaminophenyl)-carbinol [Beil. XIII-628], m.p. 111° dec. (352) (corresp. carbinyl acetate, m.p. 84-85° (352)) (for study of nitration of this prod. see (348)).]

BEHAVIOR WITH ARYLHYDRAZINES

With phenylhydrazine. [Č with phenylhydrazine or chloral hydrate (3:1270) with aq. phenylhydrazine salts reacts (353) vigorously, but the products formed have not been unambiguously characterized (see also below).]

With p-nitrophenylhydrazine. [Chloral hydrate (3:1270) (large excess) with p-nitrophenylhydrazine in AcOH at 100° for 10 min. undergoes a series of reactions resulting (354) in a chlorine-free prod., m.p. 228°, regarded (354) as 1-(p-nitrophenyl)-3,5-dihydroxy-pyrazolone-4-(p-nitrophenylhydrazone).]

With 2,4-dinitrophenylhydrazine. [Chloral hydrate (3:1270) with 2,4-dinitrophenylhydrazine gives according to conditions either or both (355) glyoxylic acid p-nitrophenyl-

hydrazone, dihydrate from aq., m.p. 191° (355); anhydrous, m.p. 194-195° (355), 190° (356), or chloroglyoxal bis-(2,4-dinitrophenylhydrazone), m.p. 278° (355).]

With various halogenated hydrazines. Owing to the violence with which the product initially formed decomposes, the behavior of \tilde{C} with phenylhydrazine (see also above) has been little studied. With halogenated phenylhydrazines the decomposition is more moderate and has been extensively examined. The nature of the products has been found to depend mainly upon the solvent medium: thus in alcohols the principal product is the corresponding substituted phenylhydrazone of the appropriate alkyl glyoxylate; in water or AcOH, however, loss of both H_2O and HCl occurs leading to formation of the corresponding α,α -dichloro- β -arylazoethylenes.

[Chloral hydrate (1 mole) (3:1270) with 2,4-dichlorophenylhydrazine in ethyl alc. at 60° gives (100% yield (357)) ethyl glyoxylate 2,4-dichlorophenylhydrazone, yellow pr., m.p. 121.5°; note that other alcs. (357) give corresp. esters. — However, chloral hydrate (1 mole) (3:1270) with 2,4-dichlorophenylhydrazine (1 mole) in AcOH at 80° (or in presence of NaOAc at 60°) gives (357) α,α -dichloro- β -(2,4-dichlorobenzeneazo)ethylene, red pr. from alc., m.p. 84.5°.]

[For completely analogous behavior of chloral hydrate (3:1270) with other halogenated phenylhydrazines, such as 2,5-dichlorophenylhydrazine (358), 2,4,5-trichlorophenylhydrazine (358), 2,4,6-tribromophenylhydrazine (359), 3-bromo-4-methylphenylhydrazine (360), or 3,5-dibromo-4-methylphenylhydrazine (360), see indic. refs. — Note that a generally analogous behavior toward halogenated arylhydrazines is shown by butyrchloral (3:5910) q.v. and by tribromoacetaldehyde (bromal).]

BEHAVIOR WITH AMIDES

Č with compounds of the amide type readily undergoes an addition reaction leading to products of the general form CCl₃.CH(OH).NH.CO.R.

With Aliphatic Monamides

With formamide. [\bar{C} (1 mole) with formamide (1 mole) on stdg. gives (361) (362) an addition prod., chloralformamide, CCl₃.CH(OH).NH.CHO [Beil. II-27, II₁-(21), II₂-(37)], m.p. 124–126° (363), 118° (362), 115–116° (361); note that this product has in the literature often been confused with the isomeric β,β,β -trichloroethyl carbamate, CCl₃-CH₂O.CO.NH₂ ("Voluntal") [see also under β,β,β -trichloroethyl alcohol (3:5775)]. Note also that chloralformamide with aq. NaOH + Ac₂O (362) or with aq. NaOH + BzCl (364) cf. (362) undergoes bimolecular condensation with loss of H₂O giving anhydrochloralformamide [CCl₃.CH(NH.CHO)]₂O, m.p. 194.5–195° (362), 193° (364).]

With acetamide. [C (1 mole) with acetamide (1 mole) (72) (172), or chloral hydrate (3:1270) (1 mole) with acetamide (1 mole), or chloralammonia with AcCl or Ac₂O (128) gives chloralacetamide [Beil. II-179, II₁-(81)], m.p. 158-159° (362), 158° (172), 156°-157° (72), 156° (128); this prod. with aq. NaOH + Ac₂O undergoes bimolecular loss of aq. yielding (362) cf. (369) anhydrochloralacetamide, [CCl₃.CH(NH.CO.CH₃)]₂O, m.p. 212-213° (362), 207° (364). — For study of reduction of chloralacetamide see (365) (366).]

With higher monoamides. [For analogous condensation of \tilde{C} with propionamide, isobutyramide, n-valeramide, n-caproamide, n-caprylamide, and phenylacetamide together with study of reduction of the several products see (367) cf. (369).]

With Aromatic Monoamides

With benzamide. [C (1 mole) with benzamide (1 mole) (172) (362) cf. (369), or chloral hydrate (3:1270) with benzonitrile + dry HCl (368) gives chloralbenzamide [Beil. IX-

209, IX₁-(101)], m.p. 150-151° (72), 150° (362), 146° (172) (368); this product with aq. NaOH + BzCl or Ac_2O gives (362) by dehydrative bimolecular condensation anhydrochloralbenzamide, known (362) in two forms, higher-melting form, m.p. 199-200°, and lower-melting form, m.p. 137-138°. — For study of reduction of chloralbenzamide see (366) cf. (369).]

With toluamides. [For condensation of \tilde{C} with o-, m-, and p-toluamides see (370); for the behavior of the products with PCl₅ see (371).]

With salicylamide. [C with salicylamide on warming directly (372) or in CHCl₃ (373) gives chloralsalicylamide, sintering at 117° and melting about 10° higher (372); for the corresp. anhydro compound (cf. above), m.p. 174–175°, see (369); for studies of chloral-salicylamide on chlorination (374), bromination (375), or nitration (375) see indic. refs.]

With amides of various substituted salicylic acids. [For behavior of \bar{C} with the amides of 3-chlorosalicylic acid (3:4745), 5-chlorosalicylic acid (3:4705), and 3,5-dichlorosalicylic acid (3:4935) see (374) (376) (377); for behavior of \bar{C} with amides of various nitrosalicylic acids (378) or various aminosalicylic acids (379) see indic. refs.]

With o-aminobenzamide (anthranilamide). [For behavior of \tilde{C} with anthranilamide and its relatives see (380).]

With Amides of Dibasic Acids

Note that two series of products are formed.

With urea. [Chloral hydrate (3:1270) (1 mole) with urea (2 moles) in aq. soln. on stdg. 3 days at room temp. gives (66% yield (381)) (382) cf. (172) chloralurea, N-(β , β , β -trichloro- α -hydroxyethyl)urea [Beil. III-59, III₁-(27)], cryst. from MeOH/C₆H₆ (381) or EtOH/C₆H₆ 1:3 (382), m.p. 150° dec. (381) (382). — However, chloral hydrate (3:1270) (2 moles) with urea (1 mole) in aq. HCl at room temp. for 3 days gives (71% yield (381)) (382) cf. (383) dichloralurea [Beil. III-60, III₁-(27), III₂-(49)], cryst. from aq. alc., m.p. 196° (381), 194° dec. (382), 190° (172).]

With thiourea. [For behavior of C with thiourea see (383).]

With various substituted ureas. With monosubstituted ureas. [Chloral hydrate (3:1270) (2 moles) with N-methylurea (1 mole) in aq. soln. at room temp. gives (384) N-methyl-N'-(β,β,β -trichloro- α -hydroxyethyl) urea, m.p. 140° dec. (384). — Chloral hydrate (3:1270) with N-ethylurea behaves in analogous fashion (384). — Chloral hydrate (3:1270) (2)½ moles) with N-phenylurea in aq. HCl gives (84% yield (382)) N-phenyl-N'-(β,β,β -trichloro- α -hydroxyethyl)urea, m.p. 142° dec. (382). — For corresp. behavior of chloral hydrate (3:1270) with N-o-tolylurea, N-p-tolylurea, N-m-nitrophenylurea, and N-p-nitrophenylurea see (385).]

With disubstituted ureas. [Chloral hydrate (3:1270) with N,N-dimethylurea gives (384) cf. (386) N,N-dimethyl-N'-(β,β,β -trichloro- α -hydroxyethyl)urea, cryst. from aq. as monohydrate, m.p. 74° dec. (384) (386), which becomes anhydrous on stdg., cryst. from alc., m.p. 157° dec. (384), 156° (386). — For analogous behavior of \bar{C} with N,N-diethylurea giving prod., m.p. 146° dec. (384), 142° (386), see indic. refs. — \bar{C} with N,N-diphenylurea gives analogous prod., m.p. 170° dec. (384).]

With amides of other dibasic acids. [For generally analogous behavior of C with oxamide (384), malonamide (384) (369), succinamide (369), and their relatives see indic. refs.]

With Urethanes

With ethyl carbamate. [\bar{C} with ethyl carbamate ("urethane") in conc. HCl gives (387) (388) ethyl $N-(\beta,\beta,\beta-\text{trichloro-}\alpha-\text{hydroxyethyl})$ carbamate ("chloralurethane") [Beil. III-24, III₁-(12), III₂-(22)], m.p. 103° (362) (388). — This product on htg. alone or

in aq. at 100° regenerates (388) chloral and ethyl carbamate. — With AcCl under reflux it gives (80% yield (387)) the corresp. acetate, m.p. 47-49°, b.p. 165° at 15 mm. (387). — With aq. NaOH + Ac₂O (362) (387) or with aq. KOH + BzCl (364) chloralurethane undergoes dehydrative bimolecular condensation yielding anhydro-chloralurethane [Beil. III₁-12], which exists in both high-melting (161-162°) and low-melting (149-150°) forms (362).]

With other alkyl carbamates. [For generally analogous behavior of \bar{C} with methyl carbamate (362), n-propyl carbamate (389), isobutyl carbamate (389), isoamyl carbamate (362), and menthyl carbamate (362) see indic. refs.]

- Preliminary tests for Č: Owing to the length of the text of this compound, a brief summary of the tests most significant as preliminary indications is given here; for details refer back as indicated and also see chloral hydrate (3:1270).
- C reduces NH₃/AgNO₃ and Fehling's soln. but only on warming (see above under oxidn. of C̄). C̄ gives fuchsin-aldehyde test with Schiff's reagent (but chloral hydrate (3:1270) does not). C̄ with conc. H₂SO₄ readily polymerizes (see above under polymerization of C̄). C̄ with aq. or alc. alkali on warming undergoes hydrolytic cleavage to CHCl₃ (3:5050) + alkali formate (see above under behavior of C̄ with alkalies); therefore, C̄ with alc. alkali + annline gives characteristic odor of phenyl isocyanide.
- Trichloroacetaldioxime: m.p. 56° (135). [See above under behavior of $\bar{\mathbf{C}}$ with hydroxylamine.]
- Trichloroacetaldehyde phenylhydrazone: unreported. [See above under behavior of C with arylhydrazines.]
- Trichloroacetaldehyde p-nitrophenylhydrazone: unreported. [See above under behavior of C with arylhydrazines.]
- —— Trichloroacetaldehyde 2,4-dinitrophenylhydrazone: a prod. of m.p. 131° has been claimed (390) but could not be confirmed (391). [See also above under behavior of C with arythydrazines.]
- Trichloroacetaldehyde semicarbazone: unreported. [Note that chloral hydrate (3:1270) with semicarbazide in aq. (392) (394) cf. (393) or chloral ethylalcoholate (3:0860) with semicarbazide in alc. (392) gives an addn. prod., m.p. 90°, which on boilg. with aq. yields (392) glyoxylic acid semicarbazone [Beil. III-600, III₁-(209) III₂-(389)], m.p. 235-236° (392), 235-238° (393), 207° (395), 206-208° dec. (396), 202-203° (397), 202° dec. (394) (note that these results may represent two stereoisomeric forms (397)).]
- 3:5210 (1) Perkin, J. Chem. Soc. 51, 808-819 (1887). (2) Lecat, Rec. trav chim. 45, 623 (1926). (3) Passavant, J. Chem. Soc. 39, 53-57 (1881). (4) Goslawski, Marchlewski, Bull. intern. acad. Polonaise, 1931A, 383-391; Cent. 1932, I 1491; [C.A. 27, 231 (1933)]. (5) Jefremov, J. Russ. Phys.-Chem. Soc. 56, 361 (1918); Cent. 1923, III 826; not in C.A. (6) Thorpe, J. Chem. Soc., 37, 191-192 (1880). (7) Friend, Hargreaves, Phil. Mag (7) 35, 626 (1944). (8) Johns, Hixon, J. Am. Chem. Soc. 56, 1333-1336 (1934). (9) van Rossem, Z. physik. Chem. 62, 681-712 (1908). (10) Brühl, Ann. 203, 11-12 (1880).
- (11) Cheng, Z. physik. Chem. B-26, 295 (1934). (12) Stauff, Schumacher, Z. physik. Chem. B-48, 1 4-175 (1941). (13) Klug, Schumacher, Z. physik. Chem. B-47, 67-92 (1940). (14) Coomber, Partington, J. Chem. Soc. 1938, 1450 (15) Jefremov, Ann. inst. anal. physico-chim. Leningrad, 4, 118-159 (1 28); Cent. 1929, I 729-730; not in C.A. (16) von Auwers, Ber. 62, 1319 (1929). (17) Breuer, J. Am. Chem. Soc. 57, 2236-2237 (1935). (18) Böeseken, Schimmel, Rec. trav. chim. 32, 112-127 (1913). (19) Kurnakow, Efremov, Z. physik. Chem. 85, 401-413 (1913). (20) Excelsior Feuerlöschgerate, A. G., Ger. 554,521, Sept. 9, 1932; Cent. 1932, II 1335; C.A. 26, 6083 (1932).
- (21) Lecat, Ann. soc. sci. Bruxelles 45, I 175 (1926). (22) Liebig, Ann. 1, 189-198 (1832). (23) Brochet, Bull. soc. chim. (3) 17, 228-230 (1897); Ann. chim. (7) 10, 332-335 (1897). (24)

Trillat, Bull. soc. chim. (3) 17, 230-234 (1897). (25) Kraemer, Ber. 3, 257-262 (1870). (26) Altschul, Meyer, Ber. 26, 2756-2759 (1893). (27) Besson, Ger. 133,021, July 31, 1902; Cent. 1902 II 553. (28) Ohse (to Chem. Fabrik von Heyden), Ger. 734,723, March 25, 1943; C.A. 38, (29) Page, Ann. 225, 209-211 (1884). (30) Pinner, Ber. 4, 256-257 (1871). 3671 (1944).

(31) Pinner, Ann. 179, 24-29 (1875). (32) Fuchs, Katscher, Ber. 57, 1258 (1924). (33) Städeler, Ann. 61, 101-121 (1847). (34) Goldschmidt, Schüssler, Ber. 58, 569-570 (1925). (35) Consortium für Elektrochem. Ind., French 706,320, June 23, 1931, Cent. 1931, II 1489; [C.A. 28, 1302 (1932)]. (36) Ingold, J. Chem. Soc. 125, 1536-1537 (1924). (37) Mason, J. Chem. Soc. 97, 866-867 (1910). (38) Moruen, Dufraisse, Berchet, Bull. soc. chim. (4) 43, 942-957 (1928). (39) Byasson, Compt. rend. 87, 26 (1878); Bull. soc. chim. (2) 32, 304-305 (1879). (40) Paterno, Ann. 150, 256 (1869).

(41) Reichert, Bailey, Nieuwland, J. Am. Chem. Soc. 45, 1556-1557 (1923). (42) Hirwe, J. Univ. Bombay, 6, Pt. II, 182-198 (1937); Cent. 1938, I 4031. (43) Busch, Stöve, Ber. 49, 1068 (1916). (44) Kelber, Ber. 50, 308 (1917). (45) Self, Pharm. J. (4) 25, 4-7 (1907); Cent. 1907, II 1019. (46) Vogt, Arch. exptl. Path. Pharmakol. 178, 628-638 (1935); Cent. 1936, I 801; [C.A. 29, 6945 (1935)]. (47) Griebel, Weiss, Z. Untersuch. Lebensm. 56, 163 (1928). (48) Personne, Ann. 157, 113-115 (1871). (49) Jona, Giorn. farm. chim. 61, 57-59 (1912); Cent. 1912, I 1148; C.A. 6, 1337-1338 (1912). (50) Meillere, J. pharm. chim. (8) 11, 145-147 (1930); Cent. 1930, I 3221; C.A. 24, 4586 (1930).

(51) Cotton, Bull. soc. chim. (2) 42, 622-625 (1884). (52) Deodhar, J. Indian Chem. Soc. 11, 83-86 (1934). (53) Sandonnini, Borghello, Att. accad. Lincei (6) 21, 30-35 (1935); Cent. 1935, II 1860; C.A. 29, 4679 (1935). (54) Meerwein, Schmidt, Ann. 444, 234 (1925). (55) Chalmers, Org. Syntheses, Coll. Vol. 1 (1st ed.) 598-601 (1943); 15, 80-84 (1935). (56) Boeseken, Tellegen, Plusje, Rec. trav. chim. 57, 74-75 (1938). (57) Callsen (to Winthrop-Chem. Co.), U.S. 1,725,054, Aug. 20, 1929; [Cent. 1936, I 434]; C.A. 23, 4709 (1929): Ger. 437,160, Nov. 18, 1926; Cent. 1927, I 802; not in C.A.: Brit. 286,797, April 5, 1928; Cent. 1928, I 2750; C.A. 23, 395 (1929). (58) Nagai, Biochem. Z. 152, 272 (1924); Cent. 1925, I 637; [C.A. 19, 2807 (1925)]. (59) Meerwein (to Bayer and Co.), U.S. 1,572,742, Feb. 9, 1926; Cent. 1926 I 3627, [C.A. 20, 1243 (1926)]; Brit. 235,584, June 27, 1926; [Cent. 1926, II 1097]; C.A. 20, 917 (1926). (60) Dworzak, Monatsh. **47.** 12–13 (1926).

(61) Callsen (to I.G.), Ger. 489,281, Jan. 15, 1930; Cent 1930, I 3104; [C.A. 24, 2140 (1930)]: Swiss 126,293, July 16, 1928, Cent. 1929, I 1741; C.A. 23, 852 (1929). (62) Nord, Ger. 434,726, Oct. 5, 1926; Cent. 1926, II 2845; not in C.A. (63) Callsen (to I.G.), Ger. 565,157, Nov. 26, 1932; Cent. 1933, I 1514; C.A. 27, 992 (1933): Brit. 384,156, Dec. 22, 1932; Cent. 1933, I 1351; [C.A. 27, 4240 (1933)]. (64) I.G., Brit. 370,490, May 5, 1932; Cent. 1932, II 3303-3304; C.A. 27. 2961 (1933). (65) Garzarolli-Thurnlackh, Ann. 210, 64-68 (1881). (66) Delacre, Bull. soc. chim. (2) 48, 784-788 (1887). (67) Meerwein, Hinz, Majert, Sonke, J. prakt. Chem. (2) 147, 236, 243 (1936). (68) Willstätter, Duisberg, Ber. 56, 2284-2285 (1923). (69) Lintner, Lüers, Z. physiol. Chem. 88, 122-123 (1913). (70) Judson, Ber. 3, 782-784 (1870).

(71) Kolbe, Ann. 54, 183-185 (1845). (72) Wallach, Ber. 5, 254-256 (1872). (73) Khotinskii, Aleksandrova, Proc. Kharkov State Univ. 4, 59-61 (1936); C.A. 31, 6615 (1937). (74) Plump (to Pennsylvania Salt Mfg. Co.) U.S. 2,370,577, Feb. 27, 1945; C.A. 39, 4085 (1945). (75) Moureu, Dufraisse, J. Soc. Chem. Ind. 47, 819-828, 849-854 (1928). (76) Clermont, Ann. 161, 128 (1872); Compt. rend. 73, 113 (1871). (77) Clermont, Ann. 166, 64 (1873); Compt. rend. 74, 1492 (1872). (78) Seubert, Ber. 18, 3336-3339 (1885). (79) Ssuknewitsch, Tschilingarjan, Ber. 68, 1215 (1935). (80) Bhatnagar, Mathur, Kapur, Phil. Mag. (7) 8, 466-467 (1929).

(81) Städeler, Ann. 106, 253 (1858). (82) Karaoglanov, Z. anal. Chem 121, 206-207 (1941). (83) Cotton, Bull. soc. chim. (2) 43, 420-423 (1885). (84) Vanino, Z. anal. Chem. 79, 369-371 (1930). (85) Hartwagner, Z. anal. Chem. 52, 19-20 (1913). (86) Wieland, Ber. 45, 2610 (1912). (87) Amato, Jahresber. 1875, 473. (88) Alexander, Schumacher, Z. physik. Chem. B-44, 313-(89) Verhoek, Hinshelwood, Proc. Roy. Soc. London, A-146, 327-333, 334-344 326 (1939). (1934). (90) Verhoek, Trans. Faraday Soc. 31, 1521-1524 (1935).

(91) Combes, Ann. chim. (6) 12, 267-271 (1887). (92) Böeseken, Rec. trav. chim. 29, 95-96, 104-108 (1910). (93) Mouneyrat, Bull. soc. chim. (3) 19, 260-261 (1898). (94) Böeseken, Schimmel, Rec. trav. chim. 32, 128-133 (1913). (95) Boeseken, Schimmel, Rec. trav. chim. 32. 112-127 (1913). (96) Gauthier, Bull. soc. chim. (2) 45, 86-88 (1886). (97) Alexander, Schumacher, Z. physik. Chem. B-44, 57-68 (1939). [98] Mouneyrat, Bull. soc. chim. (3) 17, 794-797 (1897). (99) Oglialoro, Ber. 7, 1461-1462 (1874). (100) Vorländer, Ann. 341, 21-22 (1905).

(101) Gaathaug, Norwegian 54,575, Nov. 5, 1934; Cent. 1935, I 1617; not in C.A. (102) Böeseken, Chem. Weekblad 7, 121-132 (1910); Cent. 1910, I 1002; C.A. 5, 1419 (1911). (103) Grabowski, Ber. 8, 1433-1437 (1875). (104) Kekulé, Ann. 105, 293-295 (1858). (105) Otto, Ann. 239, 262-263 (1887). (106) Wallach, Ann. 193, 4, 8, 11-19 (1878). (107) Fuchs, Katscher, Ber. 62, 2381-2386 (1929). (108) Chattaway, Kellett, J. Chem. Soc. 1928, 2709-2714. (109) Mallett, Am. Chem. J. 19, 809-810 (1897). (110) Erdmann, Ger. 139,392, March 4, 1903: Cent. 1903, I 743.

(111) Helferich, Besler, Ber. 57, 1279-1280 (1924). (112) Hibbert, Gillespie, Montonna. J. Am. Chem. Soc. 50, 1953-1955 (1928). (113) Mulder, Rec. trav. chim. 7, 322-323 (1888). (114) Belohoubek, Cent. 1898, I 558. (115) Rosenthaler, Reis, Cent. 1907, II 891. (116) Reicher, Rec. trav. chim. 4, 347-350 (1885). (117) Bottger, Kotz, J. prakt. Chem. (2) 65, 481-499 (1902). (118) Werner, J. Chem. Soc. 85, 1376-1381 (1904). (119) Enklaar, Rec. trav. chim. 23, 419-438 (1904). (120) Enklaar, Rec. trav. chim. 24, 419-443 (1905).

(121) Enklaar, Rec. trav. chim. 25, 297-310 (1906). (122) Enklaar, Rec. trav. chim. 29, 173-184 (1910). (123) Benrath, Ann. 382, 225 (1911). (124) Kotz, Cent. 1909, II, 2136. (125) Kekulé, Ann. 119, 187-189 (1861). (126) Arenson, Roller, Brown, J. Phys. Chem. 36, 623-625 (1926). (127) Truchet, Compt. rend. 202, 1997-1998 (1936). (128) Schiff, Ber. 10, 166-168 (129) Aschan, Ber. 48, 880-882, 889-891 (1915). (130) Délepine, Bull. soc. chim. (3)

19, 171-173 (1898).

(131) Chattaway, Irving, J. Chem. Soc. 1929, 1038-1048. (132) Schiff, Gazz. chim. ital. 21, 490-497 (1891). (133) Béhal, Choay, Ann. chim. (6) 26, 5-12, 59-60 (1892). (134) Meyer, Ann. 264, 118-121 (1891). (135) Palazzo, Egidi, Gazz. chim. ital. 43, I 57-68 (1913). (136) Hantzsch, Ber. 25, 705-712 (1892). (137) Ponzio, Baldracco, Gazz. chim. ital. 60, 415-429 (1930). (138) Houben, Kaufmann, Ber. 46, 2824-2825 (1913). (139) Hantzsch, Ber. 25, 701-705 (1892).

(140) Knopfer, Monatsh. 32, 768-769 (1911).

(141) Stollé, Helwerth, J. prakt. Chem. (2) 88, 315-318 (1913). (142) Knopfer, Monatch. 37, 357, 364 (1916). (143) Knopfer, Monatsh. 34, 769-776 (1913). (144) Giolitti, Gazz. chim. ital. 34, I, 247-253 (1904). (145) Paterno, Ann. 151, 116-121 (1869). (146) Paterno, Gazz. chim. tal. 1, 590-592 (1871). (147) Paterno, Oghaloro, Ber. 7, 81 (1874). (148) Balfe, Webber, J. Chem. Soc. 1942, 719-720. (149) Kerp, Bauer, Cent. 1907, II 270. (150) Rathke, Ann. 161. 154-166 (1872).

(151) Backer, Rec. trav. chim. 48, 571-574 (1929). (152) Bayer, Villiger, Ber. 33, 2481-2484 (1900). (153) Frankforter, Kritchevsky, J. Am. Chem. Soc. 36, 1511-1529 (1914). (154) Dinesmann, Compt. rend. 141, 201 (1905). (155) Chattaway, Muir, J. Chem. Soc. 1934, 701-703. (156) Florence, Bull. soc. chim. (4) 49, 926-927 (1931). (157) Baeyer, Ber. 5, 1098-1099 (1872). (158) van Laer, Bull. soc. chim. 28, 346-350 (1919). (159) Iozitsch, J. Russ. Phys.-Chem. Soc. 34, 97 (1902). (160) Howard, Stephens, J. Am. Chem. Soc. 60, 228 (1938).

(161) Fischer, Ber. 7, 1191 (1874). (162) Harris, Frankforter, J. Am. Chem. Soc. 48, 3144-3147 (1926). (163) Brand, Busse-Sundermann, Ber. 75, 1819-1829 (1942). (164) Frankforter, Kritchevsky, J. Am. Chem. Soc. 37, 385-392 (1915). (165) Howard, J. Am. Chem. Soc. 57, 2317-2318 (1935). (166) Hebert, Bull. soc. chim. (4) 27, 49, 53-54 (1920). (167) Brand, Krucke-Amelung, Ber. 72, 1031-1032 (1939). (168) Zeidler, Ber. 7, 1180-1181 (1874). (169) Grabowsky, Herold, Z. physik. Chem. B-28, 290-302 (1935). (170) Post, J. Org. Chem. 6, 830-836 (1941).

(171) Kuntze, Arch. Pharm. 246, 97-110 (1908). (172) Jacobsen, Ann. 157, 243-248 (1871). (173) Houben, Fischer, Ber. 64, 243 (1931). (174) Martius, Mendelssohn-Bartholdy, Ber. 3, 443-445 (1870). (175) Sprongerts (to Kalle and Co.), Ger. 430,732, June 19, 1926; Cent. 1926, II 1160-1161; not in C.A. (176) Magnanni, Gazz. chim. ital. 16, 332 (1886). (177) Meerwein, Bersin, Burneleit, Ber. 62, 1007 (1929). (178) Gabutti, Gazz. chim. ital. 31, I 86-89 (1901). (179) Vitoria, Bull. acad. roy. Belg. 1904, 1087-1123 (1904); Cent. 1905, I 345. (180) Fourneau. Florence, Bull. soc. chim. (4) 47, 350-356 (1930).

(181) Perganni, Gazz. chim. ital 26, II 470-472 (1896). (182) Whitmore, Homeyer. J. Am. Chem. Soc. 55, 4195 (1933). (183) Hoffmann-LaRoche and Co., Ger. 151,188, May 11, 1904; Cent. 1904, I 1506. (184) Hibbert, Morazain, Paquet, Can. J. Research 2, 131-143 (1930); [Cent. 1930, I 3770]; [C.A. 24, 2109 (1930)]. (185) de Forcrand, Bull. soc. chim. (3) 2, 256 (1889). (186) Meldrum, Vad, J. Indian Chem. Soc. 13, 118-122 (1936). (187) White, Hixon, J. Am. Chem. Soc. 55, 2438-2444 (1933). (188) Coles, Goodhue, Hixon, J. Am. Chem. Soc. 51, 519-524 (1929). (189) Goodhue, White, Hixon, J. Am. Chem. Soc. 52, 3191-3195 (1930). (190) Hanriot, Kling. Ann. chim. (9) 12, 129-150 (1919).

(191) Hanriot, Ann. chim. (8) 18, 466-502 (1909). (192) Hanriot, Bull. soc. chim. (4) 5, 819-826 (1909). (193) Genot, J. pharm. chim. Belg. 8, 407-410 (1926); Cent. 1926, II 803; C.A. 21, 3706 (1927). (194) Cheramy, J. pharm. chim. (9) 1, 233-234 (1940); Cent. 1941, I 2837; cf. C.A. 34, 2878 (1940). (195) Lespagnol, Paris, Merville, Bull. soc. chim. biol. 24, 117-119 (1942); Cent. 1943, II 1742; C.A. 38, 5863 (1944). (196) Truffert, Bull. soc. chim. biol. 24, 195-199 (1942); Cent. 1944, I 303; C.A. 39, 1820-1821 (1945). (197) Haakh, Smola, Austrian 141,159, March 25, 1935; Cent. 1935, II 439; C.A. 29, 4021 (1935). (198) Meldrum, Lonkar, J. Univ. Bombay 6, Pt. II, 116-119 (1937); Cent. 1938, I 4034; C.A. 32, 3760 (1938). (199) Pauly, Schanz, Ber. 56, 981-985 (1923). (200) ter Meer, Ber. 7, 1201-1202 (1874).

(201) Elbs, J. prakt. Chem. (2) 47, 59-79 (1893). (202) Harden, Reid, J. Am. Chem. Soc. 54, 4333-4334 (1932). (203) Mazzara, Gazz. chim. ital. 13, 271-272 (1883). (204) Spengler, Pfanenstiehl (to Winthrop Chem. Co.), U.S. 1,819,132, Aug. 18, 1931; Cent. 1932, II 1381; C.A. 25, 5678 (1931). (205) Pauly, Strassberger, Ber. 62, 2279 (1929). (206) Mauthner, J. prakt. Chem. (2) 119, 128 (1925). (207) Chattaway, Morris, J. Chem. Soc. 1927, 2013-2017. (208) Moore, Iowa State Coll. J. Sci. 16, 99-102 (1941); C.A. 36, 4396 (1942). (209) Fritsch, Feldmann, Ann. 366, 77-79 (1899). (210) Feuerstein, Ber. 34, 415 (1901).

(211) Erdtman, Ann. 505, 199 Note (1933). (212) Kaufmann, Burr, Ber. 40, 2359 (1907). (213) Pinner, Ber. 31, 1926–1938 (1898); cf. Ber. 33, 1432–1433 (1900). (214) Staudinger, Kon, Ann. 384, 87 (1911). (215) Schering-Kahlbaum, Brit. 459,462, Feb. 4, 1937; Cent. 1937, I 3518; C.A. 31, 3942 (1937): Swiss 187,423, Feb. 1, 1937; Cent. 1937, II 626; not in C.A. (216) Garsarolli-Thurnlackh, Monatsh. 12, 556–565 (1891). (217) von Auwers, Schmidt, Ber. 46, 487–494 (1913). (218) McKenzie, Plenderleith, J. Chem. Soc. 123, 1092–1093 (1923). (219) Kurien, Pandya, Surange, J. Indian Chem. Soc. 11, 826 (1934). (220) von Auwers, Wissebach, Ber. 56, 735 (1923).

(221) Nelson, J. Am. Chem. Soc. 52, 2929-2933 (1930). (222) Fittig, Miller, Ann. 255, 43-51 (1889). (223) Wislicenus, Nassauer, Ann. 285, 7-10 (1895). (224) Wallach, Ann. 193, 35-47 (1878). (225) Wallach, Heymer, Ber. 9, 545-547 (1876). (226) Nencki, J. prakt. Chem. (2) 17, 239-240 (1878). (227) Boescken, Blok, Cent. 1927, I 2987; not in C.A. (228) Meldrum, Bhatt, J. Univ. Bombay, 3, 149-152 (1934); Cent. 1935, I 3128; C.A. 29, 4734 (1935). (229) Shah, Alimchandani, J. Univ. Bombay 5, Pt. 2, 132-136 (1936); Cent. 1938, I 57; C.A. 31, 3002 (1937). (230) Yorston, Rec. trav. chim. 46, 711-714 (1927).

(231) Shah, Alimchandani, J. Indian Chem. Soc. 11, 545-550 (1934). (232) Bistrzycki, Brenken, Helv. Chim. Acta 3, 455 (1920). (233) Calvet, Mejuto, J. Chem. Soc. 1936, 554-556; Anales soc. españ. fis. quím. 34, 641-649 (1936); Cent. 1938, I 586; C.A. 31, 5756 (1937). (234) Shah, Alimchandani, J. Indian Chem. Soc. 13, 475-477 (1936). (235) Hurry, Meldrum, J. Indian Chem. Soc. 11, 535-538 (1934). (236) Alimchandani, Meldrum, J. Chem. Soc. 11, 201-209 (1921). (237) Shah, Alimchandani, J. Indian Chem. Soc. 11, 467-469 (1934). (238) Shah, Alimchandani, J. Indian Chem. Soc. 11, 467-469 (1934). (238) Indian Chem. Soc. 2, 1-9 (1925). (240) Schleussner, Voswinckel, Ann. 422, 111-133 (1921).

(241) Meldrum, Chandani, J. Indian Chem. Soc. 6, 253-258 (1929). (242) Brass, Fiedler, Ber. 65, 1655, 1657 (1932). (243) Fritsch, Ann. 296, 344-345, 350-352 (1897). (244) Chattaway, Calvet, Anales soc. españ. Its. quím. 26, 75-91 (1928); Cent. 1928, I 2618; C.A. 22, 1965 (1928). (245) Chakravarti, Perkin, J. Chem. Soc. 1929, 196-201. (246) Buehler, Block, J. Am. Chem. Soc. 68, 532-533 (1946). (247) Meldrum, Kapadia, J. Indian Chem. Soc. 9, 483-491 (1932). (248) Meldrum, Parikh, Proc. Indian Acad. Sci. A-1, 431-436 (1935). (249) Alimchandani, J. Chem. Soc. 125, 539-543 (1924). (250) Feist, Dschu, Festschrift A. Tschirch 1926, 23-29; Cent. 1927, II 58; C.A. 22, 3405 (1928).

(251) Chopra, Ray, J. Indian Chem. Soc. 13, 480 (1936). (252) Bargellini, Molina, Gazz. Chim. ital. 42, II 403-408 (1912). (253) Alimchandani, Meldrum, J. Chem. Soc. 117, 964-970 (1920). (254) Horzig, Ann. 421, 283-289 (1921). (255) Chattaway, Calvet, J. Chem. Soc. 1927, 685-692. (256) Meldrum, Tata, J. Univ. Bombay 6, Pt. II, 120-122 (1937); Cent. 1938, I 4035; C.A. 32, 3761 (1938). (257) Chattaway, Irving, J. Chem. Soc. 1934, 325-330. (258) Irving, Curtis, J. Chem. Soc. 1943, 319-321. (259) Chattaway, Calvet, J. Chem. Soc. 1928, 2913-2918; Anales soc. españ. fis. quím. 26, 320-326 (1928); Cent. 1929, I 528; C.A. 23, 599 (1929). (260) Schiff, Ber. 31, 1304-1306 (1898).

(261) Marvel, Dreger, Org. Syntheses, Coll. Vol. 1 (2nd ed.) 238-240 (1941); (1st ed.) 233-235 (1932); 6, 40-42 (1926). (262) Kulkarni, Shah, J. Univ. Bombay 10, Pt. 3, 120-121 (1941); C.A. 36, 3795 (1942). (263) Meyer, Dulk, Ann. 171, 65-78 (1874). (264) Delacre, Bull. soc. chim. (2) 48, 716 (1887). (265) Deodhar, J. Indian Chem. Soc. 11, 83-86 (1934). (266) Gabutti, Bargellini, Gazz. chim. ital. 31, I 82-85 (1901). (267) Bayer and Co., Ger. 121,223, June 3, 1901; Cent. 1901, II 69. (268) Spath, Monatsh. 36, 37 (1915). (269) Wegscheider, Spath, Monatsh. 36, 847 (1909). (270) Parlee, Dacey, Coffin, Can. J. Research 15-B, 254-259 (1937) Cent. 1938, I 4307; C.A. 31, 6538 (1937).

(271) Coles, J. Am. Pharm. Assoc. 27, 477-480 (1938); Cent. 1939, I 96; C.A. 32, 7671 (1938).
(272) Einhorn, Ann. 265, 209-238 (1891).
(273) Einhorn, Liebrecht, Ber. 20, 1592-1594 (1887).
(274) Feist, Arch. Pharm. 240, 180-184 (1902).
(275) Löffler, Kaim, Ber. 42, 96-97 (1909).
(276) Koller, Monatsh. 47, 394 (1926).
(277) Clemo, Ramage, J. Chem. Soc. 1932, 2972.
(278) Winterfeld, Holschneider, Arch. Pharm. 277, 198, 200-201 (1939).
(279) Boehringer and Sons,

Ger. 42,987, May 27, 1887; Friedländer 1, 194 (1888). (280) Tulloch, McElvain, J. Am. Chem. Soc. 61, 963 (1939).

(281) Brand, Reuter, Ber. 72, 1668-1678 (1939). (282) Düring, Ber. 38, 167 (1905). (283) Rabe, Kindler, Ber. 52, 1847-1850 (1919). (284) Rabe, Kindler, Wagner, Ber. 55, 535-536 (1922). (285) Alberts, Bachman, J. Am. Chem. Soc. 57, 1285-1286 (1935). (286) Webb, Corwin, J. Am. Chem. Soc. 66, 1458 (1944). (287) Rabe, Huntenberg, Schultze, Volger, Ber. 64, 2493-2496 (1931). (288) Koenigs, Ottmann, Ber. 54, 1345-1347 (1921). (289) Takahaski, J. Pharm. Soc. Japan, 49, 168-170 (1929); Cent. 1930, I 1308; C.A. 24, 1380 (1930). (290) Schubert, Ber. 27, 86-90 (1894).

(291) Koenigs, Mengel, Ber. 37, 1335-1337 (1904). (292) Kondo, Matsumo, J. Pharm. Soc. Japan 49, 79-83 (1929); Cent. 1929, II 1006; C.A. 23, 4218 (1929). (293) Gerngross, Ber. 42, 400-401 (1909). (294) Einhorn, Ber. 18, 3465-3468 (1885); 19, 904-911 (1886). (295) von Miller, Spady, Ber. 18, 3402-3405 (1885); 19, 130-134 (1886). (296) Clemo, Hoggarth, J. Chem. Soc. 1939, 1242. (297) Koenigs, Muller, Ber. 37, 1337-1340 (1904). (298) Chattaway, Witherington, J. Chem. Soc. 1935, 1178-1179. (299) Jones, Kenner, J. Chem. Soc. 1939, 927. (300) Henry, Bull. acad. roy. Belg. (3) 32, 17-32 (1896); Bull. soc. chim. (3) 15, 1223 (1896); Compt. rend. 120, 1262 (1895).

(301) Chattaway, Drewitt, Parkes, J. Chem. Soc. 1936, 1693-1694. (302) Irving, J. Chem. Soc. 1936, 797-801. (303) Chattaway, Drewitt, Parkes, J. Chem. Soc. 1936, 1530-1532. (304) Chattaway, Witherington, J. Chem. Soc. 1935, 1623-1624. (305) Chattaway, Drewitt, Parkes, J. Chem. Soc. 1936, 1294-1295. (306) Khaiasch, Kleiger, Martin, Mayo, J. Am. Chem. Soc. 63, 2305-2307 (1941). (307) Victoria, Rec. trav. chim. 24, 268-271 (1905); Bull. acad. roy. Belg. 1904, 1087-1123; Cent. 1905, I 344-345. (308) Bayer and Co., Ger. 151,545, May 20, 1904; Cent. 1904, I 1586. (309) Gilman, Abbott, J. Org. Chem. 8, 224-229 (1943). (310) Howard, J.

Am. Chem. Soc. 48, 774-775 (1926).

(311) Iotsitch, J. Russ. Phys.-Chem. Soc. 36, 445 (1904); Bull. soc. chim. (3) 34, 329 (1905). (312) Howard, J. Am. Chem. Soc. 49, 1068-1069 (1927). (313) Floutz, J. Am. Chem. Soc. 67. 1615-1616 (1945). (314) Floutz, J. Am. Chem. Soc. 65, 2255 (1943). (315) Iotsitch, J. Russ. Phys.-Chem. Soc. 34, 96 (1902). (316) Howard, Brown, J. Am. Chem. Soc. 58, 1657 (1936). (317) Dean, Wolf, J. Am. Chem. Soc. 58, 332 (1936). (318) Pinner, Bischoff, Ann. 179, 77-85 (1875). (319) Pinner, Ber. 17, 1997 (1884). (320) Bischoff, Pinner, Ber. 5, 208-212 (1872).

(321) Behrend, Kolln, Ann. 416, 231-233 (1918). (322) Hagemann, Ber. 5, 151-152 (1872). (323) Francis, Davis, J. Chem. Soc. 95, 1407 (1909). (324) Pinner, Fuchs, Ber. 10, 1061 (1877). (325) Cocker, Lapworth, Peters, J. Chem. Soc. 1931, 1382-1391. (326) Crowther, McCombie, Reade, J. Chem. Soc. 105, 933-947 (1914). (327) Wallach, Ann. 173, 288-302 (1874). (328) Cope, Clarke, Connor, Org. Syntheses, Coll. Vol. 2 (1st ed.), 181-183 (1943); 19, 38-39 (1939). (329) Clarke, Shibe, Connor, Org. Syntheses 20, 37-39 (1940). (330) Arndt, Eistert, Ber. 61, 1121 (1928).

(331) Schlotterbeck, Ber. 42, 2561 (1909). (332) Meerwein, Bersin, Burneleit, Ber. 62, 1006-1007 (1929). (333) Wallach, Ann. 173, 274-284 (1874); Ber. 5, 251-256 (1872); 4, 668-669 (1871). (334) Eibner, Ann. 302, 335-370 (1898). (335) Jordan, J. Am. Chem. Soc. 32, 973-977 (1910). (336) Rugheimer, Ber. 39, 1653-1664 (1906). (337) Marvel, Hiers, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 327-330 (1941); (1st ed.) 321-324 (1932); 5, 71-74 (1925). (338) Sandmeyer, Helv. Chim. Acta 2, 234-242 (1919). (339) Geigy A.G., Ger. 313,725, July 21, 1919; Cent. 1919, IV 665; not in C.A.: Brit. 128,122 [C.A. 13, 2375 (1919)]. (340) Wibaut, Geerling. Rec. trav. chim. 50, 41-43 (1931).

(341) Geigy A.G., Ger. 320,647, April 26, 1920; Cent. 1920, IV 223; not in C.A. (342) Wheeler, Weller, J. Am. Chem. Soc. 24, 1063-1066 (1902). (343) Wheeler, J. Am. Chem. Soc. 30, 136-142 (1910). (344) Wheeler, Jordan, J. Am. Chem. Soc. 31, 937-943 (1909). (345) Gulland, Robinson, Scott, Thornley, J. Chem. Soc. 1929, 2924-2941. (346) Boessneck, Ber. 21, 782-784 (1888). (347) Meldrum, Advani, J. Indran Chem. Soc. 10, 107-110 (1933). (348) Advani, Wheeler, Rec. trav. chim. 52, 257-266 (1933). (349) Advani, J. Indian Chem. Soc. 10, 621-624 (1933). (350) Zierold, Ger. 61,551, Feb. 10, 1892; Friedlander 3, 109 (1896).

(351) Knöfler, Boessneck, Ber. 20, 3193-3196 (1887). (352) Boessneck, Ber. 18, 1516-1521 (1885). (353) Causse, Bull. soc. chim. (3) 17, 547-553 (1897). (354) Stepanow, Kusin, Ber. 65, 1239-1241 (1932). (355) Torres, Brosa, Anales soc. españ. fis. quim. 32, 509-518 (1934): Cent. 1935, I 382; C.A. 28, 6104 (1934). (356) Brady, J. Chem. Soc. 1931, 756-759. (357) Chattaway, Bennett, J. Chem. Soc. 1927, 2850-2853. (358) Chattaway, Adair, J. Chem. Soc. 1933, 1488-1490. (359) Chattaway, Daldy, J. Chem. Soc. 1928, 2756-2762. (360) Chattaway. Browne, J. Chem. Soc. 1931, 1088-1092.

(361) Chem. Fabrik Schering, Ger. 50,586, Dec. 18, 1889; Friedländer 2, 524 (1891). (362)

Feist, Ber. 45, 945-962 (1912). (363) Bennett, Campbell, Quart. J. Pharm. Pharmacol. 8, 398-400 (1935); Cent. 1936, I 1916; C.A. 30, 813 (1936). (364) Moscheles, Ber. 24, 1803-1805 (1891). (365) Meldrum, Vad, J. Indian Chem. Soc. 13, 117-118 (1936). (366) Yelburgi, Wheeler, J. Indian Chem. Soc. 11, 217-223 (1934). (367) Meldrum, Bhajraj, J. Indian Chem. Soc. 13, 185-186 (1936). (368) Pinner, Klein, Ber. 11, 10-11 (1878). (369) Meldrum, Deodhar, J. Indian Chem. Soc. 11, 529-533 (1934). (370) Hirwe, Deshpande, Proc Indian Acad. Sci. A-13, 275-276 (1941).

(371) Hirwe, Deshpande, Proc. Indian Acad. Sci. A-13, 277-280 (1941). (372) Kaufmann, Arch. Pharm. 265, 237-238 (1927). (373) Ritsert (to Goedecke and Co.), Ger. 498,432, May 28, 1930; Cent. 1930, II 584; C.A. 24, 3861 (1930). (374) Hirwe, Rana, Ber. 72, 1346-1350 (1939). (375) Hirwe, Gavankar, Patil, Proc. Indian Acad. Sci. A-11, 512-516 (1940). (376) Hirwe, Rana, J. Indian Chem. Soc. 16, 677-680 (1939). (377) Hirwe, Rana, J. Univ. Bombay 7, Pt. III, 174-177 (1938); Cent. 1939, II 383; C.A. 33, 3778 (1939). (378) Hirwe, Gavankar, J. Univ. Bombay 6, Pt. II, 123-126 (1937); Cent. 1938, I 4172; C.A. 32, 3762 (1938). (379) Rana, J. Indian Chem. Soc. 19, 299-302 (1942). (380) Hirwe, Kulkarni, Proc. Indian Acad. Sci. A-13, 49-52 (1941).

(381) Coppin, Titherly, J. Chem. Soc. 105, 32-36 (1914). (382) Chattaway, James, Proc. Roy. Soc. (London), A-134, 372-384 (1931). (383) Feist, Ber. 47, 1188-1193 (1914). (384) Chattaway, James, J. Chem. Soc. 1934, 109-113. (385) Chattaway, Kerr, Lawrence, J. Chem. Soc. 1933, 30-32. (386) van der Zande, Rec. trav. chim. 8, 238-241 (1889). (387) Diels, Seib, Ber. 42, 4062-4072 (1909). (388) Bischoff, Ber. 7, 631-632 (1874). (389) Meldrum, Pandya, J. Univ. Bombay, 6, Pt. II, 114-115 (1937); Cent. 1938, I 3462; C.A. 32, 3760 (1938). (390)

Roduta, Quibilan, Rev. filipina med. farm. 27, 123-130 (1936); C.A. 31, 98 (1937).

(391) Allen, Richmond, J. Org. Chem. 2, 225 (1937). (392) Kling, Bull. soc. chim. (4) 5, 412-414 (1909); Compt. rend. 148, 569 (1909). (393) Knopfer, Monatch. 32, 768-771 (1911). (394) Darapsky, Prabhakar, Ber. 45, 2624-2625 (1912). (395) Müller, Ber. 47, 3021 (1915). (396) Sah, Kao, Chang, J. Chinese Chem. Soc. 2, 236 (1934). (397) Busch, Achterfeldt, Seufert, J. prakt. Chem. (2) 92, 24 (1915). (398) Koenigs. Ber. 25, 794-797 (1892). (399) Wislicenus, Kircheisen, Sattler, Ber. 26, 908-915 (1893). (400) Sen, Barat, J. Indian Chem. Soc. 2, 403-414 (1926).

(401) Uschakoff, J. Russ. Phys.-Chem. Soc. 29, 113-118 (1897); Cent. 1897, I 1019. (402) Koenigs, Wagstaffe, Ber. 26, 554-556 (1893). (403) Sumerford, Dalton, J. Org. Chem. 9, 81-84 (1944). (404) Frolich, Wiezevich (to Standard Oil Dev. Co.), U.S. 2,042,303, May 26, 1936; Cent. 1936, II 3193; C.A. 39, 4871 (1936); Ger. 629,897, May 26, 1936; Cent. 1936, II 2448; C.A. 30, 6006 (1936). (405) Cristol, Hayes, Haller, J. Am. Chem. Soc. 68, 913-914 (1946).

3:5220 2,3-DICHLOROBUTADIENE-1,3 Cl Cl
$$C_4H_4Cl_2$$
 Beil. S.N. 12 $H_2C=C-C=CH_2$

B.P. 98° at 760 mm. (1) (2)
$$D_4^{20} = 1.1829$$
 (1) $n_D^{20} = 1.4890$ (1) $41-43^\circ$ at 85 mm. (1) $40-43^\circ$ at 85 mm. (3)

[For prepn. of \overline{C} (86% yield (1)) from 1,2,3-trichlorobutene-3 (2,3,4-trichlorobutene-1) (3:9064) with excess MeOH/KOH at 10-15° see (1) (2); for formn. (together with other products) from 1,2,3,4-tetrachlorobutane (3:1760) with MeOH/KOH at 10-18° see (1) (2); from chloroprene (3:7080) by addn. of ICl followed by treatment with alc. KOH (3),

Č polymerizes completely within 24 hrs. at room temp., in about 40 min. at 85–90°; this is about 10 times as fast as chloroprene (3:7080) and 7000 times as fast as isoprene (1:8020). The polymer is a white opaque tough hard mass, non-plastic and lacking extensibility. It is insol. in and separates from liquid Č but is partly soluble in CHCl₃ (1). The polymerization is inhibited by hydroquinone and accelerated by benzoyl peroxide (2).

C does not (1) react with maleic anhydride (1:0625) or with 1,4-naphthoguinone (1:9040).

3:5220 (1) Carothers, Berchet, J. Am. Chem. Soc. 55, 2004-2008 (1933). (2) Carothers, Berchet, U.S. 1,965,319, July 3, 1934; Cent. 1935, I 3724; C.A. 28, 5716 (1934). (3) Petrov, J. Gen. Chem. (U.S.S.R.) 13, 155-158 (1943); C.A. 38, 1466-1467 (1944).

3:5225-3:5235

3:5225 METHOXYACETYL CHLORIDE
$$C_3H_5O_2Cl$$
 Beil. S.N. 220 CH_3OCH_2 — C =O Cl

B.P. 99° (1)
$$D_4^{20} = 1.1871$$
 $n_D^{20} = 1.41945$ (2) 50-51° at 69 mm. (2)

[For prepn. of C from methoxyacetic acid (1:1065) with SOCl₂ (yields: 70% (1), 45% (2)) see indic. refs. (note that best yield is obtd. with 10% less than 1 mole SOCl₂ (1) since cleavage of the methoxy group is thus minimized); from methoxyacetic acid anhydride [Beil. III₁-(92)] with COCl₂ (3:5000) at 160° under reduced press. over CaCl₂ on pumice see (3); from chloromethyl methyl ether (3:7085) contg. 4.67% dislvd. ZnCl₂ on shaking with CO at 25-50° and 275-625 pounds press. for 8 hrs. see (4).

 $[\bar{C}]$ with alcs. + pyridine in CHCl₃ soln. gives (1) corresp. esters; for reactn. of \bar{C} with benzyl alc. (1:6480), with β -phenylethyl a c. (1:6505), citronellol, or geraniol (1:6270) see (1); with menthol (1:5940) see (5); for study of rate of reactn. of \bar{C} with benzyl alc. (1:6480), cyclohexanol (1:6415), or ethylene chlorohydrin (3:5552) in dioxane soln, see (2).]

Č on hydrolysis yields methoxyacetic acid (1:1065); for the amide, anilide, and other derivs. corresp. to C see methoxyacetic acid (1:1065).

3:5225 (1) Rothstein, Bull. soc. chim. (4) 51, 840 (1932). (2) Leimu, Ber. 70, 1044, 1050 (1937). (3) Stellmann, French 785,075, Aug. 1, 1935; Cent. 1935, II 3301. (4) Scott (to du Pont Co.). U.S. 2,084,284, June 15, 1937; Cent. 1937, II 2261; C.A. 31, 5383 (1937). (5) Rule, Smith, J. Chem. Soc. 127, 2191 (1925).

3:5230 1,2,3-TRICHLORO-2-(CHLOROMETHYL)-C₅H₈Cl₄ Beil. S.N. 10 BUTANE

[For prepn. of C from 3-chloro-2-(chloromethyl)butene-1 (3:9206) with Cl₂ + NaHCO₃ at 0° (90% yield) see (1); for formn. from other sources see (2).]

[Č with alc. KOH gives (2) (by loss of 1 HCl) 1,3-dichloro-2-(chloromethyl)butene-1 (3:9201) and (by further loss of 1 HCl or perhaps 2 HCl from C) also 1-chloro-2-(chloromethyl)butadiene-1,3 (3:9195).]

 \bar{C} on hydrolysis with aq. $K_2CO_3 + KOH$ yields (2) an alcohol.

3:5230 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4222; C.A. 33, 4190 (1939). (2) Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1116-1132 (1936); Cent. 1937, I 573; C.A. 31, 1003 (1937).

B.P.
$$105.0^{\circ}$$
 at 750 mm. (1) $D_4^{20} = 1.4202$ (1); $n_D^{20} = 1.4541$ (1) $104.7-105.2^{\circ}$ (2) 1.4177 (4) 1.4535 (4) $103-106^{\circ}$ at 750 mm. (3)

[For prepn. of \tilde{C} from chloroacetic acid (3:1370) with PCl₃ (5) (40), or in HCl atm. under press. at 150° (6), or with ZnCl₂ (67% yield (7)) see indic. refs.; with P₂O₅ + HCl gas at 200° see (8); with SOCl₂ (yields: 95% (9), 55% (10), 50% (7)) (11) see indic. refs.; with benzoyl chloride (3:6240) (yield 71-76%) see (12); with oxalyl dichloride (3:5060) (80% yield) see (3); with physical properties (3:5000) over activated carbon at 200° see (13); with benzotrichloride (3:6540) + ZnCl₂ at 80-90° (80% yield) see (14); with Cl₂ + S₂Cl₂ (95% yield (15)) or Cl₂ + lower chlorides of sulfur + FeCl₃, SnCl₄, etc., at 50-60° (82% yield (16)) see indic. refs.]

[For prepn. of \tilde{C} from chloroacetic acid anhydride (3:0730) with oxalyl dichloride (3:5060) see (3); from ketene with NOCl see (17); from α,β -dichlorovinyl ethyl ether (3:5540) + HCl gas see (18); from α,β -dichloroethylene + O₂ in pres. of Br₂ or conc. H₂SO₄ see (19); from acetyl chloride (3:7065) with Cl₂ in sunlight (20) or in CCl₄ in u.v. light (21) or in pres. of I₂ (22) see indic. refs.; from α -chloroethyl chloroacetate on htg. with 0.02% ZnCl₂ see (23); from 2-(chloroacetoxy)hexene-1 with HCl gas see (24), from CH₂Cl₂ (3:5020) + AlCl₃ + CO gas at 200° and 900 atm. see (41).

Č on htg. with Na₂CO₃ (25) or with KNO₃ (81% yield (26)) gives chloroacetic acid anhydride (3:0730) q.v., m.p. 46°. — Č treated at −5° with HI gas gives (68% yield (27)) chloroacetyl iodide, b.p. 36.5° at 4 mm. (27). [For behavior of C with HBr gas see (40).]

Č with MeOH yields (28) methyl chloroacetate (3:5585), b.p. 131°; Č with EtOH (29) or with triethyl orthoformate (1:3241) at 100-110° (90% yield (30)) gives ethyl chloroacetate (3:5700), b.p. 144°.

[$\bar{\mathbf{C}}$ with ethylene + AlCl₃ gives (small yield (31)) 1,4-dichlorobutanone 2, b.p. 63-65° at 3 mm. (31). — $\bar{\mathbf{C}}$ with C₆H₆ + AlCl₃ gives (32) ω-chloroacetophenone (phenacyl chloride) (3:1212); $\bar{\mathbf{C}}$ with m-dichlorobenzene (3:5960) + AlCl₃ gives (33) 2,4-dichlorophenacyl chloride [Beil. VII-283], m.p. 57° (33); $\bar{\mathbf{C}}$ with biphenyl + AlCl₃ gives (77% yield (34)) p-phenylphenacyl chloride (3:3934), m.p. 122-123° (34); $\bar{\mathbf{C}}$ with naphthalene + AlCl₃ in CS₂ gives (35) cf. (36) chloromethyl β-naphthyl ketone.]

[\bar{C} with large excess (4 moles) MeMgBr or MeMgI gives (48-51% yield (37)) (38) 2-methylbutanol-3 (1:6170); \bar{C} with large excess C_6H_5MgBr in ether gives (31% yield (39)) 1,2,2-triphenylethanol-1 [Beil. VI-721], m.p. 87.5-88.5° (39); note that the isomeric 1,1,2-triphenylethanol-1 [Beil. VI₁-(354)] has almost same m.p., viz., 89°.]

Č hydrolyzes with aq. yielding chloroacetic acid (3:1370) q.v. — For the amide, anilide, p-toluidide, and other derivs. corresp. to Č see chloroacetic acid (3:1370).

3:5235 (1) Martin, Partington, J. Chem. Soc. 1936, 162. (2) Cheng, Z. physik. Chem. B-26, 295 (1934). (3) Adams, Ulich, J. Am. Chem. Soc. 42, 604, 606 (1920). (4) Vanderstichele, J. Chem. Soc. 123, 1228 (1923). (5) de Wilde, Ann. 130, 372-373 (1864). (6) Scheuble, Ger. 251,806, Oct. 8, 1912; Cent. 1912, II 1503-1504. (7) Clark, Bell, Trans. Roy. Soc. Canada (3) 27, III 97-103 (1933). (8) Frankland, Patterson, J. Chem. Soc. 73, 190 (1898). (9) Barnett, Chem. News 122, 220-221 (1921); Cent. 1921, III 463. (10) McMaster, Ahmann, J. Am. Chem. Soc. 50, 146 (1928).

(11) Böeseken, Rec. trav. chim. 32, 5 (1913). (12) Brown, J. Am. Chem. Soc. 60, 1325-1328 (1938). (13) Hochstetter, Ger. 283,896, April 27, 1915; Cent. 1915, I 1190. (14) Raboewicz-Zubkowski, Roczniki Chem. 9, 526-527 (1929); Cent. 1929, II 2767; CA. 24, 61 (1930). (15) Read, J. Am. Chem. Soc. 44, 1751 Note (1922). (16) Britton (to Dow Chem. Co.), U.S. 1,805,162, May 12, 1931; Cent. 1931, II 631; C.A. 25, 3670 (1931). (17) Deakin, Wilsmore, J. Chem. Soc. 97, 1977 (1910). (18) Consortium für Elektrochem. Ind., Ger. 222,194, May 19, 1910; Cent. 1910, I 1999. (19) Consortium für Elektrochem. Ind., Ger. 340,872, Sept. 19, 1921; Cent. 1921, IV 1101. (20) Wurtz, Ann. chim. (3) 49, 60 (1857).

Benrath, Hertel, Z. wiss. Phot. 23, 35 (1924).
 Jazukowitsch, Zeit. für Chemie 1868, 234.
 Soc. Usines Chimiques Rhone-Poulenc, Brit. 329,721, June 19, 1930; Cent. 1930, II
 Janina, Hennion, J. Am. Chem. Soc. 59, 856 (1937).
 Patterson, Ber. 38, 211-212 (1905).
 Diels, Okada, Ber. 44, 3335 (1911).
 Gustus, Stevens, J. Am. Chem.

Soc. 55, 375 (1933). (28) Meyer, Ber. 8, 1152-1158 (1875). (29) Willm, Ann. 102, 109-111

(1857). (30) Levaillant, Compt. rend. 195, 882 (1932).

(31) Carroll, Smith, J. Am. Chem. Soc. 55, 372-373 (1933). (32) Friedel, Crafts, Ann. chim. (6) 1, 507 (1884). (33) Kunckell, Ber. 40, 1702-1703 (1907) (34) Silver, Lowy, J. Am. Chem. Soc. 56, 2429-2431 (1934). (35) Morgan, Stanley, J. Soc. Chem. Ind. 44, 494-T (1925). (36) Widman, Ber. 51, 911 (1918). (37) Duston, Jackson, Spero, J. Am. Chem. Soc. 63, 1459-1460 (1941). (38) Henry, Compt. rend. 145, 24 (1907). (39) Boyle, McKenzie, Mitchell, Ber. 76, 2159 (1937). (40) Aschan, Ber. 46, 2168 (1913).

(41) Theobald (to du Pont Co.) U.S. 2,378,048, June 12, 1945; C.A. 39, 4085 (1945).

B.P.
$$105^{\circ}$$
 (1) (2) (8) $D_{20}^{20} = 1.315$ (1) $n_{\rm D}^{21} = 1.435$ (2) $104-106^{\circ}$ (3) $D_{4}^{15} = 1.328$ (2)

Liq. fumg. in moist air.

 \ddot{C} dis. slowly in cold and rapidly in warm aq. owing to hydrolysis to formaldehyde (1:0145) + HCl. [For quant. study see (5).]

[For prepn. from formalin (1:0145), paraformaldehyde (1:0080) (95% yield (6)), or hexamethylenetetramine + chlorosulfonic ac. + conc. H_2SO_4 see (6) (7); from paraformaldehyde (1:0080) + conc. H_2SO_4 + HCl gas (85% yield (8)) see (8); for prepn. from dimethyl other by chlorination see (9) (10).]

[For use in production of halogenated higher ethers by addn. to olefins see (11).]

3:5245 (1) Regnault, Ann. 34, 31 (1840). (2) Brochet, Ann. chim. (7) 10, 297 (1897). (3) Grassi, Maselli, Gazz. chim. ital. 28, II 485 (1898). (4) Litterschied, Ann. 330, 116 (1903). (5) Bohme, Ber. 74, 248-256 (1941); C.A. 35, 3972-3973 (1941). (6) Stephen, Short, Gladding, J. Chem. Soc. 117, 513-515 (1920). (7) Carr, J. Soc. Chem. Ind. 38, 468R (1919). (8) Schneider, Angew. Chem. 51, 274 (1938). (9) Salzberg, Werntz (to du Pont, U.S. 2,065,400, Dec. 22, 1936; C.A. 31, 1046 (1937); Cent. 1937, I 3715. (10) Booth (to Westinghouse Electric Co.), U.S. 2,066,905, Jan. 5, 1937; C.A. 31, 1037 (1937); Cent. 1937, I 3529.

(11) Scott (to du Pont), U.S. 2,024,749, Dec. 17, 1935, Brit. 423,520; C.A. 30, 1067 (1936); C.A. 29, 4374 (1935).

3:5270 1,1,1-TRICHLOROPROPANE CH₃.CH₂.CCl₃ C₃H₅Cl₃ Beil. S.N. 10 ("Ethylchloroform")

B.P.
$$106.5 - 108.5^{\circ}$$
 (4) $D_4^{23} = 1.287$ (1) $106 - 107^{\circ}$ (1) (2)

[For prepn. from 1,1-dichloropropene-1 (3:5120) + HCl + AlCl₃ at 5-10° see (1) (2) (4).]

[The compd. listed in Beil. I-106 as C is erroneous (1) (3).]

3:5270 (1) Levine, Cass (to du Pont), British 503,615, May 11, 1939; Cent. 1339, II 1572. (2) Levine, Cass (to du Pont), U.S. 2,179,218, Nov. 7, 1939; C.A. 34, 1336 (1940). (3) Van Arkel, Rec. trav. chim. 51, 1101 (1932). (4) Henne, Whaley, J. Am. Chem. Soc. 64, 1157 (1942).

3:5275 CHLOROMETHYL CHLOROFORMATE
$$C_2H_2O_2Cl_2$$
 Beil. III — (Chloromethyl chlorocarbonate) $ClCH_2-O-C=O$ $III_{1^-}(6)$ $III_{2^-}(11)$ B.P. 106.5-107° at 760 mm. (1) $D_-^{15} = 1.465$ (1) $n_D^{22} = 1.4286$ (2) 106.5° (2)

 $D_{-}^{14} = 1.456 (2)$

See also text.

104-107°

52.5-53°

[See also dichloromethyl chloroformate (3:5315).]

at 100 mm. (1)

(3)

Coloriess lachrymatory oil. — Note that \tilde{C} cannot by distillation be completely separated from dichloromethyl chloroformate (3:5315); the constants listed above are on samples contg. (1) about 9% of the latter, or (3) about 7% of dichloromethyl chloroformate + 2% dimethyl carbonate.

A mixt. of \bar{C} with dichloromethyl chloroformate (3:5315) has been employed as a chem. warfare agent under the names "K-Stoff," "Palite" (6). — [For studies of physiological action see (4) (5); for action on plant tissue see (7).]

[For prepn. of \tilde{C} from methyl chloroformate (3:5075) or from methyl formate (1:1000) with Cl_2 under various conditions see (1) (2) cf. (6) (8) (9).]

 \bar{C} with aq. at ord. temp. or more rapidly on boilg. or \bar{C} with aq. alk. in çold undergoes hydrolysis (1) yielding formaldehyde (1:0145) + 2 HCl + CO₂; by detn. via oxidn. with I_2 + NaOH of the formaldehyde so produced \bar{C} may be quant. estimated cf. (10) (6); note also that this hydrolysis to formaldehyde distinguishes \bar{C} from various other closely related compounds, e.g., methyl chloroformate (3:5075), dichloromethyl chloroformate (3:5315), trichloromethyl chloroformate ("Diphosgene") (3:5515), trichloromethyl trichloroacetate (3:0290), bis-(trichloromethyl) carbonate ("Triphosgene") (3:1915), or phosgene (3:5000).

 \bar{C} (1 mole) with NaI (2 moles) in dry acetone at 20° (11) liberates I₂ also yielding formal-dehyde (1:0145) + CO, but the reaction is *not* quantitative proceeding only to about 70% theoretical (11); but \bar{C} with dry NaI at 90-100° gives (1) CO + CO₂. Note that \bar{C} with LiBr in dry acetone does *not* (11) liberate bromine; in this respect \bar{C} is like methyl chloroformate (3:5075) but different from dichloromethyl chloroformate (3:5315) and trichloromethyl chloroformate ("Diphosgene") (3:5515).

[Č with FeCl₃ or AlCl₃ dec. rapidly at 70° (1) (12) yielding phosgene (3:5000) and formaldehyde (1:0145).]

[$\ddot{\mathbf{C}}$ with methyl hydrogen sulfate gives (13) methyl chlorosulfonate, formaldehyde, $\mathbf{CO_2} + \mathbf{HCl}$; $\ddot{\mathbf{C}}$ with chlorosulfonic acid at 100° for 4 hrs. gives (13) chloromethyl chlorosulfonate + $\mathbf{CO_2} + \mathbf{HCl}$; $\ddot{\mathbf{C}}$ with dimethyl sulfate gives (78% yield (13)) methyl chlorosulfonate.]

[\tilde{C} with alcohols or \tilde{C} with alkali salts of phenols reacts as an acid chlorine yielding (6) the corresp. alkyl or anyl chloromethyl carbonates (1).]

[Č with K phenylcyanamide also reacts as an acid chloride giving (14) chloromethyl N-cyano-N-phenylcarbamate, m.p. 48°.]

3:5275 (1) Kling, Florentin, Lassieur, Schmuts, Compt. rend. 169, 1046-1047 (1919); Ann. chim. (9) 13, 44-59 (1920). (2) Grignard, Rivat, Urbain, Compt. rend. 169, 1074-1077 (1919); Ann. chim. (9) 13, 246-248 (1920). (3) Herbst, Kolloidchem. Beihefte, 23, 330-331 (1927). (4) van Nieuwenberg, Chem. Weekblad 19, 328 (1922). (5) Fegler, Compt. rend. soc. biol. 160, 222-224

(1929); Cent. 1929, I 3114; C.A. 24, 5373 (1930). (6) Sartori, "The War Gases," pp. 104-109, 123-124, D. Van Nostrand Co., Inc., New York City, 1940. (7) Guerin, Lormand, Compt. rend. 176, 401-403 (1920). (8) Hood, Murdock, J. Phys. Chem. 23, 509-511 (1919). (9) Hentschel, J. prakt. Chem. (2) 36, 104-107, 212 (1887). (10) Delépine, Bull. soc. chim. (4) 27, 39-45 (1920).

(11) Perret, Biechler, Bull. soc. chim. (5) 3, 957-958 (1936); Compt. rend. 283, 84-87 (1936). (12) Kling, Florentin, Compt. rend. 169, 1166 (1919). (13) Kraft, Alekseev, J. Gen. Chem. (U.S.S.R.) 2, 726-729 (1932); Cent. 1933, II 1666; C.A. 27, 2426-2427 (1933). (14) Perret, Biechler, Bull. soc. ind. Mulhouse, 103, 168-173 (1937); Cent. 1937, II 374; [C.A. 32, 2087 (1938)].

3:5280 1,8-DICHLOROPROPENE-1 CH₂—CH=CH C₈H₄Cl₂ Beil. I-(199)
$$(\alpha,\gamma$$
-Dichloropropylene; Cl Cl Cl I_1 — I_2 -(170) Higher-boilg. B.P. 112.0° (1) $D_4^{20} = 1.217$ (1) $n_D^{20} = 1.4730$ (1) stereoisomer Lower-boilg. B.P. 104.3° (1) $D_4^{20} = 1.224$ (1) $n_D^{20} = 1.4682$ (1) stereoisomer Ordinary \bar{C} B.P. 110° (14) $D_2^{25} = 1.218$ (5) 109–110° (2) 109° (3) $D_2^{22} = 1.222$ (2) $n_D^{22} = 1.4735$ (2) 107–108° (31) 106° (5) 105.5–106° at 730 mm. (7)

[See also 3,3-dichloropropene-1 (3:5140).]

Note that \bar{C} has frequently been given the extremely unfortunate designation " β -chloroallyl chloride," a practice which has often led to confusion with 2,3-dichloropropene-1 (3:5190). — Note furthermore that, in addition to existing in *cis* and *trans*-configurations, the structure \bar{C} also represents the synionic mesomer of 3,3-dichloropropene-1 (3:5140); reactions of either mesomer may under certain conditions lead also to derivatives of the other. — Finally note further that in all reports prior to 1944 the material designated as \bar{C} was in all probability a mixture of the two geometrical stereoisomers.

C is a colorless oil with odor suggesting chloroform (4).

[For prepn. of the two geometrical stereoisomers by careful fractional distillation of a higher-boilg fraction obtd. from the chlorination of propylene in the semi-comml. prepn. of allyl chloride (and contg. abt. $60\% \ \bar{C} + 30\% \ 1,2$ -dichloropropane (3:5200)) see (1).]

[For prepn. of ord. \bar{C} from 1,3-dichloropropanol-2 (β , β' -dichloroisopropyl alc.) ("glycerol α -dichlorohydrin") (3:5985) by elimination of H₂O with POCl₃ (yields: 75% (4), 54% (7), 34–39% (8)) (5) or with P₂O₅ (3) (5) (10) (14) in C₅H₆ (30–40% yield (4)) see indic. refs.; note that none of the other conventional dehydrating agents (such as 85% H₃PO₄ conc. H₂SO₄, KHSO₄, SOCl₂, PCl₅ (11), PCl₃, ZnCl₂, I₂, B₂O₃ or anhydrous oxalic acid) gives satisfactory results (4); for prepn. of \bar{C} from β , β' -dichloroisopropyl benzenesulfonate by htg. at 240–250° (77% yield) see (9).]

[For formn. of ord. C from 3-chloropropen-2-ol-1 (3:5820) with PCl₃ see {12}; from 1,2,3-trichloropropane (3:5840) with NaOH (yielding (6) 12% C accompanied by 70% 2,3-dichloropropene-1 (3:5190)) cf. {13} (5); from acrolein (1:0115) with PCl₅ (yield 32% C accompanied by 16% of the mesomeric 1,1-dichloropropene-2 (3:5140) and also some 1,1,3-trichloropropane (3:5660) (12)) cf. (14); from 3,3-dichloropropene-1 (3:5140) by isomerization with conc. HCl in s.t. at 100° (14) see indic. refs.]

[For use as soil disinfectant of the mixt. of \bar{C} with 1,2-dichloropropene obtd. in manufacture of allyl chloride by chlorination of propylene see (15); for use of \bar{C} in prepn. of cellulose ethers see (16).]

Reactions involving unsaturated linkage of Č. [Č with Cl₂ adds 1 mole halogen yielding (14) 1,1,2,3-tetrachloropropane (3:6035), b.p. 179–180° cor. at 756.6 mm. (14).] — Č with Br₂ adds 1 mole halogen giving (72.7% yield (9)) (5) (3) (17) 1,2-dibromo-1,3-dichloropropane [Beil. I-112], b.p. 212° (3), 215–217° (9), 220–221° (17), 220–225° (5).

[C with fumg. HCl in s.t. at 150° blackens but does not add HCl (5).]

Reactions involving the one reactive chlorine atom of \bar{C} . Note that the 2 chlorine atoms in \bar{C} possess very different reactivities; that attached to the carbon directly connected with the double bond is inert, while the chlorine attached to the carbon in β -relationship to the unsaturated linkage is extremely reactive.

[\bar{C} with aq. KOH (1 mole) boiled for 30 hrs. {14}, or boiled with 10% aq. Na₂CO₃ (slight excess) for 2 hrs. {1}, or shaken with aq. silver oxide at room temp. for 24 hrs. (small yield (12)) gives 3-chloropropen-2-ol-1 (1-chloropropen-1-ol-3) (γ -chloroallyl alcohol) (3:5820); note that the high-boilg, stereoisomer of \bar{C} gives (76% yield (1)) the high-boilg, stereoisomer of the resultant alc., while the low-boilg, stereoisomer of \bar{C} gives (81% yield (1)) the low-boilg, stereoisomer of the resultant alc.; note also that aq. NaOH effects from the resultant γ -chloroallyl alc. the removal of HCl and also causes polymerization (1) so that use of hydrolytic conditions as mild as possible is desirable.] — [For reactn. of \bar{C} with NaSH or Na₂S see (18).].

[$\bar{\mathbf{C}}$ with Na alcoholates, NaOR, replaces the reactive chlorine atom by the alkoxy residue yielding ω -chloroallyl alkyl ethers of general formula RO—CH₂—CH = CHCl: e.g., $\bar{\mathbf{C}}$ with NaOMe refluxed 4 hrs. gives (12) 1-chloro-3-methoxypropene-1, b.p. 107-108°, $D^{27}=1.032,\ n^{27}=1.431$ (12) (note proximity of b.p. to that of ord. $\bar{\mathbf{C}}$) (for study of kinetics of this reactn. see (19)); $\bar{\mathbf{C}}$ with NaOEt refluxed for 4 hrs. (12) or $\bar{\mathbf{C}}$ with alc. KOH (5) yields 1-chloro-3-ethoxypropene-1 [Beil. I-439], b.p. 126-127°, $D^{16}=1.018,\ n^{16}=1.438$ (12); for corresp. reactns. of $\bar{\mathbf{C}}$ with Na derivs. of benzyl alc. (1:6480), β -phenylethyl alc. (1:6505), γ -phenyl-n-propyl alc. (1:6520), and cinnamyl alc. (1:5920) together with physical consts. of prods. see (20).]

[C with alkali metal phenolates replaces the reactive chlorine atom by the aryloxy residue yielding ω-chloroallyl aryl ethers of general formula RO.CH₂.CH = CHCl; e.g., $\bar{\mathbf{C}}$ with Na phenolate in abs. alc. refluxed $\frac{1}{2}$ hr. (21), or $\bar{\mathbf{C}}$ with phenol (1:1420) + dry K₂CO₃ in boilg. acetone (8), gives (yields: 75% (21), 72% (8)) ω-chloroallyl phenyl ether, b.p. 120-121° at 20 mm. (21), 122-127° at 27 mm. (8), $D_4^{15} = 1.146$ (21), $n_D^{20} = 1.5421$ (8), $n_D^{15} = 1.5447$ (21); for corresp. reactn. with salts of o-cresol (1:1400) (21), m-cresol (1:1730) (21), p-cresol (1:1410) (21) (8), carvacrol (1:1760) (21), thymol (1:1430) (21), β -naphthol (1:1540) (21), hydroquinone (1:1590) (21), and several other phenols (21) see indic. refs. — Note that these ω-chloroallyl aryl ethers upon treatment with Br₂ do not add halogen to the unsatd. linkage but instead undergo cleavage: e.g., w-chloroallyl phenyl ether (above) in CHCl₃ with Br₂ (1 mole) at 0° yields (22) phenol (1:1420) + p-bromophenol + 3-bromo-1-chloropropene-1 (see below) + ω -chloroallyl p-bromophenyl ether, b.p. 153° at 13 mm., $D_4^{11} = 1.521$, $n_D^{11} = 1.5785$ (22). — Note furthermore that these ω-chloroallyl aryl ethers with HBr or HI do not add hydrogen halide to the unsaturated side chain but instead undergo cleavage similar to that with halogens: e.g., ω -chloroallyl phenyl ether in AcOH with HBr gas (1 mole) gives (70% yield (23)) 3-bromo-1-chloropropene-1, lachrymatory oil, b.p. 130° at 760 mm., $D_4^{9.5} = 1.670$, $n_D^{9.5} = 1.5255$ (23); similarly action of HI yields (23) 1-chloro-3-iodopropene-1, lachrymatory oil, b.p. 162° at 760 mm. sl. dec., 58° at 19 mm., $D_4^{9.5} = 2.029$, $n_D^{9.5} = 1.5993$ (23).]

[C with phenols under suitable conditions can also react to effect direct nuclear alkenyla-

tion: e.g., \bar{C} with phenol (1:1420) + Na in C_6H_6 refluxed for 17 hrs. gives (17% yield (8)) o-(γ -chloroallyl)phenol, b.p. 151-156° at 31 mm., $n_2^{23} = 1.5638$ (8) (soluble in alk.), accompanied by some ω -chloroallyl phenyl ether (insol. alk.) (see above).]

[$\bar{\mathbf{C}}$ with phenol ethers undergoes Friedel-Crafts reactn. of the reactive halogen atom with resultant introduction of the ω -chloroallyl group into the aromatic nucleus: e.g., $\bar{\mathbf{C}}$ (1 mole) with anisole (1:7445) (10 moles) + AlCl₃ gives (70% yield (24)) 1-(ω -chloroallyl)-4-methoxybenzene, b.p. 126° at 15 mm. (24); $\bar{\mathbf{C}}$ (1 mole) with pyrocatechol dimethyl ether (veratrole) (1:7560) (2 moles) + Zn dust (1 g.) (AlCl₃ unsuitable) gives 1-(ω -chloroallyl)-3,4-dimethoxybenzene, b.p. 162° at 15 mm., D_4^{14} = 1.168, n_D^{14} = 1.551 (24); $\bar{\mathbf{C}}$ with pyrogallol trimethyl ether (1:7145) similarly yields 1-(ω -chloroallyl)3,4,5-trimethoxybenzene, b.p. 174° at 15 mm., D_4^{18} = 1.176, n_D^{18} = 1.539 (24). — Note that such ω -chloroallyl arylethers (1 mole) upon treatment with KOH (3 moles) in an alcohol R'.OH (5 moles) give (by reactn. of the ω -chlorine and rearr. or vice versa) substituted cinnamyl ethers of the type RO.C₆H₄.CH = CH.CH₂OR', used for prepn. of various natural prods. (24).]

[\bar{C} with aromatic hydrocarbons undergoes Friedel-Crafts reactn. of the reactive halogen atom with resultant introduction of the ω -chloroallyl group into the aromatic nucleus e.g., \bar{C} with $C_6H_6+AlCl_3$ yields (25) γ-chloroallylbenzene (1-chloro-3-phenylpropene-1) (3:8737) (see below); for analogous reactions of \bar{C} with toluene (1:7405), ρ -xylene (1:7430), m-xylene (1:7420), p-xylene (1:7415), ethylbenzene (1:7410), cumene (1:7440), pseudocumene (1:7470), mesitylene (1:7455), p-cymene (1:7505), etc., see (25). — Note that the resultant γ -chloroallyl hydrocarbons add Br₂ normally (26) to the unsatd. linkage (diff. from ω -chloroallyl aryl ethers (above) which undergo cleavage); e.g., γ -chloroallylbenzene (above) with Br₂ gives γ -chloro- β , γ -dibromo- η -propylbenzene, b.p. 160° at 12 mm., $D_4^{10} = 1.727$, $n_{10}^{10} = 1.611$ (26) (for use of this prod. in prepn. of hydrocinnamaldehyde (1:0225) see (35).)]

[The direct actn. of \tilde{C} with NH₃ appears to be unreported; however, \tilde{C} with KSCN followed by alk. hydrolytic cleavage is claimed (27) to yield the expected γ -chloroallylamine. — \tilde{C} with methylamine (3 moles) in C_6H_6 gives (53% yield (28)) N-methyl- γ -chloroallylamine [Beil. IV₂-(668)], b.p. 125° (B.PkOH, m.p. 91° (28)), accompanied by a little N-methyl-bis-(γ -chloroallylamine [Beil. IV₂-(668)], b.p. 88° at 16 mm. (28). — \tilde{C} with diethylamine reacts vigorously and on making alkaline gives (75% yield (29)) (12) N,N-diethyl- γ -chloroallylamine [Beil. IV₂-(668)], b.p. 57-58° at 17 mm. (12), 55° at 9 mm. (29) (B.HCl, pl. from acetone, m.p. 221° (29); B.PkOH, ndls. from aq., m.p. 78° (29), 91° (12); B.H₂PtCl₆, m.p. 169-170° (12)). — For reactns. of \tilde{C} with tertiary amines, e.g., with Mc₃N (29), Et₃N (29), or pyridine (19), see indic. refs.]

[\bar{C} (1 mole) with aniline (2 moles) in C_6H_6 under reflux ppts. aniline hydrochloride and from the solvent gives (68% yield (30)) N-phenyl- γ -chloroallylamine, b.p. 137° at 13 mm., $D_4^{13} = 1.1456$, $n_D^{13} = 1.590$ (30); for analogous reactns. of \bar{C} with o-toluidine and m-toluidine see (30).]

[\bar{C} with excess CaBr₂ refluxed for 40 hrs. (12) or actn. of HBr on ω -chloroallyl aryl ethers (23) (discussed above) gives (58% yield (12)) 3-bromo-1-chloropropene-1 (consts. given above); similarly \bar{C} with excess powdered CaI₂ shaken at room temp. for 20 hrs. gives (65% yield (12)) (14) 1-chloro-3-iodopropene-1 (consts. given above).]

[\bar{C} with NaOAc in AcOH at 110° for 16 hrs. ppts. NaCl (70% theory (12)) and gives (50% yield (12)) γ -chloroallyl acetate [Beil. II-136], b.p. 156-159° (10), b.p. 57° at 15 mm., $D_{-}^{17} = 1.140, n_{-}^{17} = 1.444$ (12).]

 \bar{C} reacts very slowly if at all with most metals: e.g., \bar{C} with Zn dust in boilg. acetone or C with Mg in dry ether (even in pres. of I_2 , EtBr, or HgCl₂) is inert (12); however, \bar{C} with Na in tetralin (1:7550) reacts violently giving only gaseous products (12), possibly including allene (propadiene-1,2) cf. (3) (31).

[$\bar{\mathbf{C}}$ reacts readily with aryl MgBr cpds., with replacement of its active halogen atom by the aryl radical: e.g., $\bar{\mathbf{C}}$ with C_0H_5Mg Br in toluene (26) or ether (32) gives (alm. 100% yield (26)) γ -chloroallylbenzene (1-chloro-3-phenyl-propene-1 (3:8737), b.p. 76° at 13 mm. (32), $D_4^{14} = 1.073$ (26), $n_D^{15} = 1.545$ (26). — For analogous reactns. of $\bar{\mathbf{C}}$ with o-tolyl-, p-tolyl-, p-cumyl-, 2-cymyl-, p-bromophenyl-, and p-methoxyphenyl-MgX cpds. see (26); for corresp. reactn. of $\bar{\mathbf{C}}$ with α -naphthyl MgBr see (34). — For reactn. of $\bar{\mathbf{C}}$ with n-propyl MgBr see (2).]

[For reactn. of Č with diethyl sodiomalonate giving (26% yield (4)) diethyl γ-chloroallylmalonate, with diethyl disodiomalonate giving (32% yield (4)) diethyl bis-(γ-chloroallyl)malonate, or with diethyl sodio-ethyl-malonate giving (20% yield (4)) diethyl γchloroallyl-ethyl-malonate see indic. refs.]

3:5280 (1) Hatch, Moore, J. Am. Chem. Soc. 66, 285-287 (1944). (2) Kirrmann, Grard, Compt. rend. 190, 876-878 (1930). (3) Hartenstein, J. prakt. Chem. (2) 7, 308-314 (1873). (4) Hill, Fischer, J. Am. Chem. Soc. 44, 2582-2595 (1922). (5) Friedel, Silva, Compt. rend. 75, 81-85 (1872). (6) Bon, Uchenye Zapiski Leningrad Gosudarst Univ., Ser. Khim. Nauk. 3, 3-37 (1938); Cent. 1939, II 366; C.A. 33, 3755 (1939). (7) Bert, Dorier, Bull. soc. chim. (4) 39, 1573-1575 (1926). (8) Hurd, Webb, J. Am. Chem. Soc. 58, 2191-2193 (1936). (9) Foldi, Ber. 60, 659-660 (1927). (10) Martinoff, Ber. 8, 1318-1319 (1875).

(11) Berthelot, Luca, Ann. chim. (3) 52, 437-438 (1858). (12) Kirrmann, Pačaud, Dosque, Bull. soc. chim. (5) 1, 860-871 (1934). (13) Reboul, Ann. chim. (3) 60, 37-38 (1860). (14) van Romburgh, Bull. soc. chim. (2) 36, 549-557 (1881); (2) 37, 98-103 (1882). (15) Carter, Science 97, 383-384 (1943). (16) du Pont Co., Brit. 429,949, July 11, 1935; Cent. 1936, I 4098; C.A. 29, 7073 (1935). (17) Reboul, Ann. Suppl. 1, 231 (1861). (18) Lilienfeld, French 758,359, Jan. 15, 1934; Cent. 1934, I 3653. (19) Tronow, Gerschewitsch, J. Russ. Phys.-Chem. Soc. 59, 727-739 (1927); Cent. 1928, I 2924. (20) Dorier, Compt. rend. 196, 1325-1327 (1933).

(21) Bert, Compt. rend. 192, 1565-1567 (1931); Cent. 1931, II 2318. (22) Bert, Andor, Compt. rend. 194, 1079-1081. (1932); Cent. 1932, I 3429. (23) Bert, Andor, Compt. rend. 194, 722-724. (1932); Cent. 1932, I 2447. (24) Bert, Compt. rend. 213, 797-798 (1941); Cent. 1942, II 1564; C.A. 67, 4710 (1943). (25) Bert, Compt. rend. 213, 619-620 (1941), Cent. 1942, II 30, C.A. 37, 4373 (1943). (26) Bert, Bull. soc. chim. (4) 37, 879-881 (1925); Compt. rend. 180, 1504-1506 (1925). (27) I.G., Dutch 52,449, May 15, 1942; Cent. 1942, II 1180. (28) von Braun, Kühn, Weismantel, Ann. 449, 254-265 (1926). (29) Ingold, Rothstein, J. Chem. Soc. 1929, 11-12. (30) Dorier, Compt. rend. 196, 1677-1678 (1933); Cent. 1933, II 1020; C.A. 27, 4222 (1933).

(31) Béhal, Ann. chim. (6) 16, 363-366 (1889). (32) von Braun, Kuhn, Ber. 58, 2171 (1925). (33) Bert, Dorier, Compt. rend. 191, 332-333 (1930); Cent. 1930, II 2376; C.A. 24, 5739 (1930). (34) Bert, Dorier, Bull. soc. chim. (4) 37, 1600-1602 (1925). (35) Bert, Compt. rend. 215, 356-357 (1942); C.A. 38, 3633 (1944).

B.P. 108° (1) 107-108° (2) 105-107° (3) (4) 106.1-107.1° at 739 mm. (5)

Oil with penetrating odor; fumes in moist air.

[For prepn. of \tilde{C} from dichloroacetic acid (3:6208) with PCl₃ (2), with HCl gas + P_2O_5 (7), with SOCl₂ (poor yield apparently because of much formation (9) of dichloro-acetic anhydride (3:6430)) (8) (9) (10) (11), with benzoyl chloride (3:6240) (73% yield (4)), or with benzotrichloride (3:6540) (12) (13) see indic. refs.; for prepn. of \tilde{C} from trichloroethylene (3:5170) by photochemical oxidn. (14) (15) (16) (3) (17) see indic. refs.; for prepn. of \tilde{C} from pentachloroethane (3:5880) with fumg. H_2SO_4 at 50-60° see (18); for prepn. of \tilde{C} from α,β -dichlorovinyl ethyl ether (3:5540) by actn. of Cl_2 see (19) (20).]

 $[\bar{C}$ with alcohols gives corresp. esters (for studies of rate of alcoholysis see (1) (21)); for reactn. of \bar{C} with various carbohydrates (22) and with cellulose (23) see indic. refs.; \bar{C} + phenol yields (20) phenyl dichloroacetate, m.p. 48°, b.p. 247.5° cor. (20); \bar{C} with β -naphthol yields (20) β -naphthyl dichloroacetate, m.p. 92-93° (20).]

[Č on warming with AlCl₃ yields (24) (25) 1,1,1,2,2,3,3-heptachloropropane (3:0200) + chloroform (3:5050) + CO + HCl.]

[$\tilde{\mathbf{C}}$ treated with dry HI gas at -5° gives (58% yield (5)) dichloroacetyl iodide, b.p. 54-54.5° at 15 mm. (5).]

Č with aq. hydrolyzes very rapidly yielding dichloroacetic acid (3:6208) q.v.; for the amide, anilide, p-toluidide, and other derivs. corresp. to Č see dichloroacetic acid (3:6208).

3:5290 (1) Branch, Nixon, J. Am. Chem. Soc. 58, 2499-2504 (1936). (2) Otto, Beckurts, Ber. 14, 1618-1619 (1881). (3) Erdmann, J. prakt. Chem. (2) 85, 78-89 (1912). (4) Brown, J. Am. Chem. Soc. 60, 1325-1328 (1938). (5) Gustus, Stevens, J. Am. Chem. Soc. 55, 374-377 (1933). (6) Vanderstichele, J. Chem. Soc. 123, 1228 (1923). (7) Frankland, Patterson, J. Chem. Soc. 73, 187 (1898). (8) Böeseken, Rec. trav. chim. 29, 99-100 (1910). (9) Blaise, Bull. soc. chim. (4) 15, 729 (1914). (10) Carré, Libermann, Compt. rend. 199, 1423 (1934).

(11) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (12) Mills (to Dow Chem. Co.), U.S. 1,921,767, Aug. 8, 1933; Cent. 1933, II 2595; C.A. 27, 5085 (1933). (13) Mills (to Dow Chem. Co.), U.S. 1,965,565, July 3, 1934; Cent. 1934, II 2899; C.A. 28, 5474 (1934). (14) Müller, Ehrmann, Ber. 69, 2207-2210 (1936). (15) Muller, Schumacher, Z. physik. Chem. B-37, 365-373 (1937). (16) Müller, Schumacher, Z. Elektrochem. 43, 807-808 (1937). (17) Consortium für Elektrochem. Ind., Ger. 391,674, Mar. 3, 1924, Cent. 1924, II 887; Ger. 340,872, Sept. 19, 1921; Cent. 1921, IV 1101; French 706,320, June 23, 1931; Cent. 1931, II 1489. (18) Chem. Fabrik Weiler-ter-Meer, Ger. 362,748, Oct. 31, 1922; Cent. 1923, II 405. (19) McKie, J. Chem. Soc. 123, 2214-2215 (1923). (20) Crompton, Triffett, J. Chem. Soc. 119, 1874-1875 (1921).

(21) Leimu, Ber. 70, 1046 (1937). (22) Bell, J. Chem. Soc. 1935, 1180-1182. (23) Barnett, J. Soc. Chem. Ind. 40, T-253-256, 274 (1921). (24) Ref. 8, p. 108. (25) Boeseken, Prins, Cent. 1911, I 466.

3:5300 1,1-DICHLORO-2-METHYLPROPENE-1 CH₃ C₄H₆Cl₂ Beil. I-209
$$(\alpha,\alpha$$
-Dichloroisobutylene) H_3 C—C=CCl₂ I_1 — I_2 —

B.P.
$$108.7-109.1^{\circ}$$
 (1) $D_0^{20} = 1.449$ (3) $108-109^{\circ}$ (2) $107.5-108.5^{\circ}$ (3)

Note: $\ddot{\mathbf{C}}$ by virtue of allylic transposition may yield derivatives of its synionic isomer 1,3-dichloro-2-methylpropene-1 (3:5590) q.v.

[For prepn. of \bar{C} from β,β,β -trichloro-ter-butyl acetate (3:6180) (85% yield (3) (2)) or from β,β,β -trichloro-ter-butyl alcohol ("Chloretone") (3:2662) (very poor yield (1)) with Zn dust in alc. see (1) (2) (3); for prepn. of \bar{C} from 1,1,1-trichloro-2-bromo-2-methyl-propane by htg. in quinoline (2), or from 1,1,1,2-tetrachloro-2-methyl-propane (3:4725) by htg. with K in tetralin (5% yield (2)), see (2).]

C with Br₂ yields (2) 1,2-dibromo-1,1-dichloro-2-methylpropane, m.p. 209° (s.t.) (2).

3:5300 (1) Bruyne, Davis, Gross, Physik. Z. 33, 720 (1932). (2) Jacob, Bull. soc. chim. (5) 7, 581-586 (1940); C.A. 36, 3507 (1942). (3) Favorskii, Jozitsch, Cent. 1899, I 778. (4) Jozitsch, Cent. 1899, I 606.

3:5310 DICHLOROACETALDEHYDE ETHYL
$$C_4H_8O_2Cl_2$$
 Beil. I - 614 ALCOHOLATE C_1 OH I_1 — I_2 —(677) hemiacetal) C_1 C_1 C_2 — C_2H_5 C_1 C_2 — C_3 — C_4 — C_4 — C_5 — C_5 — C_5 — C_5 — C_6 — C_7 —

Oil, spar. sol. aq. or lgr. but misc. with alc., C6H6, CHCl3.

[For prepn. of \bar{C} from dichloroacetaldehyde (3:5180) with a limited amt. abs. EtOH see (1).]

C readily changes to dichloroacetaldehyde diethylacetal (3:6110), b.p. 184°, and dichloroacetaldehyde hydrate (3:1085), m.p. 56°.

Č with boilg, aq. HCl yields (1) 2,2-dichloroethanol-1 (3:5745) + acetaldehyde (1:0100).

Č with powdered KCN (1 mole) in EtOH at 20° for 5 mm., then poured into aq., gives (38% yield (2)) ethyl chloroacetate (3:5700), b.p. 144°.

[For condensations of \bar{C} with phenol (3), p-nitrophenol (3), p-hydroxybenzoic acid (4), or p-methoxybenzoic acid (6) to yield substituted benzdioxins see indic. refs.]

Č in AcOH on warming with 2 moles phenylhydrazine yields (5) glyoxal bis-phenylosazone, yel. pl. from boilg. alc., m.p. 169-171° (5).

3:5310 (1) Oddo, Mameli, Gazz. chim ital 33, II 399-408 (1903). (2) Chattaway, Irving, J. Chem. Soc. 1929, 1042-1043. (3) Chattaway, Morris, J. Chem. Soc. 1928, 3241-3246. (4) Chattaway, Farinholt, J. Chem. Soc. 1931, 1737-1740. (5) Chattaway, Farinholt, J. Chem. Soc. 1931, 1828-1834.

3:5315 DICHLOROMETHYL CHLOROFORMATE
$$C_2HO_2Cl_3$$
 Beil. III — (Dichloromethyl chlorocarbonate) Cl_2CH — C — C III_1 -(6) III_2 -(11)

B.P. 110-111° at 760 mm. (1)
$$D_{-}^{17} = 1.558$$
 (2) $n_{D}^{22} = 1.44322$ (2) 111° (2) 114° (4) $D_{-}^{15} = 1.560$ (1) 54-55° at 100 mm. (1) 46° at 62 mm. (2)

See also text.

[See also chloromethyl chloroformate (3:5275).]

Colorless lachrymatory oil. — Note that \bar{C} cannot by distillation be completely separated from chloromethyl chloroformate (3:5275); the constants listed above from (2) represent preprs. contg. about 2.5% chloromethyl chloroformate (3:5275).

A mixt. of \bar{C} with chloromethyl chloroformate (3:5275) has been employed as a chem. warfare agent under the names "K-Stoff" or "Palite" (3).

[For prepn. of C from methyl chloroformate (3:5075) or from methyl formate (1:1000) with Cl₂ under various conditions see (1) (2) cf. (3) (4).]

 \bar{C} with aq. at ord. temp. or more rapidly on boilg., or \bar{C} with aq. alk. in cold, undergoes hydrolysis (1) yielding quantitatively CO + CO₂ + 3HCl; note that formaldehyde is not formed [dif. from chloromethyl chloroformate (3:5275)].

 \tilde{C} (1 mole) with NaI (2 moles) in dry acctone at 20° (5) liberates both I₂ and CO quant. according to the equation $2\tilde{C} \rightarrow I_2 + 2CO + 2NaCl + HCl$ [compare behavior of methyl

chloroformate (3:5075) which gives no I_2 and that of chloromethyl chloroformate (3:5275) trichloromethyl chloroformate ("diphosgene") (3:5515), and bis-(trichloromethyl)-carbonate ("triphosgene") (3:1915) all of which also give I_2]. — \bar{C} with NaBr or LiBr in dry acetone behaves in analogous fashion (5) setting free Br₂; in this respect \bar{C} is like trichloromethyl chloroformate ("diphosgene") (3:5515) but unlike methyl chloroformate (3:5075) or chloromethyl chloroformate (3:5275).

[C with FeCl₃ or AlCl₃ dec. even in cold or rapidly at 80° giving (1) phosgene (3:5000) + CO + HCl.]

[Č with aq. sodium phenolate reacts as an acid chloride giving (1) dichloromethyl phenyl carbonate, b.p. 124-125° at 14 mm., m.p. 14.5° (1).]

 $[\bar{C}]$ with aniline in aq. or C_6H_6 gives (1) both N,N-diphenylures and formanilide.

3:5315 (1) Kling, Florentin, Lassieur, Schmutz, Compt. rend. 169, 1046-1047 (1919); Ann. chim. (9) 13, 44-59 (1920). (2) Grignard, Rıvat, Urbain, Compt. rend. 169, 1074-1077 (1919); Ann. chim. (9) 13, 248-251 (1920). (3) Sartori, "The War Gasses," pp. 104-109, 123-124, D. Van. Nostrand Co, Inc., New York City, 1940. (4) Hood, Murdock, J. Phys. Chem. 23, 509-511 (1919). (5) Perret, Biechler, Compt. rend. 203, 86 (1936) Bull. soc. chim. (5) 3, 350 (1936).

3:5320
$$d,l$$
- α -CHLOROPROPIONYL CHLORIDE Cl C₃H₄OCl₂ Beil. II - 249 CH₃-C C=O II₁- II₂- II₂-

B.P.
$$110.7-111.2^{\circ}$$
 at 760 mm. (1) $D_4^{20}=1.2851$ (1) $n_D^{20}=1.43965$ (1) $109-110^{\circ}$ at 744 mm. (2) $107-110^{\circ}$ (3)

[For prepn. of \bar{C} from α -chloropropionic acid (3:6125) with SOCl₂ see (1); from propionic acid (1:1025) with SO₂Cl₂ + I₂ (4) (no β -chloropropionyl chloride being formed) or with SO₂Cl₂ + Bz₂O₂ in CCl₄ (45% yield \bar{C} + 55% yield β -chloropropionyl chloride (3:5690)) see (4); from propionyl chloride (3:7170) with Cl₂ + I₂ (45% yield (3)) (5) see indic. refs.; from calcium lactate (6) or anhydrous lactic acid (1:0400) (7) with PCl₅ see indic. refs.]

 \bar{C} on hydrolysis with aq. yields α -chloropropionic acid (3:6125); for the amide, anilide, p-toluidide, and other derivs. corresp. to \bar{C} see 3:6125.

3:5320 (1) Leimu, Ber. 70, 1049 (1937). (2) Henry, Compt. rend. 100, 116 (1885); J. prakt. Chem. (2) 31, 127 (1885). (3) Wolffenstein, Rolle, Ber. 41, 735 (1908). (4) Kharasch, Brown, J. Am. Chem. Soc. 62, 927-928 (1940). (5) Michael, Ber. 34, 4035, 4037 (1901). (6) Wurts, Ann. 107, 194 (1858). (7) Bruhl, Ber. 9, 35 (1876).

3:5330 1,1,2-TRICHLOROETHANE (unsym.-Trichloroethane, chloroethylidene (di)chloride)

F.P.

[114.2° at 757.7 mm. (1)]
$$-37.4^{\circ}$$
 (8)

114° at 760 mm. (2) -35.5° (5)

113.65° at 760 mm. (4)

113.5° at 760 mm. (8)

113.3° cor. at 760 mm. (8)

113.2° (9)

112.5-113° (10)

Care must be taken to avoid confusion of \tilde{C} with the isomeric 1,1,1-trichloroethane (3:5085). \tilde{C} is now comml. prod. in U.S. (14).

MISCELLANEOUS PHYSICAL PROPERTIES

Various solubility relationships. \bar{C} is almost insol. aq.: e.g., 100 g. aq. at 0° dis. 0.466 g. \bar{C} , at 20° 0.436 g. \bar{C} , at 35° 0.458 g. \bar{C} , at 55° 0.532 g. \bar{C} (15). — [For soly. of aq. in \bar{C} at 0°, 25°, and 30° (as detd. by Karl Fischer reagt.) see {16}.]

[For solv. of HCl gas in C at various temps. and press. see (10).]

[For soly. of I_2 in \bar{C} see (17).]

Binary systems contg. \bar{C} . (See also below under uses of \bar{C} .) \bar{C} + 1,2-dichloroethane (ethylene dichloride) (3:5130): for f.p./compn. data, eutectic f.p. -79° (11), and for D and vapor/liq. equil. (13), see indic. refs.

Azeotropes contg. C. C with EtOH (1:6130) forms a const.-boilg. mixt., b.p. 77.8° (4), 77.3° (6) at 760 mm., contg. 35 (6), 30 (4) wt. % C.

Other physical props. [For study of thermal conductivity of \bar{C} sec (18).]

USES OF C

 \bar{C} is now widely used as industrial solvent and in other ways [e.g., for use of \bar{C} (40%) 1,1,1-trichloroethane (3:5085) + 20% pet. hydrocarbons as dry-cleaners' solv. see (19); for use of \bar{C} + ethylene dichloride (3:5130) as hair wash see (20); for use of \bar{C} + n-heptane (1:8575), \bar{C} + cyclohexane (1:8405), or \bar{C} + C_6H_6 (1:7400) as test mixts. for detn. of number of theoret. pl. in fractionating columns see (21); for use of \bar{C} in dewaxing of oils see (22)].

PHYSIOLOGICAL ACTION AND TOXICITY

Full treatment of this topic is beyond the scope of this work [however, for lead references see (23) (24) (25) (26) (27) (67). — For study of Č as anthelmintic see (28)].

PREPARATION OF C

From vinyl chloride (3:7010). (See also below under acetylene.) [For prepn. of Č from vinyl chloride with Cl₂ at 0-80° in light or at 180-250° in absence of light or solv. see (29) (30) (31) cf. (32); for study of photochemical addn. of Cl₂ to vinyl chloride yielding Č see (33).]

From 1,2-dichloroethylene (3:5030). [For prepn. of \tilde{C} from 1,2-dichloroethylene by addn. of HCl gas at 30-40° in pres. of AlCl₃ (88% yield) see (34) (37) (note that 1,1,2,3,4-pentachlorobutane (3:0750) is also obtd. as a by-product (35)).]

From 1,1-dichloroethane (ethylidene (di)chloride) (3:5035). [For formn. of C from ethylidene (di)chloride with SbCl₅ (3 wt. parts) on refluxing see (36).]

From 1,2-dichloroethane (ethylene (di)chloride) (3:5130). [For prepn. of \bar{C} from ethylene (di)chloride with Cl₂ in ultra-violet light at 50° (38) (39) or 25° (40), or with Cl₂ + suitable cat. at not above 60° (41), or \bar{C} (as liquid) with Cl₂ (7), or with Cl₂ in pres. of AlCl₃/NaCl/FeCl₃ at 300-425° as directed (42), or with SO₂Cl₂ + trace dibenzoyl peroxide refluxed 2 hrs. in dark (12) (yields: 80% (41), 70% (40) (12), 50% (42)), see indic. refs.]

From ethylene. [For prepn. or formn. of \tilde{C} from ethylene with Cl_2 + cat. see (43) (44) (45) (46) (47).]

From acetylene. [For prepn. of \bar{C} from acetylene with $HCl + Cl_2 + cat$. (doubtless via formn. of vinyl chloride (and subsequent addn. of Cl_2 as above) see (48) (30).]

From other sources. [For formn. of \bar{C} as by-prod. of prepn. of chloral (3:5210) see (49); for prepn. of \bar{C} from 2,2-dichloroethanol-1 (3:5745) with PCl₅ (50), or from α,β -dichloroethyl chloroformate by loss of CO under influence of AlCl₃ (51), see indic. refs.; for formn. of \bar{C} from trichloroethylene (3:5170) with HI for 2 weeks in sunlight see (68).]

CHEMICAL BEHAVIOR OF C

Dehydrochlorination. \bar{C} under suitable conditions may lose HCl in either or both of two modes yielding either or both 1,1-dichloroethylene (vinylidene (di)chloride) (3:5005) or a mixt. of the stereoisomeric 1,2-dichloroethylenes (3:5030). — [E.g., \bar{C} with alc. KOH (52) (53) (54), or with excess aq. Ca(OH)₂ at 70-80° (55) (56), or with aq. or alc. NH₃ (57), or even with Na in ether (58) gives (yields: 100% (57), 90% (55) (56)) 1,1-dichloroethylene (3:5005). — On the other hand, \bar{C} pyrolyzed at 400° over pumice contg. CuCl₂ (59) is claimed to give mainly 1,2-dichloroethylene (3:5030). — Note also that \bar{C} with MeOH over Al₂O₃ at 290° gives (60) a mixt. of both prods. together with MeCl (3:7005).]

[Note in this connection that \bar{C} with aq. + Zn, Fe, or Al at 100–120° under press. yields (61) vinyl chloride (3:7010); perhaps this occurs by way of the above dichloroethylenes as intermediate.]

Halogenation of \bar{C} . Chlorination. $[\bar{C} \text{ with } Cl_2 + AlCl_3 \text{ at } 70-80^{\circ} \text{ yields (62) } 1,1,2,2-$ tetrachloroethane (acetylene tetrachloride) (3:5750).]

Fluorination. [\bar{C} with HgF₂ under press. at 140° gives (63) 50% 1,2-dichloro-1-fluoro-ethane + 10% 2-chloro-1,1-difluoroethane; for behavior of \bar{C} with SbF₃ + Br₂ at 160°, with SbF₃ + SbCl₅, or with SbF₃Cl₂ see (63).]

Behavior of C with other inorganic reactants. [C with alkali hydroxide on fusion at 250-300° yields (64) salts of glycolic acid (1:0430).]

Behavior of \tilde{C} with organic reactants. [\tilde{C} with 1,2-dichloroethylene (3:5030) + 1% AlCl₃ at 35-40° for 5 days yields (37) a mixt. of two stereoisomeric 1,1,2,3,4-pentachlorobutanes, viz., the liq. isomer (3:9068) and the solid isomer (3:0750). — \tilde{C} + trichloroethylene (3:5170) + 1-2% AlCl₃ at 40° for 7 days yields (37) 1,1,1,4,4-pentachlorobutene-2 (3:9054).]

[\bar{C} with C_6H_6 + AlCl₃ gives (31% yield (65)) 1,1,2-triphenylethane, b.p. 211° at 14 mm., accompanied by diphenylmethane and 1,2-diphenylethylene (stilbene).]

[C with C6H5MgBr in toluene does not react even at 100° (66).]

Comment on Fujiwara reaction. Č does not respond to Fujiwara reactn. (pyridine + NaOH) (23).

3:5330 (1) Pierre, Ann. 80, 127 (1851). (2) Mumford, Phillips, J. Chem. Soc. 1928, 159. (3) Staedel, Ber. 15, 2563 (1882). (4) Lecat, Ann. soc. sci. Bruxelles 47, I, 112 (1927); Cent. 1927, II 1677. (5) Timmermans, Bull. soc. chim. Belg. 27, 334-343 (1913); Cent. 1914, I 618. (6)

Lecat, "L'Azeotropisme," 1918, p. 84. (7) Hamai, Bull. Chem. Soc. Japan 9, 542-548 (1934).
(8) Henne, Hubbard, J. Am. Chem. Soc. 58, 404 (1936). (9) Köhlrausch, Koppl, Monatsh. 65, 197 (1935). (10) Hamai, Bull. Chem. Soc. Japan 10, 207-211 (1935).

(11) Timmermans, Vesselovsky, Bull. soc. chim. Belg. 40, 505 (1931). (12) Kharasch, Brown, J. Am. Chem. Soc. 61, 2145 (1939). (13) Portnov, Seferovich, Trans. State Inst. Applied Chem. (U.S.S.R.) 24, 81-89 (1935); not in Cent.; C.A. 29, 7272 (1935). (14) McLure, Chem. Eng. News 22, 421 (1944). (15) van Arkel, Vles, Rec. trav. chim. 50, 836-841 (1941); Cent. 1942, I 1352; C.A. 37, 2638 (1943). (16) Staverman, Rec. trav. chim. 60, 836-841 (1941); Cent. 1942, I 1352; C.A. 37, 2638 (1943). (17) Margosches, Hinner, Friedmann, Z. anorg. allgem. Chem. 137, 87-90 (1924). (18) Bates, Hazzard, Palmer, Ind. Eng. Chem. 33, 375-376 (1941). (19) Parkhurst (to Standard Oil of California), U.S. 1,948,045, Feb. 20, 1934; Cent. 1934, II 863; C.A. 28, 2924 (1934). (20) Cathala, French 598,518, Dec. 18, 1925; Cent. 1926, I 2752; not in C.A.

(21) Stage, Schultze, Oel u. Kohle 40, 90-95 (1944); C.A. 38, 6134 (1944). (22) Sharples Specialty Co., French 801,583; Aug. 7, 1936; Cent. 1937, I 263; C.A. 31, 535 (1937). (23) Barrett, Cunningham, Johnston, J. Ind. Hyg. Toxicol. 21, 479-480 (1939). (24) von Oettingen, J. Ind. Hyg. Toxicol. 21, 479-480 (1939). (24) von Oettingen, J. Ind. Hyg. Toxicol. 39, 398-399 (1937). (25) Schwander, Arch. Gewerbepathol. Gewerbehyg. 7, 109-116 (1939); Cent. 1938, II 1331; not in C.A. (26) Barsoun, Saad, Quart. J. Pharm. Pharmacol. 7, 205-214 (1934); Cent. 1934, II 2550; C.A. 28, 6194 (1934). (27) Lazarev, Arch. expll. Path. Pharmakol. 141, 19-24 (1929); Cent. 1929, II 451; C.A. 25, 3074 (1931). (28) Wright, Schaffer, Am. J. Hyg. 16, 372-374 (1932). (29) Ernst, Lange (to I G.), U.S. 1,833,358, 1,833,393, Nov. 24, 1931; C.A. 26, 1301 (1932): Ger. 489,454, Jan. 17, 1930, [Cent. 1930, I 3829; C.A. 24, 2145 (1930)]: Brit. 298,084, Nov. 28, 1928; Cent. 1929, I 1396, C.A. 23, 2724 (1929). (30) I.Ç., French 690,655, Sept. 24, 1930; Cent. 1931, I 1164; C.A. 25, 1264 (1931): Brit. 349,097, March 11, 1029; C.A. 26, 5314 (1932); not in Cent.

(31) Consortium fur Elektrochem. Ind., French 690,767, Sept. 25, 1930; Cent. 1931, I 1164; C.A. 25, 1264 (1931). (32) Biltz, Ber. 35, 3526-3527 (1902). (33) Schmitz, Schumacher, Z. physik. Chem. B-52, 73-80 (1942). (34) Prins, Rec. trav. chim. 45, 80-81 (1926). (35) Muller, Hönn, J. prakt. Chem. (2) 133, 289-290 (1932). (36) Moyer, Muller, J. prakt. Chem. (2) 46, 174-175 (1892). (37) Prins, Rec. trav. chim. 56, 119-125 (1937). (38) Coleman, Moore (to Dow Chem. Co.), U.S. 2,174,737, Oct. 3, 1939; C.A. 34, 779 (1940). (39) Compagnie des Prod. Chim. d'Alais, etc., French 804,491, Oct. 24, 1936; Cent. 1937, I 1545; C.A. 31, 3509 (1937). (40) Maier, Ger. 522,959, April 20, 1931, [Cent. 1931, I 3607]; C.A. 25, 3670 (1931). French 655,930, April 25, 1929; Cent. 1929, II 1347; C.A. 23, 3931 (1929).

(41) Jung, Zimmermann, Ger. 545,993, March 8, 1932; Cent. 1932, I 2893; C.A. 26, 3520 (1932). (42) Reilly (to Dow Chem. Co.), U.S. 2,140,549, Dec. 20, 1938, Cent. 1939, I 3625, C.A. 33, 2540 (1939). (43) Gavat, Ber. 76, 1115-1118 (1943); C.A. 38, 4901 (1944). (44) Golev, Sbornik Dikhloretan 1939, 18-20; C.A. 36, 2523 (1942). (45) Bahr, Zieler, Z. angew. Chem. 43, 233-236 (1930). (46) Stewart, Smith, J. Am. Chem. Soc. 51, 3082-3095 (1929). (47) Askenasy, Heller, Ger. 549,341, April 26, 1932; Cent. 1932, II 286; C.A. 26, 3807 (1932). (48) I.G., French 687,307, Aug. 7, 1930; Cent. 1930, II 3637; C.A. 25, 715 (1931); Brit 344,592, Jan. 31, 1929; C.A. 26, 155 (1932); not in Cent. (49) Kraemer, Ber. 3, 261 (1870). (50) Delacre, Compt. rend. 104, 1186 (1887).

(51) Muller, Ann. 258, 58 (1890). (52) Brockway, Beach, Pauling, J. Am. Chem. Soc. 57, 2695 (1935). (53) Regnault, J. prakt. Chem. (1) 18, 82-85 (1839); Ann. chim. (2) 69, 155-159 (1838). (54) Klimont, Chem. Ztg. 46, 521 (1922). (55) I.G., Brit. 349,872, July 2, 1931; Cent. 1931, II 1191; C.A. 26, 5314 (1932); French 702,361, April 7, 1931; Cent. 1931, II 1191; C.A. 25, 4285 (1931); Ger. 529,604, July 4, 1929; C.A. 25, 5178 (1931); not in Cent. (56) Howell (to Imp. Chem. Ind., Ltd.), Brit. 534,733, March 17, 1941; C.A. 36, 1336 (1942). (57) Engel, Bull. soc. chim. (2) 48, 97 (1887). (58) Brunner, Brandenburg, Ber. 10, 1497-1499 (1877); 11, 61-62 (1878). (59) Hermann, Baum (to Consortium für Elektrochem. Ind.), U.S. 1,921,879, Aug. 8, 1933; (C.A. 27, 5086 (1933)), not in Cent.: Ger. 570,954, Feb. 22, 1933; C.A. 27, 4252 (1933); not in Cent.: French 694,054, Nov. 28, 1930; Cent. 1931, I 1514, [C.A. 25, 1843 (1931)]. (60) I.G., French 805,563, Nov. 24, 1936; Cent. 1937, I 2258; [C.A. 31, 4345 (1937)].

(61) I.G., Ger. 525,309, May 21, 1931; Cent. 1931, II 1055; C.A. 25, 4012 (1931): French 703,767, May 6, 1931; Cent. 1931, II 1055; [C.A. 25, 4557 (1931)]. (62) Tzurikh, Trans. State Inst. Applied Chem. (U.S.S.R.) 24, 77-80 (1935); C.A. 29, 7272 (1935); not in Cent. (63) Henne, Renoll, J. Am. Chem. Soc. 58, 889-890 (1936). (64) Strosacker, Pelton (to Dow Chem. Co.), U.S. 1,884,354, Oct. 25, 1932; Cent. 1933, I 307; [C.A. 27, 1006 (1933)]. (65) Bert, Compt. rend. 213, 792-793 (1941); Cent. 1942, II 1785; C.A. 37, 4065 (1943). (66) Bert, Bull. soc. chim. (4) 41, 1173 (1927). (67) Lehman, Schmidt-Kehl, Arch. Hyg. Bakt. 116, 131-268 (1936); C.A. 31, 477 (1937); not in C.A. (68) Kharasch, Norton, Mayo, J. Org. Chem. 3, 49-50 (1938).

3:5345-3:5350

3:5345 3,3,3-TRICHLOROPROPENE-1
$$Cl_3C$$
— CH — CH_2 $C_3H_3Cl_3$ Beil. I-200 (1,1,1-Trichloropropene-2) I_1 — I_0 —

B.P. M.P. 114-115° at 760 mm. (1)
$$-30^{\circ}$$
 (2) $D_{20}^{20} = 1.369$ (1) $n_{\rm D}^{20} = 1.4827$ (3) 114-115° at 757 mm. (2) $-55--50^{\circ}$ (1) (5) (5) (5) $D_{3}^{13} = 1.359$ (2)

Liquid with penetrating odor suggesting aldehydes. [For use in dewaxing of mineral oil see (4).]

[For prepn. of \overline{C} from 1,1,1-trichloropropanol-2 (3:0846) (84% yield (3)) with P_2O_5 (3) (2) (1), with PCl_3 (5) (1), or with PCl_5 (5) (1) see indic. refs.]

Č in cold and in diffused light adds Cl₂ yielding (2) 1,1,1,2,3-pentachloropropane (3:4740), m.p. 179-180° (2). — Č adds Br₂ readily yielding (2) 1,1,1-trichloro-2,3-dibromopropane [Beil. I-112], cryst. from alc., m.p. 210° (2).

 \tilde{C} with HCl + FeCl₃ at 50° for 50-100 hrs. gives (20% yield (3)) 1,1,1,2-tetrachloro-propane (3:5785). — [For study of addn. to \tilde{C} of HBr see (3).]

3:5345 (1) Henry, Bull. acad. roy. Belg. 1905, 101-121; Cent. 1905, I 1697. (2) Victoria, Rec. trav. chim 24, 280-283 (1905). (3) Kharasch, Rossin, Fields, J. Am. Chem. Soc. 63, 2558-2560 (1941). (4) Standard Oil Development Co, French 790,852, Nov. 28, 1935; Cent. 1936, I 2672; C.A. 30, 3223 (1936). (5) Henry, Rec. trav. chim. 24, 336-344 (1905).

B.P.
$$115^{\circ}$$
 (1) $n_{\rm D}^{30.5} = 1.4550$ (1) $45-45.5^{\circ}$ at 40 mm. (1)

[For prepn. of \tilde{C} (together with other products) from butadiene-1,3 with Cl_2 , either directly or in CHCl₃, CS_2 or lgr. soln., see (1) (2); the process can be controlled so as to yield little or no 1,2,3,4-tetrachlorobutane but rather a mixt. of \tilde{C} and 1,4-dichlorobutene-2 (3:5725) in the ratio 2:1 (1) (2).]

C does not (1) rearr. to 1,4-dichlorobutene-2 (3:5725) even on htg. at 90° in a s.t. — However, C in the presence of a metal halide cat. (3) such as AlCl₃ (4) rearr. by allylic transposition to 1,4-dichlorobutene-2.

Č on htg. at 90° with 2 pts. solid KOH loses HCl yielding (1) (2) 1-chlorobutadiene-1,3 (3:7210), b.p. 85° (1) (2); under certain conditions, however, Č with KOH loses HCl to yield (5) 2-chlorobutadiene-1,3 (chloroprene) (3:7080).

Č on htg. in alc. with Zn dust yields (1) butadiene-1,3.

 $\tilde{\mathbf{C}}$ with \mathbf{Cl}_2 yields solely (1) the liq, isomer of 1,2,3,4-tetrachlorobutane (3:9082).

 \bar{C} treated directly with O_3 at 0° , then with aq., yields (1) α,β -dichloropropionaldehyde (3:9034), b.p. 73° at 50 mm. (1), + formaldehyde (1:0145). — \bar{C} on oxidn. with dil. alc. KMnO₄ gives (1) α,β -dichloropropionic acid (3:0855), m.p. 50° (1).

3:5350 (1) Muskat, Northrup, J. Am. Chem. Soc. 52, 4043-4055 (1930). (2) Muskat (to du Pont), U.S. 2,038,593, Apr. 28, 1936; Cent. 1936, II 3358; C.A. 30, 3912 (1936). (3) I.G. Farbenindustrie, Brit. 505,573, May 12, 1939; Cent. 1939, II 1572; C.A. 33, 7822 (1939). (4) Nicodemus (to I.G.), U.S. 2,242,084, May 13, 1941; C.A. 35, 5134 (1941). (5) Carothers (to du Pont), U.S. 2,038,538, Apr. 28, 1936; Cent. 1936, II 3358; C.A. 30, 3838 (1936).

3:5356 CHLOROMETHYL ACETATE CH₃.CO.O.CH₂Cl C₃H₅O₂Cl Beil. II - 152

п₁---П₂-(166)

```
B.P. 115-116^{\circ} at 757 mm. (1) D_{14,2}^{14,2}=1.1953 (1) (13) 115^{\circ} at 757 mm. (13) 115^{\circ} (5) 113-115^{\circ} (2) (12) 110-112^{\circ} (3) 58-62^{\circ} at 290 mm. (4)
```

Colorless liq. with penetrating odor. — Insol. cold aq.; sol. alc., ether. — Sol. in cold conc. H_2SO_4 with evolu. of HCl (1) (13).

[For prepn. of \bar{C} from methyl acetate (1:3005) with Cl₂ in cold (1) (5) and in sunlight (2) (6), or with SO_2Cl_2 in sunlight (6), see indic. refs.; from polyoxymethylene with AcCl (3:7065) in s.t. at 100° (6) or by htg. in pres. of $ZnCl_2$ (61% yield on AcCl (4)) cf. (7) (8) (note that crude \bar{C} may be more or less contaminated with bis-(chloromethyl ether) (3:5245), b.p. 105°, and Ac₂O (1:1015), b.p. 140°, apparently produced by disproportionation of \bar{C} itself during the htg. (7).]

C on slight warming with aq. readily dissolves by virtue of hydrolysis, yielding (1) (5) (3) formaldehyde (1:0145), AcOH (1:1010), and HCl.

[Č with alcs. or Na alcoholates (10) presumably first yields alkoxymethylacetates: e.g., Č with Na benzylate in C₆H₆ refluxed for 4 hrs. gives (15% yield 4)) benzyloxymethyl acetate, b.p. 152-155° at 29 mm. (4); however, the usual type of prod. consists of a mixture of formaldehyde dialkylacetal and alkyl acetate (perhaps formed by interchange of radicals between the initial product and the alcohol (9)): e.g., Č with benzyl alc. (1:6480) gives (9) (10) (13) formaldehyde dibenzylacetal, b.p. 188-190° at 13 mm., + benzyl acetate (1:3751), b.p. 217°; Č with n-propyl alc. (1:6150) gives (9) (13) formaldehyde din-propylacetal [Beil. I-575, I₁-(301), I₂-(639)], b.p. 137° at 760 mm., + n-propyl acetate (1:3075), b.p. 101.6°; for analogous behavior of Č with MeOH (1:6120) and EtOH (1:6130) see (10).]

[C with Na phenolate does not yield phenoxymethyl acetate but instead (45% yield (11)) phenyl acetate (1:3571); this may be accounted for in a fashion completely analogous to that suggested above in the case of alcs., but no attempt was made (11) to verify the pres. of formaldehyde diphenylacetal (diphenoxymethane) although the latter [Beil. VI-150] is well known.]

 $\bar{\mathbf{C}}$ with NH₃ in dry ether gives {12} {13} acetamide, NH₄Cl + formaldehyde (often in the form of hexamethylenetetramine {13}). — $\bar{\mathbf{C}}$ with aniline (1.5 moles) in dry ether gives (80% yield {12}) acetanilide, m.p. 114–115°, + 1,3,5-triphenyltrimethylenetriamine ("anhydroformaldehydeaniline") [Beil. XXVI-3], yel. pr., m.p. 140–141° (produced by actn. of the liberated formaldehyde upon the excess of aniline). — $[\bar{\mathbf{C}}$ (1 mole) with N,N-dimethylaniline (2 moles) + ZnCl₂ at 110–120° gives (5) salt of 4,4'-bis-(dimethylamino)-diphenylmethane [Beil. XIII-239, XIII₁-(71)], m.p. 91°.]

Č with pyridine forms an unstable addn. cpd. (12); Č with quinoline forms (12) an addn. cpd., m.p. 214-216° dec., eas. sol. in abs. alc. but easily pptd. with dry ether (12).

[Č with N-potassiopyrrole in dry ether gives (18% yield (14)) N-pyrrylmethyl acetate, b.p. 59-63.5° at 3 mm., $D_{\rm s}^{20} = 1.0916$, $n_{\rm D}^{20} = 1.4907$ (14).]

[For study of rate of reactn. of C with KI in acetone at 20° and 25° see (2).]

3:5356 (1) Henry, Ber. 6, 740-741 (1873). (2) Conant, Kirner, Hussey, J. Am. Chem. Soc. 47, 497, 499 (1925). (3) Descude, Compt. rend. 132, 1568 (1901). (4) Gupta, Kaushal, Deshapande, J. Indian Chem. Soc. 18, 638-640 (1941). (5) Censi, Bull. soc. ind. Mulhouse 76, 311-

313 (1899); Cent. 1906, I 594-595. (6) Henry, Bull. acad. roy. Belg. 1906, 48-56; Cent. 1906, I 1122-1123. (7) Descude, Bull. soc. chim. (3) 27, 867-869 (1902); Compt. rend. 132, 1568 (1901). (8) Henry, Compt. rend. 133, 97 (1901). (9) Descude, Bull. soc. chim. (3) 27, 47-48 (1903). (10) Descude, Bull. soc. chim. (3) 27, 1215-1219 (1902).

(11) Kirner, J. Am. Chem. Soc. 48, 2748 (1926). (12) Ulich, Adams, J. Am. Chem. Soc. 43, 663, 665-666 (1921). (13) Descude, Ann. chim. (7) 29, 504-508 (1903). (14) Taggart, Richter, J. Am. Chem. Soc. 56, 1386 (1934).

3:5358 3-CHLORO-1,2-EPOXYPROPANE ("Epichlorohydrin";
$$\gamma$$
-chloropropylene oxide; (chloromethyl)ethylene oxide) CH₂Cl C_3H_5OCl Beil. XVII - 6 XVII₁-(4)

B.P			M.P.			
[118-119°	(1	(50)]	-48°	(10)	$D_4^{25} = 1.17495 (23)$	
117°	(2) (3) (4) (5)			1.1723 (24)	
116.5-117.5°	at 765 mm.	(6)			$n_{\rm D}^{25} = 1.43585$	(23)
116.75-117.00	° at 762.2 mm	. (7)			$D_4^{20} = 1.184 \qquad (26)$	
116.56°	at 760 mm.	(7)			1.1812 (10)	
116.5°	at 761 mm.	(8)			1.181 (17)	
116.45°	at 760 mm.	(9)			1.1801 (25)	
117°	at 758 mm.	(10)			1.18 (18)	
117° cor.	at 755 mm.	(11)			$n_{\rm D}^{20}=1.4382$	(26)
116-118°		(12)			1.438	(17)
116-117°	at 760 mm.	(13)			$D_4^{16.1} = 1.1848 (25)$	
116°		(14) (1	.5)		$n_{\rm D}^{161}=1.43969$	(25)
115-117°		(16)			$D_4^{11.5} = 1.1928 (26)$	
115-116°		(17) (1	l8) (4 8)		$n_{\rm D}^{11.5}=1.44195$	(26)
115.4°	at 764 mm.	(19)				
115° cor.	at 740 mm.	(20)				
		(21)				
60-61°	at 100 mm.	(17)				
30-32°	at 10 mm.	(22)				

 $\bar{\mathbf{C}}$ is also sometimes designated as " α -epichlorohydrin" to distinguish it from the less common " β -epichlorohydrin" = β -chlorotrimethylene oxide.

 $\ddot{\mathbf{C}}$ is liq. with odor suggesting chloroform. — $\ddot{\mathbf{C}}$ is spar. sol. aq. (see also below) but misc. with alc. or ether.

MISCELLANEOUS PHYSICAL PROPERTIES

Solubility relations. \tilde{C} with aq. forms two layers: the lower layer conts. the following no. of g.'s \tilde{C} per 100 g. satd. soln.: at 25° 98.48 g., at 45° 97.43 g., at 70° 95.82 g., at 80.4° 94.17 g.; the upper layer conts. per 100 g. satd. soln.: at 30.2° 6.60 g., at 52.0° 7.53 g., at 65.0° 8.45 g., at 72.0° 9.34 g., at 80.2° 10.43 g. (5).

Binary azeotropes contg. \bar{C} . \bar{C} with aq. forms a homogeneous const. boilg. mixt., b.p. 88°, contg. 75% \bar{C} ; at 25° this azeotrope seps. into two layers contg. respectively 98% \bar{C} and 7% \bar{C} (17).

[$\bar{\mathbf{C}}$ with AcOH (1:1010) forms (9a) a const.-boilg. mixt., b.p. 115.05° at 760 mm., contg. 65.5 wt. % $\bar{\mathbf{C}}$; $\bar{\mathbf{C}}$ with tetrachloroethylene (3:5460) forms (9b) a const.-boilg. mixt., b.p. 110.12° at 760 mm., contg. 51.5 wt. % $\bar{\mathbf{C}}$.]

[Note that \bar{C} with EtOH (1:6130) (9c) or with formic acid (1:1005) (9d) forms no azeotropes.]

Ternary systems contg. \bar{C} . [For extensive study of system $\bar{C} + AcOH + aq. see (5).]$

MISCELLANEOUS PHYSIOLOGICAL AND BIOCHEMICAL BEHAVIOR OF Č

[For study of toxicity of \tilde{C} see (27); for effect on proteins see (28); for effect on wire worms see (29).]

USES OF C

The uses of \bar{C} both as solvent and as chemical intermediate (see below) are manifold and cannot here be reviewed in detail [however, for use of \bar{C} in stabilization of nitrate esters (30), in refining of mineral oil (31), or in treatment of cellulose fibers to improve dyeing with acid dyes (32) see indic. refs.].

PREPARATION OF C

[For prepn. of \bar{C} from 1,3-dichloropropanol-2 (" α -dichlorohydrin") (3:5985) with aq. Ca(OH)₂ (22) (16) (33), with aq. NaOH (4) (13) (17) (34) (37) cf. (35), with alc. NaOH (36), with ether + NaOH (38), with solid NaOH (39), or with aq. KOH (2) (1) (yields: 95% (33), 92.5% (36), 90% (13) (16) (34),85% (17),79% (2),76-81% (38),67-72% (22),70% (17),60% (4)) see indic. refs.; for patents on prepn. of \bar{C} from this source by use of various alk. materials see (40) (41) (33) (37), note that during this type of prepn. of \bar{C} some glycerol (1:6540) is also formed (38) (44).]

[For prepn. of \tilde{C} from 2,3-dichloropropanol-1 (" β -dichlorohydrin") (3:6060) with aq. alk. see (42) (for studies of kinetics of this loss of HCl see (43)).]

[For form. of \bar{C} from glycerol (1:6540) with PCl₃ (45), with HCl (1) (50), or S₂Cl₂ (50) see indic. refs.]

[For form. of \tilde{C} from sodium salt of γ -chloro- β -hydroxy-n-propyl hydrogen sulfite (itself obtd. from \tilde{C} + NaHSO₃) on treatment with NaOH see (46).]

[For formn. of C from 1-bromo-3-chloropropanol-2 (see below) by loss of HBr by actn. of conc. KOH see (1).]

CHEMICAL BEHAVIOR OF C WITH INORGANIC REACTANTS

Reduction of C. [C with Na/Hg in moist ether is very slowly attacked and some allyl alc. (1:6145) (together with other prods.) is formed (47). — Note, however, that reactn. of C with Na in ether is very complicated and the prods. and mode of their formn. are disputed (48) (49) (44) (50) (51).] — (For behavior of C with HI see below.)

Oxidation of \tilde{C} . [\tilde{C} on oxidn. with HNO₃ (D=1.38) gives (52) β -chloro- α -hydroxy-propionic acid (β -chlorolactic acid) [Beil. III-286, III₁-(110), III₂-(209)], eas. sol. aq., alc., ether, cryst. from C_6H_6 (53), m.p. 77° (53), 77-78° (52) (for resolution of this prod. into opt. act. forms, d-form, m.p. 91.5°, see (54)). — Note that this prod. is also obtd. by oxidn. of 3-chloropropanediol-1,2 (" α -monochlorohydrin") (3:9038) q.v.]

Halogenation of Č. [$\bar{\mathbf{C}}$ with Cl₂ in diffuse light gives (55) γ, γ -dichloropropylene oxide [Beil. XVII-9], oil, b.p. 170°. — $\bar{\mathbf{C}}$ with Br₂ at 100° gives (56) (57) x, x, x-tribromo- γ -chloropropylene oxide [Beil. XVII-9], oil, which on shaking with aq. forms a crystn. tetrahydrate, m.p. 55° (56).]

Behavior of \tilde{C} with water (or dil. acids). [\tilde{C} with aq. at 100° (6) in s.t. (1) cf. (60) or on boilg, for 14 hrs. (58) adds H₂O giving (80% yield (58)) 3-chloropropanediol-1,2 (α -

monochlorohydrin) (3:9038). This process is greatly facilitated by the pres. of dil. acids: e.g., for use of dil. H_2SO_4 (yields: 85-90% (34) cf. (59), 80% (36)) or formic acid (66% yield (212)) see indic. refs.; for study of kinetics of this reactn. incl. influence of various acids and salts see (6) (19) (61) (62); for patent on use of dil. acids or acid-reacting salts see (63). — Note, however, that \bar{C} with aq. contg. 3-20% H_2SO_4 at $100-250^\circ$ under press. gives (72) acrolein (1:0115).]

Behavior of \bar{C} with halogen hydracids (HX). With HF. [\bar{C} with 30% HF soln. reacts vigorously yielding (64a) 3-chloropropanediol-1,2 (" α -monochlorohydrin") (3:9038) and other prods.; note that \bar{C} with HF under some circumstances appears to yield (64b) polymers.]

With HCl. [\bar{C} with conc. HCl shaken several hrs. at room temp. (3) (4) cf. (19) (65), or \bar{C} with HCl gas (51) in AcOH (11), gives (80% yield (4)) 1,3-dichloropropanol-2 (" α -dichlorohydrin") (3:5985).]

With $\dot{H}Br$. [\ddot{C} with const.-boilg. HBr (D=1.48) as directed (66) cf. (1) gives alm. quant. yield 1-bromo-3-chloropropanol-2 [Beil. I-365, I₁-(185), I₂-(385)], b.p. 197° at 760 mm. (66), 92° at 20 mm. (66), $D_4^{20}=1.726$ (67), $n_D^{25}=1.5140$ (67) (corresp. bis-(N-phenylcarbamate), m.p. 73° (68)).] (See below under reactn. of \ddot{C} with metal bromides.) With HI. [\ddot{C} with 66% HI (69) cf. (66) (1) gives 3-chloro-1-iodopropanol-2 [Beil. I-366, I₁-(186), I₂-(386)], b.p. 226° (1), 107° at 19 mm. (66), 110° at 9 mm. (69).] (See also below under behavior of \ddot{C} with metal iodides.)

Behavior of \tilde{C} with oxygenated inorganic acids. [\tilde{C} with conc. H_2SO_4 (70) or 84% H_2SO_4 in cold (71) gives a corresp. mono (acid sulfate) ester [Beil. I-474, I_2 -(538)], but whether this HSO_4 group is attached through oxygen to the first or second carbon atoms of \tilde{C} is unknown.]

[\bar{C} with HNO₃ at not above 20° as directed (73) gives 42% yield of a mononitrate ester of 3-chloropropanediol-1,2 (" α -monochlorohydrin"); \bar{C} with fumg. HNO₃ at 0° gives (74) γ -chloropropylene glycol dinitrate [Beil. I-474]; \bar{C} with mixed HNO₃ + H₂SO₄ gives (75) a mixed nitrous/nitric ester [Beil. I-474] of 3-chloropropanediol-1,2 (3:9038).]

[For analogous reactns. of \bar{C} with H_3PO_4 (71) (89) or with $HClO_4$ in ether (76) see indic. refs.; for behavior of \bar{C} toward HOCl see (77).]

Behavior of C with salts of inorganic acids. (For behavior with NaCN, etc., see below under organic reactants.)

With metal chlorides. [\bar{C} in dry ether adds anhydrous ZnCl₂ giving (78) ClCH₂CH-(OZnCl).CH₂Cl; \bar{C} in dry ether adds anhydrous MgCl₂giving (78) ClCH₂CH (OMgCl)CH₂Cl; both these cpds. on hydrolysis yield (78) 1,3-dichloropropanol-2 (" α -dichlorohydrin") (3:5985). — Note also that \bar{C} (2 g.) with MgCl₂ (1 g.) + aq. (2 ml.) + abs. alc. (5 ml.) in st. at 125° for 6 hrs. (79) cf. (11) gives Mg(OH)₂ + 1,3-dichloropropanol (above); \bar{C} with alc. FeCl₃ gives (11) Fe(OH)₃ + 1,3-dichloropropanol-2 (above).] (See also below under reactn. of \bar{C} with RMgX cpds.)

With metal bromides. [C (1 mole) with MgBr₂ (1 mole) in dry ether gives (80) similarly ClCH₂.CH(OMgBr).CH₂Br which on hydrolysis yields (80) 1-bromo-3-chloropropanol-2 (props. given above under reactn. of C with HBr).] (See also below under reactn. of C with RMgX cpds.)

With metal iodides. [C with dry KI in st. at 100° for several days (1), or C with KI (2 moles) in abs. alc. at 80-85° for 11 hrs. (81), or C with NaI (1 mole) in acctone refluxed 21 hrs. (82), gives (40% yield (82)) 3-iodo-1,2-epoxypropane ("α-epiiodohydrin") [Beil. XVII-10], b.p. 167° (1), 64° at 24 mm. (82), 62° at 24 mm. (81).]

 $[\bar{C}$ with conc. aq. MgI₂ soln. gives alm. quant. yield (170) 3-chloro-1-iodopropanol-2 for whose constants see above under behavior of \bar{C} with HI.]

With alkali sulfides. [For patents on behavior of C with aq. Na₂S see (83) (84).] (See also below.)

With alkali sulfites. [C with NaHSO₃ in s.t. at 100° (11) or htd. under reflux (85) (86) or in cold (87) gives sodium salt of 3-chloro-2-hydroxy-n-propyl hydrogen sulfite [Beil. I-474, I₂-(538)].]

[\bar{C} (1 mole) with conc. aq. Na₂SO₃ (2 moles) htd. under reflux 1½-2 hrs. (46) or \bar{C} with conc. aq. K₂SO₃ (85) gives corresp. salts of "glycerol disulfonic acid."]

[For behavior of C with Na₃PO₄ (15), with Na₂HPO₄ (88), or with Na₃AsO₃ (90) see indic. refs.]

Behavior of \bar{C} with other non-nitrogenous inorganic reactants. $[\bar{C}$ with PCl₃ gives an addition prod. (91) which with aq. regenerates \bar{C} and also forms H_3PO_3 . — \bar{C} with PCl₅ yields (1) 1,2,3-trichloropropane (3:5840) + POCl₃.

[$\bar{\mathbf{C}}$ with S₂Cl₂ gives (92) 67% 1,3-dichloropropanol-2 (" α -dichlorohydrin") (3:5985) + 33% α , α '-dichloroacetone (3:0563). — $\bar{\mathbf{C}}$ with SO₂Cl₂ + AlCl₃ in CCl₄ gives (93) β , β '-dichloroisopropyl chlorosulfonate.]

[\bar{C} in alk, soln. treated with H₂S at 0° gives (94) β -chloro- α -hydroxy-n-propyl mercaptan, b.p. 60° at 1.3 mm., $D_{-}^{20} = 1.2981$, $n_{D}^{20} = 1.5257$ (94); at 50°, however, further loss of HCl occurs yielding by ring closure (94) β -hydroxytrimethylene sulfide, b.p. 57° at 1.3 mm., $D_{-}^{20} = 1.2130$, $n_{D}^{20} = 1.5433$ (94). — Note, however, that \bar{C} treated directly at 125° with H₂S gives (95) bis-(β -chloro- α -hydroxy-n-propyl) sulfide, oil, undistillable without decn. even at 2 mm. (95).]

[$\bar{\mathbf{C}}$ with AcCl₃ gives (96) tris- $(\beta,\beta'$ -dichloroisopropyl)arsine, b.p. 88–93° at 10 mm., $D_4^{10} = 2.145$ (96).]

Behavior of $\bar{\mathbf{C}}$ with NH₃ and other inorganic nitrogen cpds. $[\bar{\mathbf{C}}$ satd. repeatedly with NH₃ gas as directed (97) gives tris-(β -chloro- α -hydroxy-n-propyl)amine [Beil. IV-291], m.p. 92-93° (corresp. $\bar{\mathbf{B}}$.HCl, m.p. 173° (97)); note that from the reactn. prod. of $\bar{\mathbf{C}}$ with ethyl acetoacetate treatment with excess alc. NH₃ gives (98) 3-chloro-2-(1?)-aminopropanol-1(2?) [Beil. IV-291].]

[Č in alc. with NH₃ gas or Č in alc. with NaNH₂, or Č with aq. NH₄OH (11) (99) gives a reactn. prod. of undetermined constitution, useful in productn. (100) of vat dye printing pastes.]

[Č with hydrazine hydrate at 100° for 30 min. or in alc. under reflux for 5 hrs. gives (101) γ -hydrazinoepihydrin which with ZnCl₂ at 100° gives (101) pyrazole [Beil. XXIII-39, XXIII₁-(15)], m.p. 69.5-70° (101).]

[For behavior of \bar{C} with basic potassium iminodisulfonate, $KN(SO_3K)_2$, leading to dipotassium epihydrin-N,N-disulfonate (102) (103), or with basic potassium hydroxylaminedisulfonate, $KON(SO_3K)_2$, leading to dipotassium epihydrinhydroxylamine-N,N-disulfonate (104), see indic. refs.]

CHEMICAL BEHAVIOR OF C WITH ORGANIC REACTANTS

BEHAVIOR OF C WITH HYDROXY AND MERCAPTO COMPOUNDS

With monohydric alcohols. \bar{C} with alcohols reacts to give by opening of the oxide ring the corresp. primary ethers of 3-chloropropanediol-1,2(" α -monochlorohydrin") (3:9038). $[\bar{C}$ with MeOH (1:6120) in pres. of H_2SO_4 (105) (66) (106) (107), or \bar{C} with MeOH at elev. temp. under press. (108), or \bar{C} with MeOH + BF₃ (109), gives (yields: 88–90% (105), 89% (106), 74.5% (109)) γ -chloro- β -hydroxy-n-propyl methyl ether ("chloromethylin") [Beil. I_2 -(538)], b.p. 173° at 752 mm. (105), 172° (106), 170.5–171.5° (109), 95° at 20 mm. (106), $D_4^{20} = 1.1648$ (109), $n_2^{20} = 1.4474$ (109). — Note, however, that \bar{C} with MeOH in pres. of KOH gives (110) (111) glycerol α , α' -dimethyl ether (β , β' -dimethoxy-isopropyl alc.)

[Beil. I-512, I₂-(590)], b.p. 167-168° at 760 mm., 65.5-66.0° cor. at 9 mm. (113), $D_4^{20} = 1.0085$ (113), $D_4^{25} = 1.012$ (111), $n_D^{25} = 1.4183$ (111), $n_D^{20} = 1.4192$ (113) (corresp. p-nitrobenzoate, m.p. 43° (112)).]

[$\bar{\mathbf{C}}$ with EtOH (1:6130) in pres. of H₂SO₄ refluxed 6 hrs. (17) or 20 hrs. (106) gives (yields: 80% (106), 76% (17)) γ -chloro- β -hydroxy-n-propyl ethyl ether ("chloroethylin") [Beil. I-474, I₂-(538)], b.p. 183–184° (106), 104–106° at 60 mm. (17), 95–100° at 20 mm. (106), $D_4^{25} = 1.107$ (17), $n_D^{25} = 1.442$ (17). — Note, however, that $\bar{\mathbf{C}}$ with EtOH + KOH gives (110) glycerol α , α' -diethyl ether (β , β' -diethoxyisopropyl alc.) [Beil. I-512], b.p. 191° at 760 mm. (13) (111), 108–109° at 60 mm. (111), 61.5–62.0° cor. at 2 mm. (113), $D_4^{25} = 0.952$ (111) (13), $D_4^{20} = 0.9514$ (113), $n_D^{25} = 1.419$ (111) (13), $n_D^{20} = 1.4200$ (113).]

[For corresp. behavior of \tilde{C} with *n*-butyl alc. (1:6180) + H₂SO₄ (106), with isoamyl alc. (1:6200) + H₂SO₄ (106), see indic. refs. — \tilde{C} with dodecanol-1 (lauryl alc.) (1:5900) + FeCl₃ in s.t. at 160° for 18 hrs. (39% yield (114)) or with H₂SO₄ (115) gives γ -chloro- β -hydroxy-n-propyl n-dodecyl ether, b.p. 157° at 1 mm. (114), $n_D^{25} = 1.4525$ (114). — (For attempts to effect analogous reactn. between \tilde{C} and ter-butyl alcohol (1:6140) in pres. of H₂SO₄ and for physical constants on higher members of di(alkoxy)isopropyl alc. series see (113).)]

[\bar{C} with ethylene chlorohydrin (3:5552) + H₂SO₄ gives (70% yield (116)) γ -chloro- β -hydroxy-n-propyl β -chloroethyl ether, b.p. 123-125° at 18 mm. (116).]

With polyhydric alcohols. [\bar{C} with ethylene glycol (1:6465) + \bar{H}_2SO_4 gives (56% yield (117)) γ -chloro- β -hydroxy-n-propyl β -hydroxyethyl ether, b.p. 135–139° (117).]

[For presumably analogous behavior of \bar{C} with glycerol + H₂SO₄ see (118); for behavior of \bar{C} with cellulose + 50% NaOH see (119).]

With mercaptans. \tilde{C} with mercaptans behaves in general analogously to \tilde{C} with monohydric alcs. + H₂SO₄.

[E.g., \bar{C} with McSH is unreported. — \bar{C} with EtSH at 50° for 4 hrs. gives (90% yield (95)) γ -chloro- β -hydroxy-n-propyl ethyl sulfide, b.p. 114–115° at 16 mm.; note, however, that \bar{C} with EtSH in aq. KOH (i.e., KSEt) reacts differently yielding (95) 1,2-epoxy-n-propyl ethyl sulfide, b.p. 67–68° at 15 mm., $D_4^{22}=1.0196,\ n_D^{22}=1.4789.$ — \bar{C} with n-PrSH + activated carbon at 90° for 7 hrs. gives (95) γ -chloro- β -hydroxy-n-propyl sulfide, b.p. 95° at 4 mm.]

[\ddot{C} (1 mole) with benzyl mercaptan (1 mole) at 130° for 7 hrs. gives (95) γ -chloro- β -hydroxy-n-propyl benzyl sulfide, b.p. 154–156° at 4 mm.; note, however, that \ddot{C} (1 mole) with benzyl mercaptan (2 moles) in alc. NaOH gives (46) bis- $(\beta,\beta'$ -dibenzylmercapto)-isopropyl alc., m.p. 59°.]

[\bar{C} with thiophenol at 130° for 5 hrs. gives (95) γ -chloro- β -hydroxy-n-propyl phenyl sulfide, b.p. 141° at 4 mm.]

With monohydric phenols. Č with monohydric phenols reacts to give by opening of the oxide ring the corresp. primary aryl ethers of 3-chloropropanediol-1,2("a-mono-chlorohydrin") (3:9038).

[$\ddot{\mathbf{C}}$ with phenol (1:1420) (2 moles) at 110° for 10 hrs. (17), or at 150–160° under press. (120) (121) cf. (122), gives (86% yield (17)) γ -chloro- β -hydroxy-n-propyl phenyl ether (" α -monochlorohydrin γ -phenyl ether") [Beil. VI-147, VI_I-(85)], b.p. 155–156° at 16 mm. (123), 152–153° at 12 mm. (121), 125–126° at 2 mm. (17), D_4^{25} = 1.209 (17), n_D^{25} = 1.540 (17) (this prod. is also formed even in pres. of a very little NaOH (123)). — $\ddot{\mathbf{C}}$ (1 mole) with phenol (1:1420) (1 mole) + aq. NaOH (1½ moles) at ord. temp. for 24 hrs. gives (40% yield (17) (125)) (124) 3-phenoxy-1,2-epoxypropane (glycidol phenyl ether) [Beil. XVII-105, XVII₁-(50)], b.p. 243–244° cor. (124), 133° at 23 mm. (124), 115–116° at 3–4 mm. (17), D_4^{25} = 1.10 (17); this reactn. occurs so readily that this prod. has formerly been mistaken for glycerol α - γ -diphenyl ether (see following). — $\ddot{\mathbf{C}}$ with phenol (1:1420) +

alc. NaOEt under reflux {120} cf. (124) (127) yields glycerol α, α' -di(phenyl) ether (β, β' -diphenoxyisopropyl alc.) [Beil. VI-149, VI₁-(86)], lfts. from alc., m.p. 82° (120) (127), 81-82° (124), 80-81° (17).]

 \bar{C} (1 mole) with p-nitrophenol (1 mole) + aq. NaOH (1½ moles) at ord. temp. for some days gives (126) 3-(p-nitrophenoxy)-1,2-epoxypropane (glycidol p-nitrophenyl ether) [Beil. XVII₁-(51)], m.p. 67° cor. (126), 69° (127). — \bar{C} (1 mole) with 2,4-dinitrophenol (1 mole) in aq. KOH (1 mole) refluxed several days, or \bar{C} with Ag 2,4-dinitrophenolate in alc., gives (42-47% yield) (note that \bar{C} is in excess (128)) glycerol α,α' -bis-(2,4-dinitrophenyl)ether, m.p. 79° (128).]

[C (1 mole) with o-cresol (1:1400) (1 mole) + very dil. aq. NaOH at ord. temp. 9 days gives (30% yield (123)) γ-chloro-β-hydroxy-n-propyl o-tolyl ether ("α-monochlorohydrin γ -(o-tolyl) ether) [Beil. VI₁-(201)], oil, b.p. 165° at 14 mm. (corresp. N-phenylcarbamate, m.p. 113-114°); C (1 mole) with o-cresol (1 mole) + excess aq. NaOH at ord. temp. 4 days gives (131) 3-(o-toloxy)-1,2-epoxypropane (glycidol o-cresyl ether) [Beil. XVII-105], oil, b.p. 134.5° at 14 mm. (131); note, however, that C (1 mole) with Na o-cresolate (2 moles) in alc. refluxed 24 hrs. gives (37% yield (129)) cf. (130) glycerol α,α' -bis-(o-tolyl)ether [Beil. VI-354], m.p. 36-37°, b.p. 226° at 13 mm. (129) (130). — C (1 mole) with m-cresol (1:1730) (1 mole) + 20% aq. NaOH (1/40 mole) at ord. temp. for 56 days gives (67.5%) yield (126)) γ-chloro-β-hydroxy-n-propyl m-tolyl ether ("α-monochlorohydrin" γ-(mtolyl) ether) [Beil. VI₁-(186)], b.p. 167.5° cor. at 13 mm. (corresp. N-phenylcarbamate, m.p. 108-108.5° cor.); \bar{C} (1 mole) with m-cresol (1 mole) + excess aq. NaOH at ord. temp. gives (126) 3-(m-toloxy)-1,2-epoxypropane (glycidol m-tolyl ether) [Beil. XVII₁-(51)], b.p. 139.5-140° cor. at 15 mm.; note, however, that \tilde{C} (1 mole) with Na m-cresolate (2 moles) in alc. refluxed several days gives (23% yield (129)) (130) glycerol α, α' -bis-(m-tolyl) ether [Beil. VI-378], b.p. 232° at 13 mm. (129) (130). — \bar{C} (1 mole) with p-cresol (1:1410) (1 mole) + 20% aq. NaOH ($\frac{1}{20}$ mole) at ord. temp. for 8 days gives (47% yield (123)) γ -chloro- β -hydroxy-n-propyl p-tolyl ether (" α -monochlorohydrin" γ -(p-tolyl) ether) [Beil. VI₁-(201)], oil, b.p. 165° at 14 mm. (corresp. N-phenylcarbamate, m.p. 113-114°); \bar{C} (1 mole) with p-cresol (1 mole) + excess aq. NaOH at ord. temp. gives (124) cf. (120) 3-(p-toloxy)-1,2-epoxypropane, (glycidol p-cresyl ether) [Bul. XVII-105, XVII₁-(51)], b.p. 136° at 17 mm. (124); note, however, that C (1 mole) with Na p-cresolate in alc. under reflux gives (120) (124) glycerol α,α' -bis-(p-tolyl) ether [Beil. VI-395], m.p. 88° (120) (124).]

[The analogous behavior of \bar{C} with other monohydric phenols cannot be detailed here; however, for \bar{C} with α -naphthol (1:1500) (120) (126) (132), β -naphthol (1:1540) (126) (127) (132), carvaerol (1:1760) (126), thymol (1:1430) (126), guaiacol (1:1405) (126) (127) see indic. refs.]

With dihydric phenols. [C (1 mole) with pyrocatechol (1:1520) (1 mole) + KOH (1 mole) condenses with ring closure yielding (133) (134) 5-(hydroxymethyl)-2,3-benzo-dioxane-1,4, m.p. 96°, b.p. 160° at 17 mm. (133) (134).]

[For behavior of \bar{C} with 4-acetylresorcinol (resacetophenone) see (135).]

BEHAVIOR OF C WITH ETHERS

[\bar{C} with dimethyl ether + BF₃ at -35° after reactn. and distn. gives (86.6% yield (136)) tris-(β-chloro-β'-methoxy-isopropyl) borate, accompanied by a little γ -chloro-β-hydroxy-n-propyl methyl ether (for constants see above under behavior of \bar{C} with monohydric alcs.). — \bar{C} with diethyl ether + BF₃ at 20-25° overnight followed by treatment with aq. 2N Na₂CO₃ gives mainly (136) γ -chloro-β-hydroxy-n-propyl ethyl ether (for constants see above under behavior of \bar{C} with monohydric alcs.) accompanied by ethyl alcohol (1:6130); direct distillation of the reaction mixt. without Na₂CO₃ treatment, however,

gives (136) tris-(β -chloro- β -ethoxyisopropyl) borate, b.p. 210-216° at 12 mm., D_4^{22} = 1.148 (126).]

[\bar{C} with α -halogen-methyl alkyl ethers in pres. of HgCl₂ gives (137) (105) (by ring opening and addn.) mixed formals; e.g., \bar{C} with chloromethyl methyl ether (3:7085) + HgCl₂ gives formaldehyde β , β' -dichloroisopropyl methyl acetal, etc.]

BEHAVIOR OF C WITH CARBONYL COMPOUNDS

With aldehydes. [\bar{C} with aldehydes condenses to yield the corresp. 2-alkyl-4-(chloromethyl)-1,3-dioxolanes; (however, the prod. to be expected from \bar{C} with formaldehyde (1:0145), viz., 4-(chloromethyl)-1,3-dioxolane [Beil. XIX-8, XIX₁-(610)], b.p. 126° at 750 mm. (138), has not been so reported, but rather from 3-chloropropanediol-1,2 (" α -monochlorohydrin")(3:9038)); for behavior of this prod. with solid KOH at 110° involving loss of HCl and formn. (94% yield (139)) (140) of the formal of propen-1-diol-2,3, b.p. 93-95° at 758 mm. (139), $n_{20}^{20} = 1.4336$ (139), see indic. refs.]

[\bar{C} with acetaldehyde (1:0100) + SnCl₄ in CCl₄ at 18–25° gives (45% yield (141)) 4-(chloromethyl)-2-methyl-1,3-dioxolane ("acetaldehyde γ -chloropropylene acetal") [Beil. XIX₁-(610)], b.p. 158–162° at 760 mm. (141).— \bar{C} with propionaldehyde (1:0110) + SnCl₄ in CCl₄ gives (64% yield (141)) (142) 4-(chloromethyl)-2-ethyl-1,3-dioxolane, b.p. 65–70° at 18 mm. (142). — For analogous reactions of \bar{C} with n-butyraldehyde, octanal-1, decanal-1, and dodecanal-1 see (142); with crotonaldehyde see (141).]

With ketones. $\bar{\mathbb{C}}$ with ketones condenses in completely analogous fashion to yield the corresp. 2,2-dialkyl-1,3-dioxolanes. [E.g., $\bar{\mathbb{C}}$ (converted to 3-chloropropanediol-1,2 (" α -monochlorohydrin") (3:9038) although this may be unnecessary) gives (60% yield (58)) 4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane ("acetone-glycerol α -chlorohydrin"), b.p. 157° at 767 mm., $D_4^{20}=1.1079,\,n_D^{15}=1.43750$ (58). — $\bar{\mathbb{C}}$ with benzophenone (1:5150) + SnCl₄ in CCl₄ at 13-25° gives (73% yield (141)) 4-(chloromethyl)-2,2-diphenyl-1,3-dioxolane, m.p. 44.5°, b.p. 159-167° at 2-3 mm. (141). — For analogous behavior of $\bar{\mathbb{C}}$ with phenacyl bromide, camphor, and cyclopentadecanone see (141).

BEHAVIOR OF C WITH ORGANIC ACIDS

(For salts, acid chlorides, acid anhydrides, see below.)

With aliphatic monobasic acids. [$\bar{\mathbb{C}}$ with AcOH (1:1010) in s.t. at 180° for 24 hrs. (143) cf. (1) gives a mixt. of both glycerol α -chlorohydrin α' -acetate (3:6775) and glycerol α -chlorohydrin β -acetate (3:6517); $\bar{\mathbb{C}}$ with AcOH + a little FcCl₃ at room temp. for 24 hrs. gives (90% yield (144)) a prod. supposed originally (144) to be glycerol α -chlorohydrin α' -acetate (3:6775); note, however, that later workers (36) could obtain only 25% yield unless mixt. stood 15 days at room temp. or 2 days at 80° and regarded the product as glycerol α -chlorohydrin β -acetate (3:6517). $\bar{\mathbb{C}}$ with aliphatic monobasic acids contg. at least 4 carbon atoms + AlCl₃ (145) or $\bar{\mathbb{C}}$ with aliphatic, alicyclic, or aromatic acids (contg. no sulfonic acid groups) + pyridine (146) gives corresp. mono esters (probably mixt. of α - and β -) of 3-chloropropanediol-1,2 (3:9038).]

[\bar{C} with trichloroacetic acid (3:1150) undergoes ring closure (similar to that of \bar{C} with carbonyl cpds. above) giving (147) 4-(chloromethyl)-2-hydroxy-2-(trichloromethyl)-1,3-dioxolane, b.p. 99-101° at 0.11 mm., $n_D^{23} = 1.4892$.]

[$\bar{\mathbf{C}}$ with thiolacetic acid (CH₃.CO.SH) at 60° for 12 hrs. gives (76% yield {148}) γ -chloro- β -hydroxy-n-propyl thiolacetate, b.p. 100–101° at 1 mm., $D_{-}^{20}=1.2806$, $n_{D}^{20}=1.5186$; on longer htg., e.g., 35 hrs. at 60°, or even at ord. temp. on 2 weeks stgd. in diffuse light, largely rearr. to β -chloro- β -mercapto-isopropyl acetate, b.p. 69–70° at 1 mm., $D_{-}^{20}=1.2308$, $n_{D}^{20}=1.4855$ {148}.]

With HCN (or its salts). [\bar{C} with excess anhydrous HCN in s.t. at 75–85° for 90 hrs. (149) (150) cf. (151) (152), or \bar{C} with anhydrous HCN + some solid KCN in s.t. at ord. temp. for 3–4 days (153), or \bar{C} with aq. Ca(CN)₂ (154), gives (yields: 85% (153), 72% (150), 70% (151), 65% (149)) γ-chloro-β-hydroxy-n-butyronitrile [Beil. III-310], b.p. 250° dec. (151), 140° at 20 mm. (151), 134–135° at 15 mm. (153), 110–111° at 2 mm. (151), D_{-}^{15} = 1.233 (153), n_{D}^{15} = 1.4735 (153). — Note, however, that \bar{C} with aq. or alc. KCN splits out KCl giving (155) (85) 3-cyano-1,2-epoxypropane ("epicyanhydrin") [Beil. XVIII-261], m.p. 162°.]

BEHAVIOR OF C WITH SALTS OF ORGANIC ACIDS

[C with dry KOAc first at 110°, later at 150° (156) cf. (157), or at 120-135°, later 150° (18) (158), gives 3-acetoxy-1,2-epoxypropane (glycidyl acetate) [Beil. XVII-106], b.p. 168-169° (157), 167-168° (143), 162-164° at 750 mm. (158), accompanied by other prods. (for study of polymerization of this prod. see (18) (158)).]

Č with aq. K cyanate on boilg. (159) (160) or C with free isocyanic acid (from htg. cyanuric acid) in cold (160) adds yielding 5-(chloromethyl)oxazolidone-2 [Beil. XXVII-145, XXVII-(260)], pr. from aq., C₀H₀, or Ac₂O, m.p. 106° (161) (159), 105° (159).

[For behavior of C with disodium methyl phosphate (162) or with disodium glycerophosphate (163) see indic. refs.]

BEHAVIOR OF C WITH ACID CHLORIDES

 $\ddot{\mathbf{C}}$ with acid chlorides yields corresp. esters of β,β' -dichloroisopropyl alc. ("glycerol α -dichlorohydrin") (3:5985) as exemplified by the following illustrations.

With aliphatic acid chlorides. [$\bar{\mathbb{C}}$ with AcCl (3:7065) (164) in s.t. at 100° for 2 hrs. (165) or 30 hrs. (166) gives (73% yield (164)) β , β' -dichloroisopropylacetate (3:6318). — $\bar{\mathbb{C}}$ with propionyl chloride (3:7170) in s.t. at 135° for 3 hrs. gives (167) β , β' -dichloroisopropyl propionate [Beil. II₂-(221)], b.p. 208°, $D_{20}^{20}=1.2222$ (167). — $\bar{\mathbb{C}}$ with *n*-butyryl chloride (3:7370) in s.t. at 100° (166) or with exclusion of aq. in flask at 75° for 8 hrs. (167) gives β , β' -dichloroisopropyl *n*-butyrate [Beil II-271, II₂-(246)], b.p. 226-227° at 738 mm. (166), 223.5° (167), $D_{20}^{20}=1.1792$ (167), $n_{10}^{20}=1.4540$ (167). — $\bar{\mathbb{C}}$ with isovaleryl chloride (3:7560) gives (166) (168) β , β' -dichloroisopropyl isovalerate [Beil. II-312, II₂-(275)], b.p. 245° at 737 mm. (166), 127-140° at 36 mm. (168), $D_{20}^{20}=1.444$ (168), $n_{10}^{20}=1.450$ (168). — $\bar{\mathbb{C}}$ with stearoyl chloride (3:9960) in s.t. at 130° for $3\frac{1}{2}$ hrs. gives (167) β , β' -dichloroisopropyl stearate [Beil. II₂-(352)], m.p. 39.5°.]

BEHAVIOR OF C WITH ACID ANHYDRIDES

With anhydrides of aliphatic acids. [\bar{C} with Ac₂O (1:1015) in s.t. at 180° for 4 hrs. (166) or \bar{C} with Ac₂O + FeCl₃ at ord. temp. for 24 hrs. (144) gives (90% yield (144)) β,β' -dichloroisopropyl acetate (3:6318).]

With anhydrides of aromatic acids. [Č with phthalic anhydride (1:0725) + dimethylaniline at 100° is claimed (169) to give the monomolecular neutral phthalate [Beil. XIX-165] of 3-chloropropanediol-1,2.]

BEHAVIOR OF C WITH ORGANOMETALLIC COMPOUNDS (OR THEIR EQUIVALENTS)

Behavior with Grignard compounds. With RMgX cpds. from alkyl or alkaryl halides [Č with MeMgI in dry ether evolves gas (CH₄?) and after acidification yields (171) 3-chloro-1-iodopropanol-2 (for constants see above under behavior of Č with HI).]

[The reactn. of C with EtMgBr may give three different prods. (or mixtures of them) according to circumstances: the first of these is 1-bromo-3-chloropropanol-2 (for constants

see above under behavior of \tilde{C} with HBr); the second is the expected 1-chloropentanol-2 (3:8225); the third is cyclopropanol, b.p. $100-103^\circ$ (80) (172), $D_{20}^{20}=0.9110$ (80), $n_{0}^{20}=1.4129$ (80) (corresp. p-nitrobenzoate, m.p. $72.0-72.5^\circ$; 3,5-dinitrobenzoate, m.p. $108-109^\circ$; N-phenylcarbamate, m.p. $101.5-102.0^\circ$; N-(p-nitrophenyl)carbamate, m.p. $159-160^\circ$; N-(q-naphthyl)carbamate, m.p. $100.5-101.5^\circ$ (172)). — Note that \tilde{C} with EtMgBr gives (16-19% yield (67) (173)) 1-chloropentanol-2 (3:8225), while \tilde{C} with MgEt₂ gives 70-83% yield (80). — For review of earlier work on this rather complex system see (80) (173) (67).] [For behavior of \tilde{C} with 15 other RMgX cpds. leading in general to chlorohydrins of type RCH₂CH(OH)CH₂Cl see (173).]

With RMgX cpds. from aryl haldes. [\bar{C} with C₆H₅MgBr gives (18% yield (173)) (132) (174) (175) 3-chloro-1-phenyl-propanol-2 [Beil. VI-503], b.p. 254-257° (174), 153-154° at 28 mm. (174) (175), 142-144° at 23 mm. (173), $D_{25}^{25} = 1.1528$ (173), $n_{D}^{25} = 1.5470$ (173) (corresp. 3,5-dinitrobenzoate, m.p. 120-121° (173)). — For analogous behavior of \bar{C} with RMgX cpds. from α -bromonaphthalene and from p-bromanisole (p-bromophenyl methyl ether) see (132).]

Behavior with various sodio derivatives. [\bar{C} with diethyl sodiomalonate in abs. alc. at 50° does not split out NaCl but rather by ring opening, addn. of reactant, and elimination of EtOH ppts. (176) (177) cf. (178) the monosodium enolate (m.p. 172° dec. (176)) of α -carbethoxy- δ -chloro-n-valero- γ -lactone [Beil. XVIII-373, XVIII₁-(478)], set free (yields: 78% (177), 50% (176)) by acidification as an oil, b.p. 180–182° at 12 mm. (176), 175–180° at 12 mm. (177). — Note that this lactone with excess alc. NH₃ gives on evapn. (176) (179) γ -chloro- β -hydroxy-n-propylmalondiamide [Beil. III-450], m.p. 117–118°.]

[C with ethyl sodioacetoacetate in abs. alc. at 50° does not split out NaCl but rather by ring opening, etc., as in preceding case gives after acidification (yields: 80% (176), 74% (177)) α-aceto-δ-chloro-n-valero-γ-lactone [Beil. XVII-421, XVII₁-(230)], b.p. 168° at 16 mm. (177), 163° at 12 mm. (176).]

[$\ddot{\mathbf{C}}$ with ethyl sodio-benzoylacetate in abs. alc. behaves in analogous fashion yielding after acidification (180) α -benzoyl- δ -chloro-n-valero- γ -lactone [Beil. XVII-497], m.p. 105-106°.]

BEHAVIOR OF C WITH AMINES

With primary amines. With aliphatic primary amines. This reacts. appears not to to have been thoroughly studied [however, for reacts. of C with MeNH₂ (181) and use of prod. in preps. of vat dye printing pastes (182) see indic. refs.].

With alicyclic primary amines. [\bar{C} (1 mole) with cyclohexylamine (3½ moles) under reflux gives (18% yield (82)) β,β' -bis-(cyclohexylamino)isopropyl alc., m.p. 72-73°.]

With aromatic primary amines. [\bar{C} (1 mole) with aniline (2 moles) in toluene refluxed 95 hrs. gives (yield not stated (71)) 3-(phenylamino)-1,2-epoxypropane ("glycidanilide"). — \bar{C} (1 mole) with aniline (3 moles) at 140° is claimed (183) to yield β,β' -bis-(phenylamino)isopropyl alc. [Beil. XII-553], m.p. 53-54°, but later workers could obtain only viscid oils (184) or a further reactn. prod. supposed (185) to be β -(phenylamino)- β' -(diphenylamino)isopropyl alc., m.p. 350° dec. (185).]

[\bar{C} (1 mole) with p-toluidine (2 moles) might be expected to yield 3-(p-tolylamino)-1,2-epoxypropane, but no such cpd. appears to have been recorded. — However, \bar{C} (1 mole) with p-toluidine (1 mole) in dil. alc. (186) (184) (82) (but not in C_6H_6 (184)) opens ring to yield by addn. β -chloro- β' -(p-tolylamino)isopropyl alc., m.p. 85° (184), 81-82° (186); this prod. on htg. with p-toluidine (184) or \bar{C} (1 mole) with p-toluidine (2 moles) at 155° (186) gives β,β' -bis-(p-tolylamino)isopropyl alc., m.p. 116° (184), 113.5° (186).]

[Č with p-phenetidine hydrochloride in aq. soln. at ord. temp. especially in sunlight gives (40% yield (187)) cf. (188) N,N-bis- $(\gamma$ -chloro- β -hydroxy-n-propyl)phenetidine.]

[For behavior of \bar{C} with β -naphthylamine in xylene under reflux (189), with arsanilic acid (190), or with p-aminophenol (or its ethers) (191) see indic. refs.]

With heterocyclic primary amines. [C with α -aminopyridine gives (63% yield (192)) by addn. to oxide ring and subsequent ring closure a prod., m.p. 190°, regarded as "1,2-divinylene-5-hydroxytetrahydropyrimidine."]

With phenylhydrazine. [\bar{C} with $1\frac{1}{2}$ pts. phenylhydrazine in ether at not above 15° for 10 days ppts. phenylhydrazine hydrochloride and leaves in the other 4-hydroxy-1-phenyl-pyrazolidine [Beil. XXIII-348], m.p. $103-104^{\circ}$ (193); this prod. with phenylhydrazine hydrochloride on warming in C_6H_6 (193) or \bar{C} with 2 pts. phenylhydrazine in C_6H_6 refluxed 8-9 hrs. (194) gives (58% yield (194)) 1-phenylpyrazole [Beil. XXIII-40, XXIII₁-(15)], b.p. 246.5° cor. at 765.4 mm. (194), m.p. $11-11.5^{\circ}$ (194), $D_4^{20} = 1.1127$ (195), $n_D^{20} = 1.5966$ (195).]

With secondary amines. With aliphatic secondary amines. [\bar{C} with Me₂NH presumably gives (196) β -chloro- β' -(dimethylamino)isopropyl alc., but no constants are reported in the literature, either for it or for its ring-closure derivative, 3-(dimethylamino)-1,2-epoxypropane, cf. (196); note further that the prod. to be expected from $\bar{C} + 2$ Me₂NH, viz., β,β' -bis-(dimethylamino)isopropyl alc. [Beil. IV-290] (197), although known, has not been prepd. from \bar{C} , but only by other means.]

[Č with aq. Et₂NH gives (196) (198) cf. (199) 3-(diethylamino)-1,2-epoxypropane [Beil. XVIII-583], b.p. 155–159 at 760 mm. (198), 55–60° at 15 mm. (196), 40–50° at 8 mm. (198), $D_4^{15} = 0.8876$ (196). — Č (1 vol.) with Et₂NH (3½ vols.) refluxed 2–3 hrs. gives (82% yield (200)) β , β '-bis-(diethylamino)isopropyl alc., b.p. 114° at 9 mm. (corresp. B.2PkOH, m.p. 163° (200).]

[Č with di-n-propylamine (2 moles) gives (70% yield (215)) 1,3-bis-(di-n-propylamino)-propanol-2, b.p. 99-101° at 3 mm., $D_4^{20} = 0.8624$, $n_D^{20} = 1.4483$ (215).]

With aromatic secondary amines. [\bar{C} with N-methylaniline gives (198) cf. (199) 3-(N-methylanilino)-1,2-epoxypropane, b.p. 160-162° at 30 mm. (198), 132-135° at 8 mm. (198); note, however, that \bar{C} (1 mole) with N-methylaniline (1 mole) at 100° for 4 hrs. (82) gave none of the preceding cpd. but a very small yield (2%) of β , β '-bis-(N-methylanilino)isopropyl alc., m.p. 82°, accompanied by other prods.]

[Č with diphenylamine at 160–170° under press. splits out HCl and ring-closes with loss of H₂O yielding (201) 1-phenyl-3-hydroxy-1,2,3,4-tetrahydroquinoline [Beil. XXI₁-(205)], m.p. 79°, b.p. 200° at 5 mm.]

With heterocyclic secondary amines. [\bar{C} with piperidine gives (196) (198) by elimination of HCl 3-(piperidino)-1,2-epoxypropane, b.p. 86.5-88° at 15 mm. (196), 72-77° at 8 mm. (198), $D_4^{16} = 0.9669$ (196).]

With tertiary amines. Č with tertiary amines gives quaternary salts, but this reactn. is often followed by opening of the oxide ring and addn. of reactant.

With aliphatic tertiary ammes. [\bar{C} with alc. Et₃N (1 mole) in s.t. at 100° gives (202) a little of the corresp. quat. salt, viz., triethyl- $(\beta, \gamma$ -epoxy-n-propyl)ammonium chloride [Beil. XVIII-583]; note, however, that \bar{C} with alc. Et₃N (1 mole) in s.t. at 100° for 6 hrs. gives also (202) (203) 2-hydroxytrimethylene-1,3-bis-(triethyl-ammonium chloride) [Beil. IV-290] together with other prods.]

[For behavior of \bar{C} with N,N-dimethyl-"stenyl" amine see (204).]

With heterocyclic tertiary amines. [For study of behavior of C with pyridine see (205) (206); with quinoline see (207).]

BEHAVIOR OF C WITH OTHER NITROGENOUS REACTANTS

(Note that in the following examples reaction occurs by opening of the oxide ring and that elimination of chlorine, if it occurs at all, is effected only in a subsequent ring closure.)

- [\bar{C} (1 mole) with disodium cyanamide (1 mole) in aq. soln. at ord. temp. for 24 hrs. presumably first yields the sodium deriv. of $N-(\gamma-\text{chloro}-\beta-\text{hydroxy}-n-\text{propyl})$ cyanamide, but this immediately ring-closes giving (33% yield (208)) 5-(chloromethyl)-2-amino-oxazoline, m.p. 142°.]
- \bar{C} (1 mole) with p-toluenesulfonanilide (1 mole) + a few drops pyridine at 120° reacts vigorously giving (86% yield (209)) N-(γ-chloro-β-hydroxy-n-propyl)-N-phenyl-p-toluenesulfonamide, m.p. 96-97°; note that this prod. in boilg. alc. on treatment with NaOH loses HCl and ring-closes (92% yield (209)) to the corresp. N-(β,γ-epoxy-n-propyl)-N-phenyl-p-toluenesulfonamide, m.p. 77°.
- [Č (1 wt. pt.) with phthalimide (1 wt. pt.) at 140–150° for 3 hrs. gives (35% yield on phthalimide (210)) cf. (211) (212) N-(γ -chloro- β -hydroxy-n-propyl)phthalimide [Beil. XXI₁-(369)], m.p. 95.0–96.5° (210), 96–97° (213). Note that N-[(β , γ -epoxy)-n-propyl]phthalimide ("phthalimidoepihydrin"), m.p. 93–94° (213), has been prepd. (75% yield (213)) from 3-bromo-1,2-epoxypropane ("epibromohydrin") with K phthalimide, and in CHCl₃ with HCl gas or even directly with conc. HCl opens the oxide ring to give (213) the above N-(γ -chloro- β -hydroxy-n-propyl)-phthalimide, m.p. 96–97° (213).]

COLOR REACTION OF C

Color reaction with pyridine (and pyridine bases). \bar{C} in MeOH with pyridine and/or various "pyridine bases" gives specific color reactions; these can be used for detection of "pyridine bases," e.g., in denatured alcohol and probably vice versa; for detailed study see (214).

- 3:5358 (1) Reboul, Ann. chrm. (3) 60, 17-38 (1860), Ann Suppl. 1, 221-227 (1861). (2) Drozdov, Cherntzov, J. Gen. Chem. (U.S.S.R.) 4, 1305-1309 (1934); Cent. 1936, I 4549; C.A. 29, 3306 (1935). (3) Hibbert, Whelen, J. Am. Chem. Soc. 51, 1945 (1929). (4) Hill, Fischer, J. Am. Chem. Soc. 44, 2587-2588 (1922). (5) Leone, Benelli, Gazz. chrm. ttal. 52, II 75-86 (1922). (6) Brönsted, Mary Kilpatrick, Martin Kilpatrick, J. Am. Chem. Soc. 51, 430 (1929). (7) Thorpe, J. Chem. Soc. 37, 206 (1880). (8) Walden, Z. physik. Chem. 70, 581 (1910). (9) Lecat "L'Azeotropisme," 1918 (a) p. 70, No. 95; (b) p. 132, No. 1210; (c) p. 89, No. 485; (d) p. 70, No. 94. (10) Jaeger, Z. anorg. allgem. Chem. 101, 156 (1917).
- (11) Darmstaedter, Ann. 148, 119-131 (1868). (12) Fauconnier, Bull. soc. chim. (2) 50, 213 (1888). (13) Fairbourne, Gibson, Stephens, J. Soc. Chem. Ind. 49, 1021-1033 (1930). (14) Müller, Griengl, Mollang, Monatsh. 47, 87 (1926). (15) Bailly, Bull. soc. chim. (4) 31 848-849 (1922). (16) Braun, J. Am. Chem. Soc. 54, 1248-1250 (1932) (17) Fairbourne, Gibson, Stephens, J. Chem. Soc. 1932, 1965-1972. (18) Levene, Walti, J. Biol. Chem. 77, 685-696 (1928). (19) Smith, Z. physik. Chem. 81, 356 (1912); 92, 723 (1919). (20) Sugden, Wilkins, J. Chem. Soc. 1927, 143.
- (21) Yajnik, Sobti, J. Am. Chem. Soc. 45, 3138-3139 (1923). (22) Braun, Org. Syntheses, Coll. Vol. 2 (1st ed.), 256-258 (1943); 16, 30-32 (1936). (23) Walden, Z. physik. Chem. 59, 401 (1907). (24) Walden, Z. physik. Chem. 55, 230 (1906). (25) Bruhl, Ber. 24, 661 (1891). (26) VON Auwers, Ann. 415, 146 (1918). (27) Freuder, Leake, Univ. Calif. Pub. Pharmacol. 2, 69-77 (1921); C.A. 35, 8104 (1941). (28) Fraenkel-Conrat, J. Biol. Chem. 154, 227-238 (1944). (29) Lehman, J. Econ. Entom. 26, 1042-1051 (1933); Cent. 1934, I 1867; C.A. 28, 6917 (1934). (30) McGill (to du Pont Co.), U.S. 1,817,456, Aug. 4, 1931; Cent. 1932, I 613; C.A. 25, 5434 (1931).
- (31) Ferris (to Atlantic Refining Co.), U.S. 2,072,104, March 2, 1937; Cent. 1937, I 4719; C.A. 31, 2810 (1937). (32) I.G., Brit. 471,880, Oct. 14, 1937; Cent. 1938, I 185; not in C.A. (33) Chem. Fabrik. Griesheim-Elektron., Ger. 246,242, April 25, 1912; Cent. 1912, I 1677; C.A. 6, 2496 (1912). (34) Fourneau, Ribas y Marques, Bull. soc. chim. (4) 39, 699-700 (1926). (35) Nivière, Bull. soc. chim. (4) 13, 969-970 (1913); Compt. rend. 156, 1628 (1913). (36) Delaby, Dubois, Bull. soc. chim. (4) 47, 569-573 (1930). (37) F. Bayer & Co., Ger. 239,077, Oct. 9, 1911; Cent. 1911, II 1393. (38) Clarke, Hartmann, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 233-234 (1941); (1st ed.), 228-229 (1932); 3, 47-49 (1923). (39) Prevost, J. prakt. Chem. (2) 12, 160 (1875). (40) Engs. Fairbairn (to Shell Development Co.), U.S. 2,177,419, Oct. 24, 1939; Cent. 1940, II 689; C.A. 34, 1034 (1939).

(41) Stein, Flemming, U.S. 2,227,948, Jan. 7, 1941; C.A. 35, 2534 (1941): Ger. 735,477, April 15, 1943; C.A. 38, 2666 (1944); Brit. 496,709, Dec. 29, 1938; Cent. 1939, I 4117; C.A. 33, 3398 (1939): French 843,841, July 11, 1939; [C.A. 34, 6948 (1940)]. (42) Münder, Tollens, Zeit. für Chemie 1871, 252. (43) Smith, Z. Physik. Chem. 92, 739-740 (1917); 93, 83-85 (1919). (44) Claus; Ber. 10, 556-559 (1877). (45) Berthelot, Luca, Ann. chim. (3) 48, 305 (1856); Ann. 101, 67-68 (1857). (46) Fromm, Kapeller, Taubmann, Ber. 61, 1354, 1356 (1928). (47) Tornöe, Ber. 21, 1290 (1888). (48) Kishner, Ber. 25, Referate 506 (1892). (49) Tornöe, Ber. 24, 2676-2677 (1891). (50) Bigot, Ann. chim. (6) 22, 434-442 (1891).

(51) Hubner, Miller, Ann. 159, 184-187 (1871). (52) von Richter, J. prakt. Chem. (2) 20, 193-195 (1879). (53) Koelsch, J. Am. Chem. Soc. 52, 1106 (1930). (54) Tsunoo, Ber. 68, 1342 (1935). (55) Cloez, Ann. chim. (6) 9, 170 (1886). (56) Grimaux, Adam, Bull. soc. chim. (2) 33, 257-259 (1880). (57) Cloez, Ann. chim. (6) 9, 206 (1886). (58) Fischer, Pfahler, Ber. 53, 1608 (1920). (59) Boeseken, Hermans, Bull. soc. chim. (4) 39, 1254 (1926). (60) Hanriot,

Ann. chim. (5) 17, 75 (1879).

(61) Banerjee, Sen, J. Indian Chem. Soc. 9, 509-518 (1932). (62) Smith, Wode, Widhe, Z. physik. Chem. 130, 157-162 (1927). (63) Groll, Hearne (to Shell Development Co.), U.S. 2,086,077, July 6, 1937; Cent. 1937, II 2433; C.A. 31, 5813 (1937). (64) (a) Swarts, Cent. 1903, 12; (b) Paterno, Oliveri, Gazz. chim. ital. 24, I 305-309 (1894), Paterno, Gazz. chim. ital. 24, II 541-544 (1894). (65) Markownikow, Ann. 208, 352-353 (1881). (66) Blanchard, Bull. soc. chim. (4) 41, 825-826 (1927). (67) Koelsch, McElvain, J. Am. Chem. Soc. 51, 3390-3394 (1929). (68) Johnson, Langley, Am. Chem. J. 44, 358 (1910). (69) Ingold, Rothstein, J. Chem. Soc. 1931, 1671-1672. (70) Oppenheim, Ber. 3, 736 (1870). (72) Groll, Hearne (to Shell (71) Zetsche, Aeschlimann, Helv. Chim. Acta 9, 711-714 (1926). (72) Groll, Hearne (to Shell

(71) Zetsche, Aeschlimann, Helv. Chim. Acta 9, 711-714 (1926). (72) Groll, Hearne (to Shell Development Co.), U.S. 2,106,347, Jan. 25, 1938; Cent. 1938, II 1676; C.A. 32, 2542-2543 (1938). (73) I.G., French 846,575, Sept. 20, 1939; C.A. 35, 1071 (1941). (74) Henry, Ann. 155, 166, 168-169 (1870). (75) Henry, Ber. 4, 703 (1871). (76) Hofmann, Zedwitz, Wagner, Ber. 42, 4391 (1909). (77) Carius, Ann. 134, 73-75 (1865). (78) Ribas, Tapia, Anales soc. españ. fis. quím. 28, 636-644 (1930); Cent. 1932, II 3862; C.A. 24, 4265 (1930). (79) Delaby, Ann. chim.

(9) 20, 67-68 (1923). (80) Magrane, Cottle, J. Am. Chem. Soc. 64, 484-487 (1942).

(81) Nef. Ann. 335, 237-238 (1904). (82) Wedekind, Bruch, Ann. 471, 78, 94, 95, 97 (1929). (83) Lilienfeld, Ger. 253,753, Nov. 15, 1912, Cent. 1913, I 82, [C.A. 7, 808 (1913)]: French 436,088, Nov. 8, 1911; C.A. 6, 2494 (1912). (84) Blumfeld (to Röhm and Haas, A.G.), Brit. 314,440, Aug. 21, 1929; [Cent. 1930, II 480]; C.A. 24, 1524 (1930): French 677,431, March 7, 1930; Cent. 1930, I 3252; [C.A. 24, 3092 (1930)]. (85) Pazschke, J. prakt. Chem. (2) 1, 86-99 (1870). (86) Cohen, J. pharmacol. 46, 283 (1932); Cent. 1933, I 1109; C.A. 27, 166 (1933). (87) Lumière, French 548,343, Jan. 12, 1923; Cent. 1925, I 1010; not in C.A. (88) Bailly, Bull. soc. chim. (4) 29, 274-280 (1921). (89) Cavalier, Ann. chim. (7) 18, 482-483 (1899). (90) Oechslin (to Etab. Poulenc Frères), Brit. 191,028, Feb. 14, 1923; Cent. 1923, IV 721; C.A. 17, 2887 (1923); French 556,366, July 19, 1923; Cent. 1923, IV 721; not in C.A.

(91) Hanriot, Bull. soc. chim. (2) 22, 550-552 (1879). (92) Malinovskii, J. Gen. Chem. (U.S.S.R.) 9, 832-839 (1939); C.A. 34, 375 (1940). (93) Blanchard, Bull. soc. chim. (4) 43, 1203 (1928). (94) Sjoberg, Svensk Kem. Tid. 50, 250-254 (1938); Cent. 1939, I 2756; C.A. 33, 2106 (1939). (95) Nenitzescu, Scarlatescu, Ber. 68, 587-591 (1935). (96) Malinovskii, J. Gen. Chem. (U.S.S.R.) 10, 1918-1922 (1940); C.A. 35, 4736 (1941). (97) Fauconnier, Compt. rend. 107, 115-117 (1887); Ber. 21, Referate 646 (1888). (98) Schiff, Gazz. chim. ital. 21, II 1-6 (1891). (99) Stallmann (to du Pont Co.), U.S. 1,977,251, Oct. 16, 1934; Cent. 1935, I 2603; C.A. 29, 352 (1935). (100) Stallman (to du Pont Co.), U.S. 1,977,250, Oct. 16, 1934; Cent. 1935, I 1619;

C.A. 29, 352 (1935).

(101) Balbiano, Ber. 23, 1103-1106 (1890); Gazz. chim. ital. 20, 460-465 (1890). (102) Traube, Wolff, Ber. 53, 1498 (1920). (103) F. Bayer & Co., Ger. 330,801, Dec. 17, 1920; Cent. 1921, II 601; not in C.A. (104) Traube, Ohlendorff, Ber. 53, 1488 (1920). (105) Blanchard, Bull. soc. chim. (4) 39, 1263-1265 (1926). (106) Fourneau, Ribas, Bull. soc. chim. (4) 39, 1504-1589 (1926). (107) I.G., Brit. 271,169, June 16, 1927; Cent. 1927, II 2110; C.A. 22, 1596 (1928). (108) I.G., French 697,786, Jan. 22, 1931; Cent. 1931, I 2394; [C.A. 25, 3013 (1931)]. (109) Petrov, J. Gen. Chem. (U.S.S.R.) 10, 1918-1922 (1940); C.A. 35, 3603 (1941). (110) Zunino, Atti accad. Lincei (5) 6, II 348 (1897).

(111) Fairbourne, Gibson, Stephens, J. Chem. Soc. 1931, 450, 454. (112) Fairbourne, J. Chem. Soc. 1929, 1151-1152. (113) Henze, Rogers, J. Am. Chem. Soc. 61, 434-435 (1939). (114) Grummitt, Hall, J. Am. Chem. Soc. 66, 1229 (1944). (115) Henkel et Cie, French 744,749, April 26, 1933; Cent. 1933, II 2210; C.A. 27, 4242 (1933). (116) Fourneau, Ribas, Bull. soc. chim. (4) 41, 1053 (1927). (117) Kharasch, Nudenberg, J. Org. Chem. 8, 189 (1943). (118) Loehr (to I.G.), Ger. 510,422, Oct. 18, 1930; Cent. 1931, I 154; [C.A. 25, 964 (1931)]. (119) Dreyfus,

Brit. 166,767, Aug. 18, 1921; Cent. 1921, IV 1140; C.A. 16, 830 (1922). (120) Lindeman, Ber. **24.** 2146–2148 (1891).

(121) Fischer, Krämer, Ber. 41, 2730 (1908). (122) Fourneau, J. pharm. chim. (7) 1, 58 (1910); Cent. 1910, I 1134; C.A. 4, 3070 (1910). (123) Boyd, Marle, J. Chem. Soc. 97, 1788-1790 (1910). (124) Boyd, Marle, J. Chem. Soc. 93, 839-841 (1908). (125) Böeseken, Rec. trav. chim. 34, 102 (1915). (126) Marle, J. Chem. Soc. 101, 305-317 (1912). (127) Fourneau (to Etab. Poulence Frères), Ger. 228,205, Nov. 7, 1910; Cent. 1910, II 1790-1791; [C.A. 28, 2155 (1911)]. (128) Brenans, Bull. soc. chim. (4) 13, 529-530 (1913). (129) Boyd, J. Chem. Soc. 83, 1137-1138 (1903). (130) Boyd, Marle, J. Chem. Soc. 95, 1807-1808 (1909).

(131) Boyd, Knowlton, J. Chem. Soc. 95, 1803 (1909). (132) Fourneau, Trefouel, Bull. soc. chim. (4) 43, 454-458 (1928). (133) Fourneau, Maderin, LeStrange, J. pharm. chim. (8) 18, 185-191 (1933); Cent. 1934, I 391; C.A. 27, 5738 (1933). (134) Soc. Usines Chim. des Rhone-Poulenc, Brit. 420,978, Dec. 20, 1924; Cent. 1935, I 2216; [C.A. 29, 3468 (1935)]: French 770,485, Sept. 14, 1934; Cent. 1935, I 2216; C.A. 29, 477 (1935). (135) Nadkarni, Wheeler, J. Chem. Soc. 1936, 589-591. (136) Meerwein, Hinz, Hofmann, Kroning, Pfeil, J. prakt. Chem. (2) 147, 258-260, 268-273 (1936/7). (137) Blanchard, Bull. soc. chim. (4) 49, 281-289 (1931). (138) Bull. soc. chim. (3) 21, 276-277 (1899). (139) Fischer, Baer, Reldmann, Ber. 63, 1738-1739 (1930). (140) Fischer, Baer, Pollock, Nidecker, Helv. Chim. Acta 20, 1214 (1937).

(141) Willfang, Ber. 74, 145-153 (1941). (142) Bersin, Willfang, Ber. 70, 2167-2173 (1937). (143) Bigot. Ann. chim. (6) 22, 491, 493 (1891). (144) Knoevenagel, Ann. 402, 134-138 (1914). (145) Stein (to General Aniline and Film Corpn.), U.S. 2,224,026, Dec. 3, 1940; C.A. 35, 1802 (1941): Brit. 509,072, Aug. 10, 1939; Cent. 1939, II 4351; C.A. 34, 2862 (1940): French 850,709, Dec. 23, 1939; C.A. 36, 1947 (1942). (146) Stein (to I.G.), Ger. 708,463, June 12, 1941; C.A. 37, 3105 (1943): French 853,647, March 23, 1940; C.A. 36, 2565 (1942). (147) Hibbert, Greig, Can. J. Research 4, 262 (1931). (148) Sjoberg, Ber. 74, 64-65, 69-70 (1941). (149) Braun, J. Am. Chem. Soc. 52, 3170 (1930). (150) Linneweh, Z. physiol. Chem. 176, 217 (1928).

(151) Lespieau, Bull. soc. chim. (3) 33, 462-463 (1905); Compt. rend. 127, 965 (1898), 129, 225 (1899). (152) Hormann, Ber. 12, 23-24 (1879). (153) Rambaud, Bull. soc. chim. (5) 3, 138-139 (1936). (154) I.G., Brit. 348,134, June 4, 1931; Cent. 1931, II 1193; [C.A. 26, 2748 (1932)]: French 702,023, March 27, 1931; Cent. 1931, II 1193; C.A. 25, 4012 (1931). (155) Hartenstein, J. prakt. Chem. (2) 7, 297-298 (1873). (156) Breslauer, J. prakt. Chem. (2) 20, 188-193 (1879). (157) de Gegerfelt, Bull. soc. chim. (2) 23, 160-161 (1871). (158) Levene, Walti, J. Biol. Chem. 79, 363-376 (1928). (159) Thomsen, Ber. 11, 2136-2137 (1878). (160) Paterno, Cingolani, Gazz. chim. ital. 38, I 243-247 (1908).

(161) Johnson, Guest, Am. Chem. J. 44, 453, 460 (1910). (162) Bailly, Gaumé, Compt. rend. (164) 198, 1932-1934 (1934). (163) Bailly, Gaumé, Bull. soc. chim. (4) 39, 1420-1428 (1926). Sjoberg, Svensk Kem. Tid. 53, 454-457 (1941); Cent. 1942, II 25; C.A. 37, 4363 (1943). (165)Abderhalden, Weill, Fermentforschung 4, 84 (1920). (166) Truchot, Ann. 138, 297-299 (1866); 140, 244-246 (1866). (167) Whitby, J. Chem. Soc. 1926, 1460. (168) Humnicki, Bull. soc. chim. (4) 45, 281 (1929). (169) Weinschenk, Chem. Ztg. 29, 1311 (1905). (170) Grignard, Bull. soc. chim. (3) 29, 944, note 2 (1903).

(171) Kling, Compt. rend. 137, 756 (1903); Bull. soc. chim. (3) 31, 14-16 (1904). (172) Stahl. Cottle, J. Am. Chem. Soc. 65, 1782-1783 (1943). (173) Koelsch, McElvain, J. Am. Chem. Soc. 52, 1164-1169 (1930). (174) Fourneau, Tiffeneau, Bull. soc. chim. (4) 1, 1227-1233 (1907). (175) J. D. Riedel, A.G., Ger. 183,361, April 10, 1907; Cent. 1907, I 1607; [C.A. 1, 2336 (1907)]. (176) Traube, Lehman, Ber. 34, 1972–1980 (1901). (177) Leuchs, Ber. 44, 1509–1511 (1911). (178) Michael, Weiner, J. Am. Chem. Soc. 58, 1000, 1002 (1936); 56, 2012-2013 (1934). (179) Traube, Lehman, Ber. 32, 721 (1899). (180) Haller, Bull. soc. chim. (3) 31, 367-369 (1904); (3) 21, 564 (1899).

(181) Stallmann (to du Pont Co.), U.S. 1,977,253, Oct. 16, 1934; Cent. 1935, I 2603; C.A. 29, 352 (1935). (182) Stallman (to du Pont Co.), U.S. 1,977,252, Oct. 16, 1934; Cent. 1935, I 1620; C.A. 29, 352 (1935). (183) Fauconnier, Compt. rend. 106, 605 (1888); 107, 250 (1888). (184) Dains, Brewster, Blair, Thompson, J. Am. Chem. Soc. 44, 2641-2642 (1922). (185) Fukagawa, Ber. 68, 1344-1346 (1935). (186) Cohn, Friedländer, Ber. 37, 3034-3035 (1901). (187) Strukov, Khim. Farm. Prom. 1934. No. 2, 11; Cent. 1935, I 2806; C.A. 28, 5421 (1934). (188) Fourneau. Ranedo, Anales soc. españ fís. quím. (2) 18, 133-139 (1920); Cent. 1921, III 781; C.A. 15, 1885 (1921). (189) Dreyfus, French 702,553, April 11, 1931; Cent. 1931, II 2058; C.A. 25, 4284 (190) Lewis (to Parke-Davis Co.), U.S. 1,664,123, March 27, 1928; Cent. 1929, I 1047; C.A. 22, 1595 (1928).

(191) Kolshorn, Ger. 346,385, Dec. 29, 1921; Cent. 1922, II 574; not in C.A.: Brit. 155,575, 155,576, Jan. 13, 1921; Cent. 1921, II 601-602; C.A. 15, 1535 (1921). French 519,129, June 4, 1921: Cent. 1921, IV 803; not in C.A. (192) Knunyantz, Ber. 68, 397-399 (1935): Compt. rend. acad. sci. (U.R.S.S.) 1935, I 501-506; Cent. 1936, II 2915; not in C.A. (193) Gerhardt, Ber. 24, 352-357 (1891). (194) Balbiano, Gazz. chim. ital. 17, 177 (1887); 18, 356-357, 375 (1888); 19, 128 (1889). (195) Rosanov, J. Russ. Phys.-Chem. Soc. 48, 1227 (1916); Cent. 1923, III 1080; not in C.A. (196) Drozdov, Cherntzov, J. Gen. Chem. (U.S.S.R.) 4, 969-974 (1934); Cent. 1936, I 42; C.A. 29, 2148 (1935). (197) Gibson, Harley-Mason, Litherland, Mann, J. Chem. Soc. 1942, 172. (198) Eisleb (to I.G.), Ger. 473,219, March 13, 1929; Cent. 1929, II 350; [C.A. 23, 2987 (1929)]; Brit. 275,622, Sept. 28, 1927; Cent. 1929, II 350; C.A. 22, 2171 (1928). (199) Eisleb (to Winthrop Chem. Co.), U.S. 1,845,403, Feb. 16, 1932; Cent. 1932, I 3112; C.A. 26, 2199 (1932). (200) Ingold, Rothstein, J. Chem. Soc. 1931, 1672-1673.

(201) M.L.B., Ger. 284,291, May 19, 1915; Cent. 1915, I 110; [C.A. 10, 94 (1916)]. (202) Reboul, Compt. rend. 93, 423 (1881). (203) Schmidt, Ann. 337, 116-121 (1904). (204) du Pont Co., Brit. 477,981, Feb. 10, 1938; Cent. 1938, II 183, not in C.A. (205) Tronov, Gershevich, J. Russ. Phys.-Chem. Soc. 58, 727-739 (1927); Cent. 1928, I 2924; C.A. 22, 3389-3390 (1928). (206) Tronov, J. Russ. Phys.-Chem. Soc. 58, 1278-1301 (1926); Cent. 1927, II 1145; C.A. 22, 2737 (1928). (207) Giua, Gazz. chim. ital. 52, I 349-351 (1922). (208) Fromm, Ann. 442, 133-134, 142 (1925). (209) Ohle, Haeseler, Ber. 69, 2325 (1936). (210) Gabriel, Ohle, Ber. 50, 820-821 (1917).

(211) Tomita, Z. physiol. Chem. 158, 42-57 (1926). (212) den Otter, Rec. trav. chim. 57, 18-20 (1938). (213) Weizmann, Malkowa, Bull. soc. chim. (4) 47, 357-358 (1930); Compt. rend. 190, 495-496 (1930). (214) Lohmann, J. prakt. Chem. (2) 153, 57-64 (1939). (215) Bachman, Mayhew, J. Org. Chem. 10, 250, 253 (1945).

3:5360 1,2-DICHLOROBUTENE-2
$$Cl$$
 Cl $C_4H_6Cl_2$ Beil. S.N. 11 (low-boilg. stereoisomer) $CH_3-CH=C-CH_2$

B.P.
$$116-118^{\circ}$$
 at 765 mm. (2) $D_4^{20} = 1.1544$ (2) $n_D^{20} = 1.4642$ (2) $111.5-112.5^{\circ}$ at 742 mm. (1) $D_4^{18} = 1.1550$ (2) $n_C^{18} = 1.4576$ (2) $D_4^{16} = 1.1488$ (1) $n_C^{16} = 1.45513$ (1)

[See also high-boilg. stereoisomer (3:5615).]

[For prepn. of \bar{C} (together with its stereoisomer (3:5615)) from 1,2,3-trichlorobutane (3:5935) with KOH at 150° (2), or from 2,2-dichlorobutane (3:7415) or 2,3-dichlorobutane (3:7615) with alc. KOH (5), see indic. refs.; for formn. of \bar{C} (together with its stereoisomer and also 2,4-dichlorobutene-2 (3:5550)) from 2-chlorobutene-2 (3:7105) by actn. of Cl_2 at 350° see (3).]

 \bar{C} with 1 mole Cl₂ + 1.5 moles NaHCO₃ at 0° gives (100% yield (4)) 1,2,2,3-tetrachlorobutane (3:9078).

C on hydrolysis by htg. with 2 pts. aq. + 1 mole powdered CaCO₃ at 70° for 4 hrs. gives (1) a mixt. of about equal parts of 2-chlorobuten-2-ol-1 (3:8240) and (by allylic transposition) 3-chlorobuten-3-ol-2 (3:9115).

 \tilde{C} on oxidn. with KMnO₄ in acetone gives (1) chloroacetic acid (3:1370) + AcOH (1:1010) + HCl. — \tilde{C} in CCl₄ at -17° treated with O₃ followed by aq. gives acetaldehyde (1:0100).

3:5360 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 658-662 (1937); Cent. 1937, II 371; C.A. 31, 5754 (1937). (2) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 6, 1553-1558 (1936); Cent. 1937, I 3786; C.A. 31, 2165 (1937). (3) N. V. Bataafsche Petroleum Maatschappij, Brit. 468,016, July 22, 1937; French 810,112, March 15, 1937; Cent. 1937, II 4102. (4) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4222; C.A. 33, 4190 (1939). (5) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 663-666 (1937); Cent. 1937, II 371; C.A. 31, 5754 (1937).

3:5372
$$\alpha,\alpha$$
-DICHLOROPROPIONYL CHLORIDE C_3H_3 OCl₃ Beil. II - 251 H_1 — CH_3 — C — C =O

B.P. 117.4-117.8° at 753 mm. (1)
$$D_4^{20} = 1.4062$$
 (1) $n_D^{20} = 1.45240$ (1) $110-115^{\circ}$ (2) $68-73^{\circ}$ at 88-90 mm. (3)

Colorless lachrymatory liq. with penetrating odor.

[For prepn. of \bar{C} from α,α -dichloropropionic acid (3:6162) with SOCl₂ under reflux for 10 hrs. (1) or with PCl₃ (2) see indic. refs.; from pyruvic acid (CH₃CO.COOH) (1:1040) with PCl₅ see (2) (4).]

[For study of rate of reaction of \tilde{C} in dioxane with β -chloroethanol (3:5552) see (1).] \tilde{C} with aq. readily hydrolyzes to α,α -dichloropropionic acid (3:6162) q.v.

- α,α-Dichloropropionamide: Ifts. from dil. alc., m.p. 117-118° (3) (5), 116-117° (2), 116° (4). [From C with conc. aq. NH₄OH (2); for other ways see under α,α-dichloropropionic acid (3:6162).]
- α,α-Dichloropropion-N-ethylamide: m.p. 51-52° (3). [From C with EtNH₂ (3).]
 α,α-Dichloropropionanilide: m.p. 101° (3). [Reported only by indirect means (3).]
 α,α-Dichloropropion-p-toluidide: m.p. 84-86° (6). [Reported only by indirect means (6).]
- 3:5372 (1) Leimu, Ber. 70, 1046, 1050 (1937). (2) Beckurts, Otto, Ber. 11, 386-391 (1878). (3) von Braun, Jostes, Münch, Ann. 453, 126, 135 (1927). (4) Klimenko, Ber. 3, 465-468 (1870). (5) Otto, Ann. 132, 183 (1864). (6) Bischoff, Walden, Ann. 279, 93 (1894).

3:5385
$$\alpha$$
-CHLORO-ISOBUTYRYL CHLORIDE $\begin{array}{c} C_4H_6OCl_2 \\ Cl \\ II_1-\\ CH_3-C-C=O \\ CH_3 \end{array}$ Beil. II - 295 II_1- II_2-(263)

The b.p. of 125-126° given by (3) is incorrect (1).

113-114° (2)

[For prepn. of \bar{C} from isobutyryl chloride (3:7270) with Cl₂ (3) (4) (5) or with SO₂Cl₂ + dibenzoyl peroxide in CCl₄ (20% \bar{C} + 80% β -chloro isomer (1)) see indic. refs.; for prepn. of \bar{C} from α -hydroxyisobutyric acid (1:0431) with SOCl₂ (together with other products) see (2).]

[For reactn. of \tilde{C} with MeOH yielding methyl α -chloro-isobutyrate (3:7918) see (5).] \tilde{C} on hydrolysis with aq. yields α -chloro-isobutyric acid (3:0235) q.v.

3:5385 (1) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940). (2) Blaise, Montagne, Compt. rend. 174, 1555 (1922). (3) Michael, Garner, Ber. 34, 4054-4055 (1901). (4) Henry, Compt. rend. 142, 1024 (1906); Bull. acad. roy. Belg. 1906, 206-226; Cent. 1906, II 227. (5) du Pont Co. & Loder, Brit. 428,223, May 9, 1935; Cent. 1936, I 179; C.A. 29, 6607 (1935).

3:5395 1,1,2-TRICHLOROPROPENE-1 Cl
$$C_3H_3Cl_3$$
 Beil. I - 200 CH_3 — $C=CCl_2$ I_1 — I_2 — B.P. 118° (1) $D_{14}^{14}=1.387$ (3) $D_{14}^{14}=1.387$ (3)

[For prepn. of \bar{C} from 1,1,1,2-tetrachloropropane (3:5785) in 93% yield by htg. with aq. or alc. alk. for 3 hrs. at 95° see (1); for prepn. of \bar{C} from 1,1,2,2-tetrachloropropane (3:5825) with alc. KOH or alc. NH₄OH see (2) (3).]

[For use of \tilde{C} as dry cleaner and spot remover (4) or in degreasing of metals (5); for use in dewaxing of mineral oils see (6).]

C with Cl₂ yields (3) 1,1,1,2,3-pentachloropropane (3:4740), m.p. 179°.

3:5395 (1) du Pont Co. and Cass, Brit. 469,051, July 19, 1937; Cent. 1938, I 1218; C.A. 32, 596 (1938). (2) Szenic, Taggesell, Ber. 28, 2668 (1895). (3) Borsche, Fittig, Ann. 133, 117-119 (1865). (4) Levine (to du Pont Co.), U.S. 2,116,437, May 3, 1938; Cent. 1938, II 796; C.A. 32, 5233 (1938). (5) Levine (to du Pont Co.), U.S. 2,116,438, May 3, 1938; Cent. 1938, II 947; C.A. 32, 4936 (1938). (6) Standard Oil Development Co., French 790,852, Nov. 28, 1935; Cent. 1936, I 2672; C.A. 30, 3323 (1936).

B.P.
$$118^{\circ}$$
 cor. (1) (8) $D_4^{20} = 1.6202$ (3); $n_D^{20} = 1.4701$ (5); $117-118^{\circ}$ at 760 mm. (2) 1.6179 (5) 1.46949 (3) $116.3-118.5^{\circ}$ (4) 116.4° at 755 mm. (5) $116-117^{\circ}$ at 726 mm. (6)

[For prepn. of \bar{C} from trichloroacetic acid (3:1150) with PCl₃ (1) (7) (8), with PCl₃ + ZnCl₂ (25% yield (9)), with SOCl₂ (yield: 12% (9), 30% (23)) in C₆H₈ (60% yield (3)) or in pyridine (90% yield (10)), with P₂O₅ + HCl gas (11), with benzotrichloride (3:6540) + ZnCl₂ at 100° (77% yield (12)), with benzoyl chloride (3:6240) (51-56% yield (13)) see indic. refs.]

[For formn. of $\bar{\rm C}$ from trichloroacetic acid at 300° (together with CO, CO₂ + HCl) see (14); from acetyl chloride (3:7065) with 3 moles PCl₅ see (11); from hexachloroethane (3:4835) with SO₃ at 150° see (15); from pentachloroethane (3:5880) or sym.-tetrachloroethane (3:5750) in ultra-violet light and O₂ see (16); from tetrachloroethylene (3:5460) with SO₃ (15), with H₂SO₄ + HNO₃ (together with other products) (17), with ozone (18) (19), with oxygen in pres. of Br₂ or conc. HNO₃ (20), with oxygen by chlorine sensitized photo-oxidation (21) cf. (30) (31), or with oxygen in ultra-violet light (16) see indic. refs.; from diethyl ether on protracted chlorination in sunlight, from decachlorodiethyl ether (3:1676) on distn. see (22), or from distn. of pentachloroethyl trichloroacetate see (22), from CCl₄ (3:5100) + AlCl₃ + CO gas at 200° and 250 atm. (37% yield) see (32).]

[C on htg. (13) or on htg. with AlCl₃ (23) yields carbon tetrachloride (3:5100) + CO; C on htg. at 600° yields (24) carbon tetrachloride (3:5100) + hexachloroethane (3:4835) + CO + phosgene (3:5000).]

[\bar{C} on treatment at -5° with dry HBr gas gives (70% yield (24)) trichloroacetyl bromide, b.p. 143°; \bar{C} similarly treated with dry HI gas gives (71.5% yield (6)) trichloroacetyl iodide, b.p. 74-74.2° at 30 mm. (6).]

[C with MeOH should yield readily methyl trichloroacetate (3:5800), b.p. 153.8°; C with EtOH yields (1) ethyl trichloroacetate (3:5950), b.p. 168°. (For study of rate of reactn. see (2)).]

[\bar{C} with pure freshly distilled AlCl₃ + C₆H₆ yields (25) (26) triphenylvinyl alcohol (ω , ω -diphenylacetophenone) [Beil. VII-522, VII₁-(291)], m.p. 137°; with moist AlCl₃ + C₆H₆, however, \bar{C} gives instead (25) (27) (28) ω , ω , ω -trichloroacetophenone (3:6874), b.p. 256-257° (25). — \bar{C} with Me₂Zn yields (29) pentamethylethyl alcohol [Beil. I-418, I₁-(207), I₂-(447)]. — \bar{C} with EtMgBr in ether at 10° gives (33) 1,1,1-trichlorobutanol-2 (3:5955).]

Č hydrolyzes readily with aq. yielding trichloroacetic acid (3:1150); for the amide, anilide, p-toluidide, and other derivs. corresp. to Č see trichloroacetic acid (3:1150).

3:5420 (1) Gal, Bull. soc. chim. (2) 20, 11-13 (1873). (2) Branch, Nixon, J. Am. Chem. Soc. 58, 2499-2504 (1936). (3) Leimu, Ber. 70, 1049 (1937). (4) Cheng, Z. physik. Chem. B-26, 295 (1934). (5) Martin, Partington, J. Chem. Soc. 1936, 162. (6) Gustus, Stevens, J. Am. Chem. Soc. 55, 376 (1933). (7) Delacre, Bull. acad. roy. Belg. 1902, 189-202; Cent. 1902, I 1197. (8) Thorpe, J. Chem. Soc. 37, 189-190 (1880). (9) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (10) Carré, Libermann, Compt. rend. 199, 1422-1423 (1934).

(11) Friederici, Ber. 11, 1971 (1878). (12) Rabcewicz-Zubkowski, Roczniki Chem. 9, 528 (1929); Cent. 1929, II 2767; C.A. 24, 61 (1930). (13) Brown, J. Am. Chem. Soc. 66, 1325-1328 (1938). (14) Engler, Steude, Ber. 26, 1443-1444 (1893). (15) Pud'homme, Compt. rend. 76, 1138 (1870). (16) Müller, Ehrmann, Ber. 69, 2207-2210 (1936). (17) Biltz, Ber. 35, 1535-1536 (1902). (18) Besson, Compt. rend. 118, 1348 (1894); 121, 125 (1895). (19) Swarts, Bull. acad. roy. Belg. (3) 36, 532-552 (1898); Cent. 1898, I 588-589. (20) Consortium für Elektrochem. Ind., Ger. 340,872, Sept. 19, 1921; Cent. 1921, IV 1101.

(21) Dickinson, Carrico, J. Am. Chem. Soc. 56, 1473-1480 (1934). (22) Malaguti, Ann. chim. (3) 16, 5-28, 64 (1846). (23) Boeseken, Rec. trav. chim. 29, 100, 112 (1910). (24) Simons, Sloat, Meunier, J. Am. Chem. Soc. 61, 435-436 (1939). (25) Biltz, J. prakt. Chem. (2) 142, 196-197 (1935). (26) Biltz, Ber. 32, 654-655 (1899). (27) Staudinger, Kon, Ann. 384, 112 (1911). (28) Gautier, Ann. chim. (6) 14, 398-402 (1888). (29) Bogomolez, Ann. 209, 78-82 (1881). (30) Schott, Schumacher, Z. physik. Chem. B-49, 107-125 (1941); Cent. 1941, II 2549; C.A. 38, 3551 (1944).

(31) Kirkbride (to Imperial Chem. Ind., Ltd.), U.S. 2,321,823, June 15, 1943; C.A. 37, 6676 (1943): Brit. 534,732, March 17, 1941; C.A. 38, 1330 (1942): Brit. 546,561, July 20, 1942; C.A. 37, 4746 (1943). (32) Theobald (to du Pont Co.), U.S. 2,378,048, June 12, 1945; C.A. 39, 4085 (1945). (33) Jacob, Bull. soc. chim. (5) 7, 581-586 (1940); C.A. 36, 3507 (1942).

B.P.	B.P. (contd.)	
119-120° (1) (20)	60-62° at 50 mm. (10)	$D_4^{25} = 1.123 (189)$
119.7° at 760 mm. (2)	46° at 46 mm. (3)	$D_{-}^{20} = 1.170 (11)$
119.5° (3)	35° at 29 mm. (6)	$D_{15}^{17} = 1.164 (12)$
119.3° (4)	20° at 12 mm. (6)	
118.8-119.4° (5)		$D_{16}^{16} = 1.162$ (7) cf. (189)
119° at 760 mm. (6)		
119° at 735 mm. (7)		$D_{13}^{13} = 1.158$ (9) cf. (189)
118° at 723 mm. (8)		
117-118° (9)		$D_4^{15} = 1.135 (189)$

 \bar{C} when pure is colorless liq. — \bar{C} turns dark on exposure to light. — \bar{C} on long exposure to light, acids, or metals resinifies to a dark mass, m.p. above 350°, which fumes in air and dis. in fumg. HNO₃, but does not react with fumg. H₂SO₄, NH₂OH, or phenylhydrazine

nor hydrolyze with 50% KOH (13). — [For stabilization of \bar{C} by means of addn. of 1% CaCO₃ (14) or 0.1% aq. (15) see indic. refs.]

Č is sol. in 10 pts. aq. (7) but does *not* form crystn. hydrates with it (9) (for prepn. of anhydrous Č using CaSO₄ see (16)); Č is volatile with steam (9); sol. in alc., ether, CHCl₈. Č has very pronounced lachrymatory properties; for studies of this property see (17) (18).

 $\bar{\bf C}$ forms azeotropes with several org. liqs. (19); e.g., $\bar{\bf C}$ with toluene (1:7405) forms a const.-boilg. mixt., b.p. 109.2° at 760 mm., contg. 28.5% $\bar{\bf C}$; $\bar{\bf C}$ with isobutyl alc. (1:6165) forms a const.-boilg. mixt., b.p. 105.8° at 760 mm., contg. 36% $\bar{\bf C}$; $\bar{\bf C}$ with ethyl *n*-butyrate (1:3127) forms a const.-boilg. mixt., b.p. 117.2° at 760 mm., contg. 53% $\bar{\bf C}$; $\bar{\bf C}$ with isobutyl acetate (1:3115) forms a const.-boilg. mixt., b.p. 116.7°, contg. 30% $\bar{\bf C}$.

[For prepn. of $\bar{\mathbb{C}}$ from acetone (1:5400) with Cl_2 (188) (9) (20) (21) (22) (23) (24) (25) (yield is poor and contaminated with higher chlorination prods. especially 1,1-dichloropropanone-2 (unsym.-dichloroacetone) (3:5430) whose b.p. is very close to that of $\bar{\mathbb{C}}$); with Cl_2 in pres. of CaCO_3 (yield 82% (3)) (26) (27) (28); with Cl_2 in vapor-phase chlorination (29) (30) (21) in pres. of NiCl_2 (38); by electrolysis in HCl (97% yield (32)) (36) using Pt electrodes (with graphite or lead electrodes resultant $\bar{\mathbb{C}}$ is reduced) even using alternating current (35% yield (33)); with $\mathrm{Cl}_2\mathrm{O}$ (34); with HOCl (22) (27) (35); with EtOCl (3:7022) (1); with N-chlorourea in aq. soln. (37); or with $\mathrm{SO}_2\mathrm{Cl}_2$ (72% yield (189)) see indic. refs.]

[For prepn. of C from acctone (1:5400) with benzenediazonium chloride (solid) in pres. of CaCO₃ (39) (40), or with aq. solns. of other diazonium chlorides (especially those with negative substituents such as those from p-nitroaniline, p-chloroaniline, or 2,4-dichloroaniline) in pres. of CuCl₂ + NaOAc (41), see indic. refs.]

[For prepn. of \bar{C} from 1-chloropropanol-2 (propylene α -chlorohydrin) (3:7747) by oxidn. with $K_2Cr_2O_7 + H_2SO_4$ (42) (43) (44) (45), $CrO_3 + dil$. H_2SO_4 (43), H_2SO_4 (44), H_2SO_4 (45), H_2SO_4 (46), or $G_3 + dil$. $G_3 +$

[For prepn. of \tilde{C} from ethyl γ -chloroacetoacetate (3:6375) (50) or from α -chloroacetoacetanilide (51) by hydrolytic cleavage with HCl see indic. refs.; from 1,3-dichloropropene-2 (3:5280) by soln. in conc. H₂SO₄ and distn. with aq. see (52); from allyl chloride (3:7035) with HgO + HOCl see (53); from 1,2-epoxypropane (propylene oxide) (1:6115) with Cl₂ at 0° see (54); from diketene + Cl₂ in cold followed by treatment with aq. see (55).]

[For use of \bar{C} in refining of mineral oils see (56); in prepn. of photosensitizing cyanine dyes see (57).]

Pyrolysis. [C passed through tube at 450° pyrolyzes into acetaldehyde (1:0100), acetone (1:5400), crotonaldehyde (1:0150) + HCl (58).]

Reduction. [\tilde{C} on reduction with Zn + HCl (7) or on electrolysis in HCl soln. using graphite or lead electrodes (32) yields acetone (1:5400); \tilde{C} on reduction with AlEt₃ etherate as directed (59) gives (70% yield) 1-chloropropanol-2 (3:7747), b.p. 78-81° at 80 mm. (59); \tilde{C} on phytochemical reduction using yeast (60) gives (25% yield) 1-chloropropanol-2 (3:7747); for polarographic study of oxidn.-reductn. potential of \tilde{C} see (61).]

Oxidation. \bar{C} on oxidn. with KMnO₄ (49) (62), HNO₈, CrO₃, etc. (62), yields chloroacetic acid (3:1370) and AcOH (1:1010). — \bar{C} with moist silver oxide yields (7) glycolic acid (1:0430), acetic acid (1:1010), and formic acid (1:1005).

Halogenation. [C with Cl₂ even in cold gives (26) more highly chlorinated acetones; e.g., C with Cl₂ at 30-40° yields (63) 1,1,3-trichloropropanone-2 (3:5957) and 1,1,1-trichloropropanone-2 (3:5620); C with Cl₂ at 50-70° yields (63) cf. (64) sym.-tetrachloro-

acetone (3:6050), unsym.-tetrachloroacetone (3:6085), and pentachloroacetone (3:6205); \bar{C} with Cl₂ at 50-100° in light (63) (65) or under press. (66) yields hexachloroacetone (3:6312). — Note that \bar{C} with Ca(OCl)₂ undergoes both chlorination and subsequent cleavage yielding (46) CHCl₃ (3:5050).]

 $[\bar{C} \text{ with } Br_2 \text{ (3 moles) at } 100^\circ \text{ yields (67) } 3,3,3-\text{tribromo-1-chloropropanone-2 [Beil. I-658], b.p. 215°; 13.0° at 25 mm.]}$

Reactions of the halogen atom of \bar{C} (see also further below under formn. of heterocyclic systems). \bar{C} with excess aq. alkali presumably yields propanone-2-ol-1 (acetol) (1:5455) and therefore reduces Fehling's soln.; the halogen atom of \bar{C} is so reactive that \bar{C} slowly neutralizes 1 equiv. alk. (68); \bar{C} with NaOEt in abs. alc. yields acetol ethyl ether (ethoxyacetone) [Beil. I-822, I₁-(418), I₂-(867)], b.p. 128° at 760 mm. (for study of rate of reaction see (69)).

[\bar{C} with phenol (1:1420) + anhydrous K_2CO_3 in acetone stirred 24 hrs. at room temp. or refluxed 3 hrs. (70) (note that in pres. of KI yield jumps to 92.5% (191)), or \bar{C} with sodium phenolate in phenol (71) (72) or in toluene (73), gives (yields: 21-23% (70), 16% (73)) phenoxyacetone (1:5534), b.p. 117-124° at 19 mm. (70) (note that \bar{C} + phenol + aq. NaOH gives only black resin (73)) (for application of this type of reactn. to other monohydric phenols such as tetralol-2 (5,6,7,8-tetrahydronaphthol-2) (74) (75) or p-terbutyl)phenol (1:1510) (75) or β -naphthol (1:1540) (191) see indic. refs.). — Note that \bar{C} with phenol (3 moles) + fumg. HCl at 100° reacts in a dif. sense to give (50% yield (76)) a tris-(hydroxyphenyl)propane of undetd. struct.; for formn. of resins from \bar{C} + phenol see (77) (78).]

[\bar{C} with KI in aq. MeOH (79) (80) or in acetone (5) gives (75% yield (80)) iodoacetone [Beil. I-660, I₁-(345), I₂-(719)], oil, b.p. 58.4° at 11 mm. (79) (oxime, pr. from pet. eth., m.p. 64.5° (79)); for study of rate of this reactn. in acetone at 0° and 10° see (5). — \bar{C} with K₂SO₃ (or Na₂SO₃) yields (81) salts of acetonesulfonic acid [Beil. IV-19, IV₂-(530)]. — For study of rate of reactn. of \bar{C} with aq. Na₂S₂O₃ see (82). — \bar{C} with Na₂S in acetone yields (83) (84) bis-(acetonyl) sulfide, m.p. 49° (83), b.p. 126° at 14 mm. (83), 125° at 18 mm. (84) (earlier work (85) using alc. as solvent could not be checked (83) (84).)]

[C with aq. NaSCN.stirred 10 hrs. at 25° (86), or C with Ba(SCN)₂ directly (87) or in alc. (88) (89) cf. (90), gives (95% yield (86)) thiocyanoacetone (acetonyl thiocyanate) [Beil. III-179, III₁-(72), III₂-(125)], oil, b.p. 73.5-74.5° at 1 mm. (86), D₁₅ = 1.1892 (86) (for use of this prod. as anti-oxidant for rubber (91), as stabilizer for cellulose (92), or as 1% soln. in petroleum as insecticide (93) see indic. refs.); note that thiocyanacetone, at though insensitive to dil. aq. HCl (87), with HCl gas in cold (86) or conc. HCl on boilg. (89) adds 1 mole HCl and ring-closes to 2-chloro-4-methylthiazole, oil, b.p. 167-167.5° at 754.4 mm., 69° at 14 mm. (86); note also that thiocyanoacetone with aq. NaHCO₃ (94) (or C + aq. KSCN + NaHCO₃ (86)) yields 2-hydroxy-4-methylthiazole (4-methylthiazolone-2) ("α-methylrhodime") [Beil. XXVII-158, XXVII₁-(264)], ndls. from aq. or ether, m.p. 105-106° (94), 102-103° (86).]

[\bar{C} with Na salts of sulfinic acids gives the corresp. alkyl- (or aryl)sulfonylacetones: e.g., \bar{C} with Na methanesulfinate gives (95) methanesulfonylacetone, m.p. 54° (95) (96); \bar{C} with Na benzensulfinate in alc. gives on refluxing (95% yield (97)) benzenesulfonylacetone [Beil. VI-307, VI₁-(145)], lfts. from alc., m.p. 57° (97); \bar{C} with Na p-toluenesulfinate yields (97) p-toluenesulfonylacetone [Beil. VI-421, VI₁-(210)], m.p. 51° (97) (98); many other analogous cases are known.]

 $[\bar{C}]$ with tertiary amines gives the corresp. quaternary ammonium chloride salts: e.g., \bar{C} with dry Me₃N in abs. ether (99) or abs. alc. (100) (101) yields trimethyl-acetonyl-ammonium chloride [Beil. IV-315, IV₂-(763)], very hygroscopic white solid; \bar{C} with pyridine gives corresp. salt (for study of rate in abs. alc. at 55.6° see (102)). — \bar{C} with triphenyl-

phosphine in C_6H_6 at 75-80° for 15 hrs. yields (103) triphenyl-acetonyl-phosphonium chloride, m.p. 234° dec. (103). — \bar{C} with hexamethylenetetramine in CHCl₃ grad. ppts. an addn. prod. (poor yield (104)), ndls., m.p. 122° (104).]

[C with dry NH₃ may yield (9) a little aminoacetone (acetonylamine) [Beil. IV-314, IV₁-(450), IV₂-(763)], but the reactn. is unsatisfactory and other methods (105) are preferred for prepn. of the latter; C (in excess) with aq. soln. (30%) of Me₂NH yields (106) dimethylaminoacetone [Beil. IV-314], misc. with aq., alc., ether, b.p. 123° (106); C (1 mole) with Et₂NH (2 moles) in ether yields (106) diethylaminoacetone [Beil. IV-316], b.p. 155-156° (106). — Many analogous cases are recorded.]

Reactions of $\bar{\mathbb{C}}$ involving the H atoms of its —CH₂Cl grouping. $\bar{\mathbb{C}}$ with salicylaldehyde (1:0205) in alc. KOH refluxed for 15 min. (107) (108), or in alc. NaOH refluxed 2 hrs. (109), or $\bar{\mathbb{C}}$ + Na salt of salicylaldehyde in dry \mathbb{C}_6H_6 under reflux (110), gives (yields: 60–85% (107), 75% (109), 60% (108)) 2-(acetyl)coumarone (2-acetobenzofuran) [Beil. XVII-338], colorless lfts. from alc., m.p. 76° (107), 75–76° (109), 74–75° (108) (110) (corresp. oxime, ndls. from dil. alc., m.p. 150° (111), phenylhydrazone, cryst. from alc., m.p. 153–154° (107), semicarbazone, ndls. from dil. alc., m.p. 217° (107)). — $\bar{\mathbb{C}}$ with p-dimethylaminobenzal)acetone, yel. lfts. from alc., m.p. 115° (112) (corresp. phenylhydrazone, m.p. 206–208° (112), semicarbazone, m.p. 202–203° (112)), accompanied by a little α -chloro- α , α -bis-(p-dimethylaminobenzal)acetone, cryst. from 1:1 abs. alc. + \mathbb{C}_6H_6 , m.p. 225° (112). — $\bar{\mathbb{C}}$ with diazotized aniline in pres. of NaOAc at 0° yields (113) (49) cf. (114) 1-(benzeneazo)1-chloroacetone [Beil. XV-342], yel. ndls. from boilg. alc., m.p. 136–137° (113), 135–136° (49).

Reactions of Č involving the keto group. \bar{C} with satd. aq. NaHSO₃ soln. yields (51) a crystn. NaHSO₃ cpd. cf. (7).

[Č with HCN as directed gives (yields: 94% (119), 87–90% (192)) (21) (115) (116) β -chloro- α -hydroxyisobutyronitrile (chloroacetone cyanohydrin) [Beil. III-317], oil, b.p. 110° at 22 mm. (117) 108–110° at 20 mm. (192), 103–104° at 16 mm. (115), $D_{-}^{15} = 1.2027$ (117), $n_D^{20} = 1.4520$ (192), $n_D^{11} = 1.45362$ (117); this prod. on distillation at ord. press. or even on stdg. in the air readily dissociates into the original components; on saponification with HCl, however, it gives (62% yield (192)) (5) (115) β -chloro- α -hydroxyisobutyric acid [Beil. III-317, III₁-(120), III₂-(224)], ndls. from C_6H_6 , m.p. 110° (118) 109–110° (192). — Č (1 mole) with aq. KCN (1 mole) gives 43% yield (119) of a cpd., $C_8H_{10}O_2N_2$, m.p. 183°, formerly supposed to be α -aceto- β -hydroxy- β -methylglutaro (di)nitrile·[Beil. III-883] but now (119) regarded as 2,4-dicyano-2,5-dimethyl-5-hydroxytetrahydrofuran (for mechanism of its formn. and review of earlier literature see (119)).]

[\tilde{C} forms acetals or similar cpds.: e.g., \tilde{C} with triethyl orthoformate (1:3241) in EtOH + a drop of H₂SO₄ gives (yields: 90% (120), 87% (80)) cf. (190) chloroacetone diethylacetal [Beil. I-654, I₂-(718)], b.p. 161-162° u.c. (120) 81-82° at 50 mm. (190), 52-53° at 14 mm. (80), $D_0^{14} = 1.002$ (120); for acetals from \tilde{C} with glycerol (1:6540) (121) or pyrocatechol (1:1520) (122) see indic. refs.]

[$\ddot{\mathbf{C}}$ with phenyl isocyanide + AcOH in ether gives (123) α -acetoxy- β -chloroisobutyranilide; $\ddot{\mathbf{C}}$ with phenyl isocyanide + BzOH in ether gives (123) α -benzoyloxy- β -chloro-isobutyranilide.]

[Č with RMgX cpds. (1 mole) in ether in general reacts normally with the ketonic group to give addn. prods. which with aq. yields the corresp. tertiary alcs.: e.g., Č with MeMgBr gives (38% yield (124)) (125) 1-chloro-2-methylpropanol-2 (\$\alpha\$-isobutylene chlorohydrin) (3:7752) (accompanied as a result of reactn. of a second MeMgBr and rearr. (126) (127) by some 2-methylbutanol-2 (1:6160)); for corresp. reactn. of Č with EtMgBr yielding

1-chloro-2-methylbutanol-2 (3:8175) see (128); for corresp. reactn. of \tilde{C} with n- C_4H_7MgBr , n- C_4H_9MgBr , iso- $C_5H_{11}MgBr$, n- $C_6H_{13}MgBr$, and n- $C_7H_{15}MgBr$ see (129); for corresp. reactn. of \tilde{C} with ter-butylethynyl MgBr (130), with n-amylethynyl MgBr (131), or with ethynyl bis-(MgBr) (132) see indic. refs. — \tilde{C} with C_6H_5MgBr yields (133) 1-chloro-2-phenylpropanol-2 [Beil. VI-507]; note, however, that if the initial addn. cpd. is htd. at 130–140° prior to hydrolysis rearr. occurs and the prod. then (134) is phenylacetone (1:5118). — For reactn. of \tilde{C} with o-xenyl MgI see (70).]

[C with abs. diazomethane (free from MeOH) in dry ether yields (135) 1-chloro-2-methyl-2,3-epoxybutane, b.p. 124° (135).]

Condensation reactions of C (usually yielding heterocyclic compounds). [Č with acetal-dehyde (1:0100) + NH₄OH in pres. of Cu(OAc)₂ gives (49% yield (136)) 2,4-(or 5)-dimethylimidazole [Beil. XXIII-79, XXIII₁-(25)], b.p. 266° at 733 mm., m.p. 92° (136) (B.HCl, m.p. 205, B.PkOH, m.p. 142-143° (136)).]

[$\bar{\mathbb{C}}$ with methyl acetoacetate (1:1705) + NH₄OH at -1° gives (16% yield (137)) 3-carbomethoxy-2,5-dimethylpyrrole [Beil. XXII-29], cryst. from alc., m.p. 119.5°; $\bar{\mathbb{C}}$ with ethyl acetoacetate (1:1710) + excess conc. aq. NH₄OH (138) (140) or in ether with NH₃ gas (139) gives (yields: 44% (139), 20% (138)) 3-carbethoxy-2,5-dimethylpyrrole [Beil XXII-29, XXII₁-(496)], m.p. 116-117° (138) (other by-prods. also being formed (139)); $\bar{\mathbb{C}}$ with ethyl acetoacetate (1:1710) + prim. amines similarly gives N-substituted analogs; e.g., use of aq. MeNH₂ gives (141) 3-carbethoxy-1,2,5-trimethylpyrrole [Beil. XXII-29, XXII₁-(496)], m.p. 48° (141); use of aniline gives (139) (141) 3-carbethoxy-2,5-dimethyl-1 phenylpyrrole [Beil. XXII-30, XXII₁-(496)], m.p. 43°, b.p. 225° at 40 mm.; for corresp. use of p-toluidine see (141).]

[Č with ethyl oxaloacetate [Beil. III-780, III₁-(273), III₂-(479)] in other treated with NH₃ gas yields (139) 4-carbethoxy-5,6-dihydroxy-2(or 3)-methylpyridine [Beil. XXII-259], m.p. 223° (139) (much oxamide and other by-prods. also being formed).]

[\bar{C} with diethyl acetonedicarboxylate (1:1772) in ether (142) (143) (139) or C_6H_6 (144) with dry NH₃ gas gives (yields: 49% (143), 38% (142)) ethyl (3-carbethoxy-4-methyl-furyl-2)acetate [Beil. XVIII-333], oil, b.p. 168° at 20 mm. (139).]

[C htd. with amides yields corresp. oxazoles: e.g., C with acetamide htd. 8-10 hrs. at 120° under reflux gives (7% yield (145)) (146) 2,4-dimethyloxazole [Beil. XXVII-17], liq. with odor like pyridine, very sol. aq., b.p. 108° (145) (146); C with benzamide + powdered CaCO₃ at 115-120° for 8 hrs. gives (15% yield (147)) (148) 2-phenyl-4-methyloxazole [Beil. XXVII-58], b.p. 238-241° (148), 92-95° at 5 mm. (147) (B.HCl, m.p. 72°, B.PkOH, m.p. 111° (147)); for corresp. reactn. of C with m-nitrobenzamide see (147).]

[Č with thioamides yields corresp. thiazoles: e.g., Č with thioformamide in abs. alc. refluxed for 1 hr. (149) or Č with formamide $+ P_2S_5$ (150) gives (35–47% yield (149)) 4-methylthiazole [Beil. XXVII-16], b.p. 131° (150), 130° (149), 70–71° at 59 mm. (151) (B.PkOH, m.p. 181° (151); B.EtI, m.p. 144.5° (149)); Č with thioacetamide without solvent (152) (153) in aq. or alc. (152) (149) or Č with acetamide $+ P_2S_5$ (150) yields 2,4-dimethylthiazole [Beil. XXVII-18], b.p. 144–145.5° cor. at 719 mm. (152), 143–144° at 762 mm. (153), 143° (150) (154), $D_4^{20} = 1.0562$ (B.PkOH, m.p. 137–138° (152), B.EtI, m.p. 212° dec. (149)); Č with thiobenzamide in alc. gives (155) (147) 4-methyl-2-phenylthiazole [Beil. XXVII-58], m.p. 29.5° (156), b.p. 282° at 762 mm. (156), 275–277° at 750 mm. (147), 111° at 6 mm. (147); many other analogous cases are recorded.]

[Č with aq. thiourea (157) (158) (159) or Č with NH₄SCN (160) (161) or Č with NH₄SCN + NH₄OH (162) (86) gives (70-75% yield (157)) 2-amino-4-methylthiazole [Beil. XXVII-159], m.p. 44-45° (157), 42° (159), b.p. 231-232° sl. dec. (162), 130-133° at 18 mm. (157), 117-120° at 8 mm. (157); Č with N-methylthiourea gives (163) (164) (158) 2-(methyl-

amino)-4-methyl-thiazole [Beil. XXVII-159], pr. from alc., m.p. 71.5-72.5° cor. (163), 64° (164) (B.HCl, m.p. 228° cor. (163)); Č with phenylthiourea gives (158) (164) 2-(anilino)-4-methylthiazole [Beil. XXVII-159], ndls. from alc., m.p. 117-118° (164), 115° (158).]

[Č with O-methyl thiocarbamate on warming gives (89) 2-methoxy-4-methylthiazole, b.p. 59-60° at 18 mm. (89) (B.HCl, m.p. 78°; B.HgCl₂, m.p. 123-124° (89)) (accompanied by its dimer); Č with O-ethyl thiocarbamate + KOAc yields (89) 2-ethoxy-4-ethylthiazole, b.p. 71-72° at 15 mm. (89).]

[Č with solid ammonium dithiocarbamate in abs. alc. stood at room temp. for 12 hrs. then refluxed 1 hr. gives (85% yield (151)) 2-mercapto-4-methylthiazole [Beil. XXVII-161], cryst. from isopropyl ether/alc. or dil. alc., m.p. 89-90° (165), 88.0-88.5° (151); note that in ether these reactants yield (166) an intermediate S-acetonyl dithiocarbamate, m.p. 80-82° (166), which on stdg. changes to the above 2-mercapto-4-methyl-thiazole; for use of the latter (or its metal salts) as vulcanization accelerators see (167).]

[C with 1-phenylthiosemicarbazide in abs. alc. readily dis. at room temp. yielding on addn. of pyridine (168) 2-(phenylhydrazino) 4-methylthiazole, m.p. 179° (acetyl deriv., m.p. 179° (168)); for analogous reactions of C with the three 1-(tolyl)thiosemicarbazides (169), the three 1-(nitrophenyl)thiosemicarbazides (170), see indic. refs.]

[C with acetone thiosemicarbazone in CHCl₃ gives on warming (171) the corresp. deriv. of 4 methylthiazolone 2, viz., 2-keto-4-methyl-2,3-dihydrothiazole-2-isopropylidenehydrazone; for analogous reactn. of C with acetophenone thiosemicarbazone and benzaldehyde thiosemicarbazone see (171).

- Color reactn. with KOH: C with excess very cone. aq. KOH gives crimson red color (5) (22).
- Acetonyl acetate (acetal acetate) (acetoxyacetone) [Beil. II-155, II₁-(72), II₂-(168)]: b.p. 174-175° at 760 mm. (172), 137-138° at 230 mm. (172), $D_4^{20} = 1.0749$, $n_D^{20} = 1.4150$ (Beil.). [From \bar{C} + KOAc in MeOH (173) or abs. EtOH (172) after 2 hrs. reflux (82% yield (173)).]
- —— Acetonyl benzoate (acetol benzoate) (benzoyloxyacetone) [Beil. IX-148]: m.p. 23.5-24° (174), 25° (175); b.p. 188-190° at 60 mm. (176). [From C with KOBz on htg. together (54% yield (176)) or in alc. soln. (174).]
- **D** 1-(β -Naphthoxy)acetone (acetonyl β -naphthyl ether): cryst. from alc., m.p. 78.4° cor. (177), 78° (178), 69-73° (191), 69-72° (70). [From \dot{C} + Na β -naphtholate on htg. in β -naphthol (178) or from \dot{C} + β -naphthol (1:1540) + dry K₂CO₃ refluxed in acetone (21% yield (70)) (note that by addn. of KI yield jumps to 85% (191)).]
- ① 1-(N-phthalimido)acetone (N-acetonylphthalimide) [Beil. XXI-477, XXI₁-(371)]: lfts or ndls. from aq., m.p. 124° (105). [From $\ddot{C} + K$ phthalimide at 120° for 20 min. (179) or refluxed 1 hr. in xylene (67% yield (180)).]
- 1-(N-3-nitrophthalimido)acetone (N-(acetonyl)-3-nitrophthalimide: ndls. from alc., m.p. 152-153° (181). [From C with K 3-nitrophthalimide on htg. (181).]
- Methylglyoxal dioxime (methylglyoxime) [Beil. I-764, I₁-(396), I₂-(822)]: pr. from alc., m.p. 156° (182). [From C with aq. soln. contg. NH₂OH.HCl (3 moles) + Na₂CO₃ (2 moles) followed by acidification and ether extraction (182); note that by careful regulation of conditions chloroacetone oxime has been obtd. (82% yield (183)), but since it is an oil, b.p. 171° at 727 mm. with slight decompn., it has no value as a for C̄.]
- 1-(β-Phenylhydrazino)acetone phenylhydrazone [Beil. XV-412]: yel. cryst. from MeOH, m.p. 162.5° (184). [From C with phenylhydrazine (3 moles) in abs. alc. at -16 to -18° (184).]
- © Chloroacetone o-nitrophenylhydrazone: m.p. 83° (135).

- ♠ Chloroacetone 2,4-dinitrophenylhydrazone: yel. ndls. from alc., m.p. 124.0-125.5° (185) (51), 124° (39). [From C (0.5 g.) with 2,4-dinitrophenylhydrazine (1.0 g.) in alc. (12 ml.) + conc. HCl (1.5 g.) under reflux (185); note that this prod. on protracted (13 hrs.) boilg. in alc. disproportionates yielding (185) C + 2,4-dinitrophenylhydrazine (both sol. hot alc.) accompanied by the spar. sol. methylglyoxal-bis-(2,4-dinitrophenyl)-osazone, cryst. from pyridine, m.p. 298° (185); for various other reactans, see (185).]
- © Chloroacetone semicarbazone: m.p. 147-148° dec. (39), 141-142° (47), 136-137° (48), 165° (50), 163-165° (44). [From C with aq. semicarbazide HCl on addn. of solid NaHCO3 at room temp. (186); note that this prod. is reactive and on boilg. with aq. dissolves to a bright yel. soln. which soon becomes colorless and ppts. hydrazine dicarboxylic acid diamide leaving in the filtrate hydroxypropanone semicarbazone, m.p. abt. 192° dec. (186); these changes (which doubtless occur slowly even on standing in water at room temp.) probably account for the divergent values of m.p. reported above.]
- © Condensation prod. ($C_{17}H_{20}O_4N_3SC1$) of \tilde{C} with N-methyl- β -carbohydrazidopyridinium p-toluenesulfonate: cryst. from 1:1 alc./ether, m.p. 135° cor. (187). [From \tilde{C} + indicated react. in abs. alc. on refluxing 15 min. (187).]
- 3:5425 (1) Goldschmidt, Endres, Dirsch, Ber. 58, 576 (1925). (2) Lecat, Rec. trav. chim. 46, 245 (1927). (3) Justoni, Chimica e industria (Italy) 24, 89-94 (1942); Cent. 1943, I 383. (4) Cheng, Z. physik. Chem. B-26, 296 (1934). (5) Conant, Kirner, Hussey, J. Am. Chem. Soc. 47, 497 (1925). (6) Herbst, Kollondchem. Benhefte 23, 330-331 (1927). (7) Linnemann, Ann. 134, 170-175 (1865). (8) Mohler, Helv. Chim. Acta 21, 69 (1938). (9) Cloèz, Ann. chim. (6) 9, 156-161 (1886). (10) Jacob, Bull. soc. chim. (5) 7, 581-586 (1940), C.A. 36, 3508 (1942).
- (11) Harkins, Clark, Roberts, J. Am. Chem. Soc. 42, 703 (1920) (12) Dobrosserdow, J. Russ. Phys.-Chem. Soc. 43, 129 (1911); Cent. 1911, I 955. (13) Giua, Racciu, Atti accad. sci. Torino, Classe sci. fis. mat. at. 67, 409-412 (1932); Cent. 1933, I 3919; C.A. 27, 5719 (1933). (14) Rahrs (to Eastiman Kodak Co.), U.S. 2,263,010, Nov. 18, 1940; C.A. 36, 1331 (1942). (15) Morey (to Commerical Solvents Corp.), U.S. 2,229,625, Jan. 21, 1941; C.A. 35, 2904 (1941). (16) Wallis, Falck (to I.G.), Ger. 584,776, Oct. 1, 1934; Cent. 1935, I 156. (17) Bertrand, Compt. rend. 171, 965-967 (1920); Cent. 1921, I 779. (18) Dufraisse, Bongrand, Compt. rend. 172, 817-819 (1920); Cent. 1921, I 1006. (19) Lecat, Ann. soc. sci. Bruxelles, 41, 21-27 (1927); Cent. 1927, II 226. (20) Glutz, Fischer, J. prakt. Chem. (2) 4, 52-53 (1871).
- (21) Bischoff, Ber. 5, 863-867, 963-964 (1872). (22) Mulder, Ber. 5, 1009-1010 (1872). (23) Bischoff, Ber. 8, 1330 (1875). (24) Barbagha, Ber. 7, 467 469 (1874). (25) Tcherniac, Ber. 25, 2629-2632 (1892). (26) Fritsch, Ber. 26, 597-598 (1893); Ann. 279, 310-319 (1894). (27) Kling, Bull. soc. chm. (3) 33, 322-324 (1905); Ann. chm. (8) 5, 474-480 (1905). (28) Ger. 69,039, April 19, 1893, Friedländer 3, 9. (29) Justoni, Chimica e industria (Italy) 24, 195-201 (1942); Cent. 1943, I 1659. (30) I.G., French 813,131, May 26, 1937; Cent. 1937, II 2071.
- (31) Rahrs (to Eastman Kodak Co.), U.S. 2,235,562, March 18, 1941; C.A. 35, 4040 (1941). (32) Szper, Bull. soc. chim. (4) 51, 653-654 (1932). (33) Shipley, Rogers, Can. J. Research 17-B 147-158 (1939); Cent. 1939, II 3056; C.A. 33, 6727 (1939). (34) Goldschmidt, Schissler, Ber. 58, 567 (1925). (35) Richard, Compt. rend. 133, 878 (1901). (36) Riche, Ann. 112, 321-324 (1859). (37) Behal, Detoeuf, Compt. rend. 153, 1229 (1911). (38) Akashi, Bull. Inst. Phys.-Chem. Research (Tokyo) 12, 329-340 (1933); Cent. 1933, I 3066; C.A. 27, 3447 (1933). (39) Waters, J. Chem. Soc. 1937, 2011-2012. (40) Waters, Nature 140, 466-467 (1937).
- Chem. Rescator (Polygo 12), 3201-2012. (40) Waters, Nature 140, 466-467 (1937).
 (41) Meerwein, Büchner, van Emster, J. prakt. Chem. (2) 152, 248-251 (1939). (42) Markownikoff, Ann. 153, 254-255 (1870). (43) Morley, Green, J. Chem. Soc. 47, 133 (1885); Ber. 18, 24-25 (1885). (44) Michael, J. prakt. Chem. (2) 60, 455-457 (1899); Ber. 39, 2787 (1996). (45) Henry, Rec! trav. chim. 22, 337-338 (1903); Bull. acad. roy. Belg. 1903, 397-431; Cent. 1908, II 486. (46) Ssuknewitsch, Tschilingarjan, Ber. 69, 1539 (1936). (47) Gutner, Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1062-1067 (1938); Cent. 1939, II 4221. (48) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4223. (49) Jones, Williams, J. Chem. Soc. 1934, 834. (50) Hamel. Bull. soc. chim. (4) 29, 399 (1921).
- 1934, 834. (50) Hamel, Bull. soc. chim. (4) 29, 399 (1921).
 (51) Bülow, King, Ann. 439, 213 (1924). (52) Henry, Ber. 5, 190-191, 966 (1872). (53)
 Linnemann, Ann. 138, 123-125 (1866). (54) Dobryanskii, Davydova, Papkina, J. Gen. Chem. (U.S.S.R.) 7, 291-297 (1937); Cent. 1937, II 1998; C.A. 31, 4645 (1937). (55) Boses (to Carbide and Carbon Chem. Corp.), U.S. 2,209,683, July 30, 1940; C.A. 35, 139 (1941). (56) Ferris

(to Atlantic Refining Co.), U.S. 2,062,872, Dec. 1, 1936; Cent. 1937, I 3578; C.A. 31, 849 (1937). [57] Kodak, Ltd., Brit. 405,028, Feb. 22, 1934; French 757,767, Jan. 4, 1934; Cent. 1934, II 1250. (58) Nef, Ann. 335, 278 (1904). (59) Meerwein, Hinz, Majert, Sonke, J. prakt. Chem. (2) 147, 236 (1936). (60) Sen, J. Indian Chem. Soc. 1, 7 (1925).

 (61) Winkel, Proske, Ber. 69, 700 (1936).
 (62) N. V. de Bataafsche Petroleum Maatschappij,
 French 797,943, May 6, 1936; Cent. 1936, II 865; C.A. 30, 7124 (1936).
 (63) I.G., French 816,956, Aug. 21, 1937; Cent. 1938, I 2216. (64) Edwards, Evans, Watson, J. Chem. Soc. 1937, 1944–1945. (65) Heisel, Hendschel (to I.G.), U.S. 2,199,934, May 7, 1940; C.A. 34, 5855 (1940). (66) I.G., French 837,741, Feb. 20, 1939; Cent. 1939, II 228. (67) Cloëz, Ann. chim. (6) 9, 207-209 (1886). (68) Astruc, Munro, Compt. rend. 131, 944 (1900). (69) Hedelius, Z. physik. Chem. 96, 356-358, 364-365 (1920). (70) Bradsher, Tess, J. Am. Chem. Soc. 61, 2184-2185 (1939).

(71) Stoermer, Ber. 28, 1253-1254 (1895); Ann. 312, 273 (1900). (72) Stoermer, Wehln Ber. 35, 3553, Note (1902). (73) Whitney, Henze, J. Am. Chem. Soc. 60, 1149 (1938). (74) Thoms, Kross, Arch. Pharm. 265, 342-343 (1927). (75) Sabetay, Bull. soc. chim. (4) 45, 534-537 (1929). (76) Lippmann, Ber. 45, 2489-2491 (1912). (77) Dachlauer, Thomsen (to I.G.), Ger. 453,430, Dec. 7, 1937; French 612,035, Oct. 15, 1926; Cent. 1928, I 2456. (78) I.G., French 666,086, Sept. 26, 1929; Cent. 1930, II 1145. (79) Scholl, Matthaiopoulos, Ber. 29, 1558 (1896). (80) Evlampiev, Ber. 62, 2387-2388 (1929).

(81) Mazak, Suszko, Roczniki Chem. 9, 431-443 (1929); Cent. 1929, II 1918; C.A. 23, 4187 (1929). (82) Slator, Twiss, J. Chem. Soc. 95, 96 (1909). (83) Bohme, Pfeifer, Schneider, Ber. 75, 903-904, 908 (1942). (84) van Zuydewijn, Boeseken, Rec. trav. chim. 53, 673-674 (1934). (85) Matthaiopoulus, Zaganjaris, J. prakt. Chem. (2) 123, 333-335 (1930). (86) Tcherniac, J. Chem. Soc. 115, 1071-1076 (1919). (87) Tcherniac, Ber. 25, 2623-2628 (1892). (88) Hellon, Tcherniac, Ber. 16, 348-350 (1883). (89) Hantzsch, Ber. 60, 2541-2543 (1927); Ber. 61, 1780, 1784 (1928). (90) Tcherniac, Ber. 61, 575-577 (1928).

(91) Cadwell, Meuser (to Naugatuck Chem. Co.), U.S. 1,839,950, Jan. 5, 1932; Cent. 1932, I 3356. (92) du Pont Co., Brit. 466,877, July 8, 1937; Cent. 1937, II 3108. (93) Heckert (to Röhm and Haas Co.), U.S. 1,808,893, June 9, 1931; Cent. 1932, I 123. (94) Tcherniac, Ber. 25, 3648-3652 (1892). (95) Corvie, Gibson, J. Chem. Soc. 1934, 48. (96) Bohme, Fischer, Ber. 76, 99-106 (1943); C.A. 37, 5026 (1943). (97) R. Otto, W. Otto, J. prakt. Chem. (2) 36, 402-405, 426 (1887). (98) Arndt, Martius, Ann. 499, 280 (1932). (99) Niemilowicz, Monatsh. 7, 242-249 (1886). (100) Furnée, Arch. Pharm. 236, 343-346 (1898).

(101) Brabant, Arch. intern. pharmacodynamie 25, 295-320 (1920); Ccnt. 1921, III 124. (102) Clarke, J. Chem. Soc. 97, 427 (1910). (103) Mel'nikov, Kretov, Mel'tser, J. Gen. Chem. (U.S.S.R.) 7, 461-463 (1937); Cent. 1937, II 1564; C.A. 31, 4289 (1937). (104) Mannich, Hahn, Ber. 44, 1552 (1911). (105) Gabriel, Pinkus, Ber. 26, 2197-2202 (1893). (106) Stoermer, Dzimski, Ber. 28, 2220-2227 (1895). (107) Stoermer, Chydenius, Schinn, Ber. 57, 74-75 (1924). (108) Shriner, Anderson, J. Am. Chem. Soc. 61, 2706 (1939). (109) Stoermer, Schäffer, Ber. 36,

2864-2865 (1903). (110) Stoermer, Ber. 30, 1711-1712 (1897).

(111) Stoermer, Calov, Ber. 34, 775 (1901). (112) Bauer, Werner, Ber. 55, 2498 (1922). (113) Favrel, Bull. soc. chim. (4) 41, 1494-1497 (1927). (114) Favrel, Bull. soc. chim. (5) 1, 981-990 (1934). (115) Fourneau, Bull. soc. chim. (4) 5, 229-231 (1909). (116) Poulenc Frères et Fourneau, Ger. 198,306, May 12, 1908; Cent. 1908, I 1956. (117) Ultée, Ber. 39, 1858 (1906): Rec. trav. chim. 28, 17-19 (1909). (118) Fourneau, Tiffeneau, Bull. soc. chim. (4) 15, 24 (1914). (119) Justoni, Gazz. chim. ital. 71, 41-53 (1941); C.A. 36, 1016-1017 (1942). (120) Arbusow, Ber. 40, 3304 (1907); J. Russ. Phys.-Chem. Soc. 40, 637-652 (1908); Cent. 1908, II 1340.

(121) Evlampiev, J. Gen. Chem. (U.S.S.R.) 7, 2941-2944 (1937); Cent. 1939, I 1747; C.A. 32, 5377 (1938). (122) Druey, Bull. soc. chim. (5) 2, 2261-2264 (1935). (123) Passerini, Gazz. chim. ital. 54, 532-533, 536-537 (1924). (124) Dersin, Ber. 54, 3158-3159 (1921). (125) Honry, Compt. rend. 142, 131, 494, Note (1906); Bull. acad. roy. Belg. 1906, 523-557; Cent. 1906, II 1551; Rec. trav. chim. 26, 149 (1907). (126) Henry, Compt. rend. 145, 24 (1907). (127) Fourneau, Tiffeneau, Compt. rend. 145, 438 (1907). (128) Seyer, Chalmers, Trans. Roy. Soc. Can. (3) III 20, 337-341 (1926); Cent. 1927, II 1811. (129) Fourneau, Samdahl, Bull. soc. chim. (4) 47, 1005-1010 (1930). (130) Favorskii, Tikhomolov, Compt. rend. 203, 726-727 (1936); Cent. 1937, I 577; C.A. 31, 6188 (1937).

(131) Tiffeneau, Deux, Compt. rend. 213, 753-758 (1941); Cent. 1942, II 1557; C.A. 37, 4049 (1943). (132) Zaboev, J. Gen. Chem. (U.S.S.R.) 1, 143-149 (1931); Cent. 1931, II 1122; C.A. 25, 4525 (1931). (133) Tiffeneau, Compt. rend. 134, 775 (1902); Ann. chim. (8) 10, 176-179 (1907). (134) Tiffeneau, Compt. rend. 137, 990 (1903); Ann. chim. (8) 10, 367-368 (1907). (135) Arndt, Amende, Ender, Monatsh. 59, 206-207, 213 (1932). (136) Weidenhagen, Herrmann, Ber. 68, 1960-1961 (1935). (137) Korschun, Ber. 37, 2196-2197 (1904). (138) Hantzsch, Ber. 25, 1474-1476 (1890). (139) Feist, Ber. 35, 1539-1552 (1902). (140) Küster, Willig, Z.

physiol. Chem. 121, 144-145 (1922); Cent. 1922, III 1087.

(141) Fischer, Smeykal, Ber. 56, 2372-2374 (1923). (142) Reichstein, Zschokke, Helv. Chim. Acta 14, 1271-1272 (1931). (143) Feist, Molz, Ber. 32, 1766-1769 (1899). (144) Rinkes, Rec. trav. chim. 56, 1127-1129 (1931). (145) Oesterreich, Ber. 30, 2255 (1897). (146) Schuftan, Ber. 28, 3070-3072 (1895). (147) Friedman, Sparks, Adams, J. Am. Chem. Soc. 59, 2262-2263 (1937). (148) Lewy, Ber. 21, 2193-2194 (1888). (149) Clarke, Gurin, J. Am. Chem. Soc. 57, 1879 (1935). (150) Hromatka (to E. Merck), Ger. 670,131, Jan. 12, 1939; Cent. 1939, I 2296.

(151) Buchman, Reims, Sargent, J. Org. Chem. 6, 767-768 (1941). (152) Hantssch, Ann. 256, 265-268 (1888). (153) Dyson, Hunter, Jones, Styles, J. Indian Chem. Soc. 8, 176-177 (1931). (154) von Auwers, Ernst, Z. physik. Chem. A-122, 232, 246 (1926). (155) Hubacher, Ann. 259, 236 (1890). (156) Mills, Smith, J. Chem. Soc. 121, 2736 (1922). (157) Byers, Dickey, Org. Syntheses, Coll. Vol. 2 (1st ed.), 31-32 (1943); 19, 10-11 (1939). (158) Traumann, Ann. 249, 37-38, 43-45, 47 (1888). (159) Bogert, Chertoff, J. Am. Chem. Soc. 48, 2866 (1924). (160) Hantzsch, Traumann, Ber. 21, 938-939 (1888).

(161) Hantzsch, Weber, Ber. 20, 3121 (1887). (162) Tscherniac, Norton, Ber. 16, 345-347 (1883). (163) Burtles, Pyman, Roylance, J. Chem. Soc. 127, 589 (1925). (164) Young, Crookes, J. Chem. Soc. 89, 64, 68 (1906). (165) Miolati, Gazz chim. ital. 23, I 578-579 (1893). (166) Levi, Gazz chim. ital. 61, 721-722 (1931); Cent. 1932, I 1097; C.A. 26, 1602 (1932). (167) Bruni, Romani, Atti accad. Lincei (5) 31, I 86-88 (1922); Cent. 1922, III 676; C.A. 16, 4093 (1922). (168) Bose, J. Indian Chem. Soc. 4, 336 (1927). (169) Bose, Sen. J. Indian Chem. Soc. 5, 650, 653, 655 (1928). (170) Das-Gupta, Bose, J. Indian Chem. Soc. 6, 499, 501-502, 504.

(171) McLean, Wilson, J. Chem. Soc. 1937, 556-559. (172) Perkin, J. Chem. Soc. 59, 788-789 (1891). (173) Madelung, Oberwegner, Ber. 65, 940 (1932). (174) Breuer, Zincke, Ber. 13,

639 (1880). (175) Van Romburgh, Rec. trav. chim. 1, 53-54 (1882). (176) Kling, Ann. chim. (8) 5, 484-485 (1905). (177) Calaway, Henze, J. Am. Chem. Soc. 61, 1356 (1939). (178) Stoermer, Ann. 312, 311-312 (1900). (179) Goedeckemeyer, Ber. 21, 2684 (1888). (180)

Gabriel, Colman, Ber. 35, 3806 (1902).

(181) Sah, Ma, Ber. 65, 1630-1633 (1932). (182) Hantzsch, Wild, Ann. 290, 292 (1896). (183) Scholl, Matthaiopoulos, Ber. 29, 1552-1554 (1896). (184) Bodforss, Ber. 52, 1770-1771, 1775 (1919). (185) Bulow, Seidel, Ann. 439, 48-58 (1924). (186) Hoogeveen, Jansen, Rec. trav. chim. 51, 260-264 (1932). (187) Allen, Gates, J. Org. Chem. 6, 596-601 (1941). (188) Shilor, Kubinskaye, J. Applied Chem. (U.S.S.R.) 13, 121-126 (1945); C.A. 39, 5250 (1945). (189) Buchman, Sargent, J. Am. Chem. Soc. 67, 401-402 (1945). (190) Morey (to Commerical Solvents Corp.). U.S. 2,374,494, April 25, 1945; C.A. 39, 3545 (1945).

(191) Hurd, Perletz, J. Am. Chem. Soc. 68, 38-39 (1946). (192) Hurd, Rector, J. Org. Chem.

10, 443 (1945).

3:5430 1,1-DICHLOROPROPANONE-2
$$C_3H_4OCl_2$$
 Beil. I - 654 $(\alpha,\alpha$ -Dichloroacetone; CH_3 —C—CHCl₂ I_1 -(344) I_2 -(718) dichloromethyl methyl ketone)

B.P. 120-121° (1) (25) $D_2^{21} = 1.236$ (5) 120° (2) (10) (11) (14) 119.8-120° (3) $D_-^{20} = 1.236$ (6) 119-120° (7) 115-116° (4) $D_-^{15} = 1.234$ (1)

Colorless oil which rapidly turns yellow on expos. to light; spar. sol. aq.; eas. sol. alc., ether. — $\bar{\mathbf{C}}$ has penetrating odor, is lachrymatory, and blisters skin. — Note that b.p. of $\bar{\mathbf{C}}$ is very close to that of chloroacetone (3:5425) and that the latter is a frequent impurity in ord. samples of $\bar{\mathbf{C}}$.

[For prepn. of \tilde{C} from acetone (1:5400) with Cl_2 under various conds. see (2) (5) (7) (8) (9) (1); from acetone at b.p. with Cl_2 in pres. of I_2 , $FeCl_3$, or $SbCl_5$ (yield: 48.6% \tilde{C} accompanied by 28% sym.-dichloroacetone (3:0563) (12)) or at 70° in pres. of NiCl₂ (13)

(other prods. are also formed) or by electrolysis in HCl (9) see indic. refs.; from ethyl α,α -dichloroacetoacetate [Beil. III-663, III₁-(233), III₂-(427)] by ketonic cleavage with dil. HCl in s.t. at 170-180° for 4-6 hrs. (14) or by refluxing 4-5 hrs. with HCl (15) cf. (4) see indic. refs.; for formn. of \bar{C} from isopropyl alc. (1:6135) with Cl₂ see (16); from methylacetylene with HOCl (42% yield) see (17); from 1,1-dichloro-2-methylpropene-2 (3:7480) with O₂ see (18); from homoaspartic acid [Beil. IV-494, IV₁-(541), IV₂-(912)] by oxidn. with sodium N-chloro-p-toluenesulfonamide see (19).

[Č on reduction with Al(OEt)₃ + anhydrous acetaldehyde in dry ether gives (45% yield (20)) 1,1-dichloropropanol-2 (3:5755), b.p. 146-148°. — Č on reduction by yeast gives (54% yield (21)) levorotatory 1,1-dichloropropanol-2.]

 \bar{C} on oxidn. with conc. HNO₃, CrO₃, or KMnO₄ yields (22) dichloroacetic acid (3:6208). [\bar{C} with Br₂ (1 mole) (1) yields 3-bromo-1,1-dichloropropanone-2 [Beil. I-657], b.p. 111° at 25 mm. (1); \bar{C} with excess Br₂ at 100° yields (1) 3,3-dibromo-1,1-dichloropropanone-2 [Beil. I-658], b.p. 120° at 25 mm. (1); for study of rate of bromination of \bar{C} and influence of catalysts thereon see (4).]

 $\{\bar{C} \text{ with PCl}_5 \text{ htd. at b.p. of mixt. for 2 days yields (2) 1,1,2,2-tetrachloropropane (3:5825), b.p. 153°.\}$

 $[\bar{C}]$ with aq. in s.t. at 200° for 6 hrs. yields (23) lactic acid (1:0400). — \bar{C} with aq. alk. yields (presumably via cleavage of the expected methylglyoxal) acetic acid (1:1010) and formic acid (1:1005); by virtue of this result \bar{C} readily reduces Fehling's soln. (24). — \bar{C} with aq. 10% K_2CO_3 on boilg. loses HCl yielding (25) acrylic acid (1:1020).]

 \bar{C} with satd. aq. NaHSO₃ soln. readily yields (1) (5) an addn. prod. crystg. as a trihydrate. [\bar{C} with conc. aq. HCN slowly dis. on protracted refluxing yielding (10) the corresp. cyanohydrin (β,β -dichloro- α -hydroxy-isobutyronitrile) [Beil. III-318], an oil, which on htg. dissociates into its components; this prod., however, on hydrolysis with strong HCl yields (10) the corresp. acid, β,β -dichloro- α -hydroxyisobutyric acid (3:2145), pr. from alc./ether or cryst. from C₆H₆, m.p. 82-83° (10) (26). — Note also that \bar{C} with phenylisocyanide + aq. on stdg. yields (26) β,β -dichloro- α -hydroxy-isobutyranilide, pr. from CHCl₃, m.p. 132-133° (26).]

[C in excess McOH (5 moles) with ethyl iminoformate hydrochloride (1½ moles) 4-8 days at room temp. yields (27) unsym.-dichloroacetone dimethylacetal, b.p. 170-171° at 767 mm., 63° at 9 mm. — C in excess EtOH with ethyl iminoformate as above yields (27) unsym.-dichloroacetone diethylacetal, b.p. 183-184° at 767 mm., 76° at 8 mm.]

[\bar{C} with o-nitrobenzaldehyde in alc. treated dropwise with aq. 5% NaOH condenses yielding (28) ω , ω -dichloro-o-nitrobenzalacetone, pptd. as oil by addn. of aq., colorless pr. from C_6H_6 , m.p. 106–107° (28). — By similar procedure \bar{C} with m-nitrobenzaldehyde gives (28) ω , ω -dichloro-m-nitrobenzalacetone, colorless pr. from C_6H_6 , m.p. 116–117°; \bar{C} with p-nitrobenzaldehyde similarly gives (30% yield (28)) ω , ω -dichloro-p-nitrobenzalacetone, colorless pr. from C_6H_6 or ether, m.p. 125°.]

[$\bar{\mathbf{C}}$ with diazotized aniline in pres. of NaOAc yields (29) dichloro-bis-(benzeneazo)-methane, yel.-or. cryst. from hot alc., m.p. 81-82°; $\bar{\mathbf{C}}$ with diazotized p-toluidine in pres. of NaOAc yields (29) dichloro-bis-(p-tolueneazo)methane, or. cryst. from C₆H₆, m.p. 159-160°.

 \ddot{C} (1 mole) treated with aq. soln. of excess NH₂OH.HCl (6 moles) + Na₂CO₃ (3 moles), stood 24 hrs., and acidified yields (15) methylglyoxal dioxime (methylglyoxime) [Beil. I-764, I₁-(396), I₂-(822)], pr. from alc. or aq., m.p. 157°, 153° (15) (30); the same prod. also results if a satd. soln. hydroxylamine sulfate is used (30) in place of free hydroxylamine.

Č (1 g.) in abs. alc. (20 g.) with phenylhydrazine (2.5 g.) stood for 1½ days, then warmed with aq. (100 ml.), yields (31) as insol. residue (1 g.) methylglyoxal bis-(phenyl)osazone [Beil. XV-156, XV₁-(38)], yel. ndls. from dil. alc., m.p. 148° (31).

- ₱ 1,1-Dichloropropanone-2 semicarbazone: m.p. 163° (32). [From C in alc. with aq. semicarbazide.HCl (1 mole) without addn. of NaOAc, the semicarbazone pptg. immediately; note, however, that on stdg. the filtrate ppts. a small amt. of methylglyoxal bis-semicarbazone, m.p. 254°, also formed (together with equiv. C) on boilg. the semicarbazone with aq. (32).]
- 3:5430 (1) Cloéz, Ann. chim. (6) 9, 164-165, 175-176, 211-213 (1886). (2) Borsche, Fittig, Ann. 133, 112-117, 124 (1865). (3) Cheng, Z. physik. Chem. B-26, 296 (1934). (4) Bell, Lidwell, Proc. Roy. Soc. London, A-176, 104-106 (1940). (5) Fittig, Ann. 110, 38-43 (1859). (6) Harkins, Clark, Roberts, J. Am. Chem. Soc. 42, 703 (1920). (7) Glutz, Fischer, J. prakt. Chem. (2) 4, 53 (1871). (8) Mulder, Ber 5, 1007-1009 (1872). (9) Theegarten, Ber. 6, 897-898 (1873). (10) Bischoff, Ber. 8, 1330-1336 (1875).
- (11) Grabowski, Ber. 8, 1438-1442 (1875). (12) Consortium fur Elektrochem. Ind., French 707,852, July 16, 1931; Cent. 1931, II 2056. (13) Akashi, Bull. Inst. Phys.-Chem. Research (Tokyo) 12, 329-340 (1933); Cent. 1933, I 3066; C.A. 27, 3447 (1933), (14) Conrad, Ann. 186, 235-236 (1877). (15) Meyer, Janny, Ber. 15, 1165-1166 (1882). (16) Buc (to Standard Oil Co.), U.S. 1,391,757, Sept. 27, 1921; Cent. 1922, IV 942. (17) Wittorf, J. Russ. Phys.-Chem. Soc 32, 88-117 (1900); Cent. 1900, II 29-30. (18) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1236 (1938); Cent. 1939, II 4223. (19) Dakin, Biochem. J. 11, 91 (1917). (20) Nord, Ger. 434,728, Oct. 5, 1926; Cent. 1926, II 2845.
- (21) Sen, J. Indian Chem. Soc. 1, 1-8 (1924/25); Cent. 1925, I 537; C.A. 19, 816 (1925); Biochem. Z. 151, 51-53 (1924); Cent. 1924, II 2272; C.A. 19, 3277 (1925). (22) N. V. de Bataafsche Petroleum Mattschappij, French 797,943, May 6, 1936; Cent. 1936, II 865. (23) Linnemann, Zotta, Ann. 159, 248-251 (1871). (24) Klmont, Chem. Ztg. 69, 521 (1922). (25) Faworsky, J. prakt. Chem. (2) 51, 555-557 (1895). (26) Passerini, Gazz. chim. ital. 54, 540 (1924). (27) Wohl, Ber. 41, 3605-3606 (1908). (28) Heller, Lauth, Buchwaldt, Ber. 55, 485-486 (1922). (29) Favrel, Bull. soc. chim. (5) 1, 988-989 (1934). (30) Treadwell, Westenberger, Ber. 15, 2786-2787 (1882).
 - (31) Heller, Ann. 375, 287-288 (1910). (32) Knopfer, Monatsh. 32, 765-766 (1911).

```
B.P.
                                  -99.5^{\circ} (8) D_4^{25} = 1.1770 (11) n_D^{25} = 1.4362 (12)
120.5–120.6° (1) (2) (3) (4)
120.4°
                at 760 mm. (5)
                                              D_4^{17.6} = 1.1896 (13) \quad n_D^{20} = 1.452
                         (6) (7)
                                                                                         (9)
120.3-120.5° at 760 mm. (8)
                                                                             1.44867 (28)
120.2°
                at 750 mm. (28)
119.2°
                at 740 mm. (9)
119°
                at 740 mm. (10)
```

Colorless oil. — Note that b.p. of 125° given in I.C.T. is too high (4). — Almost insol. in aq. [for precise data see (1) (2) (3) (4)].

[For prepn. from propanediol-1,3 (trimethylene glycol) (1:6490) with fumg. HCl in s.t. at 100° (13) (10) (20–25% yield (14)) but always accompanied by 3-chloropropanol-1 (trimethylene chlorohydrin) (3:8285) see indic. refs.; with PCl₃ + ZnCl₂ (21% yield (15)), or PCl₅ + ZnCl₂ (31% yield (15)), or SOCl₂ (50% yield (15)) see (15): for prepn. of \tilde{C} from 1,3-dibromopropane (trimethylene dibromide) + HgCl₂ (8) (10) or 1,3-diiodopropane + AgCl (16) see indic. refs.: for prepn. of \tilde{C} from γ -chloropropyl p-toluenesulfonate with various RMgX cpds. see (12); for formn. of \tilde{C} (19.3% (7) together with other products) by chlorination of propane (17) (18) (19) or n-propyl chloride (3:7040) (17) (18) see indic. refs.]

[\bar{C} with Zn dust in aq. alc. (20) (21) or better in a high-boilg. solvent (7) (22) yields cyclopropane, b.p. -34° .]

Č with alc. KOH yields allyl chloride (3:7035), b.p. 46°, which then reacts with the KOEt yielding (10) allyl ethyl ether (1:7850), b.p. 66-67° at 742 mm.

- 1,8-Diphenoxypropane (1:7170) q.v.: lfts. from alc., m.p. 61° (23), 60-61° (24), 59-60° (25); b.p. 338-340° cor. at 762 mm. (26). [From C (26) (or trimethylene dibromide (24) or trimethylene diiodide (25)) with sodium phenolate.]
- **1,3-Di-**(α-naphthoxy)propane [Beil. VI-607]: ndls. from alc., m.p. 103-104° (27).
- **1,3-Di-**(β-naphthoxy)propane [Beil. VI-642]: lfts. from AcOH, m.p. 148-149° (27).
- 3:5450 (1) Gross, Saylor, Gorman, J. Am. Chem. Soc. 55, 651 (1933). (2) Gross, Physik. Z. 32, 589 (1931). (3) Gross, Z. physik. Chem. B-6, 215-220 (1929). (4) Gross, J. Am. Chem. Soc. 51, 2362-2366 (1929). (5) Hass, J. Chem. Education, 13, 493 (1936). (6) Hass, McBee, Weber, Ind. Eng. Chem. 28, 338 (1936). (7) Hass, McBee, Hinds, Gluesenhamp, Ind. Eng. Chem. 28, 1178-1181 (1936). (8) Serwy, Bull. soc. chim. Belg. 42, 485, 488 (1933). (9) Kohlrausch, Ypsilanti, Z. physik. Chem. B-32, 414 (1936). (10) Reboul, Ann. chim. (5) 14, 460-462, 493 (1878).
- (11) Dunstan, Hilditch, Thole, J. Chem. Soc. 163, 137 (1913). (12) Rossander, Marvel, J. Am. Chem. Soc. 0, 1491-1496 (1928). (13) Freund, Monatsh. 2, 638-639 (1881). (14) Rojahn, Ber. 54, 3116 (1921). (15) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89, (1929). (16) Hersfelder, Ber. 26, 2434 (1893). (17) Hass, McBee (to Purdue Research Foundation), Canadian 374,242, June 7, 1938; Cent. 1938, II 3005; C.A. 32, 5856 (1938). (18) Hass, McBee (to Purdue Research Foundation), U.S. 2,105,733, Jan. 18, 1938; Cent. 1938, I 4533. (19) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,073, June 4, 1935; Cent. 1936, I 1500. (20) Lott, Christiansen, Schackell, J. Am. Pharm. Assoc. 27, 125-120 (1938).
- (21) Lott (to E. R. Squibb and Sons), U.S. 2,261,168, Nov. 4, 1941; C.A. 36, 1049 (1942). (22) Hass, Hinds (to Purdue Research Foundation), U.S. 2,098,239, Nov. 9, 1937; Cent. 1938, I 4237. (23) Lohmann, Ber. 24, 2632 (1891). (24) Ramart-Lucus, Hoch, Bull. soc. chim. (4) 51, 837 (1932). (25) Bell, Bennett, Hock, J. Chem. Soc. 1927, 1807. (26) Henry, Bull. soc. chim. (3) 15, 1224 (1896). (27) Gattermann, Ann. 357, 378-380 (1907). (28) Smyth, McAlpine, J. Am. Chem. Soc. 57, 979 (1935).

3:5460 TETRACHLOROETHYLENE (Perchloroethylene) CI—C=C—Cl C₂Cl₄ Beil. I - 187 (Perchloroethylene) Cl Cl Cl Cl I₁₋(79) I₂₋(161) B.P. F.P. 121.20° at 760 mm.
$$\{1\}$$
 -23.5° $\{16\}$ D_4^{25} = 1.61463 $\{1\}$ n_D^{25} = 1.4993 $\{22\}$ 121.1° at 765 mm. $\{2\}$ -23° $\{17\}$ $\{3\}$ $\{4\}$ 121° at 765 mm. $\{5\}$ -22.35° $\{1\}$ D_4^{20} = 1.6230 $\{13\}$ n_D^{20} = 1.5058 $\{13\}$ 121° at 760 mm. $\{6\}$ $\{8\}$ 1.623 $\{6\}$ 1.50566 $\{2\}$ 121° $\{7\}$ -22.4° $\{18\}$ 1.62286 $\{1\}$ 1.50547 $\{20\}$ 120.8° at 760 mm. $\{8\}$ -19° $\{19\}$ 1.6226 $\{20\}$ 120.74° $\{9\}$ 1.6207 $\{2\}$ 120.5-120.8° at 770 mm. $\{10\}$ 1.9 1.6239 $\{11\}$ n_D^{15} = 1.50812 $\{1\}$ 119.0-120.0° u.c. $\{11\}$ 1.6239 $\{14\}$ 1.50831 $\{1\}$ 119-120° at 753 mm. $\{12\}$ 1.50899 $\{1\}$ 118.0-118.1° at 740 mm. $\{15\}$ 3.2° at 30 mm. $\{14\}$ See also Note 2.

Note 1. For vap. press. of $\bar{\mathbf{C}}$ from 33–118° see (14). Note 2. For D_4^t over range $t=15-90^\circ$ see (14).

Colorless liq. widely used as solvent, etc. (see also below). — \tilde{C} is pract. insol. aq., but detailed studies do not appear to be recorded. — \tilde{C} is miscible with alc., ether, CHCl₃, C₆H₆, and many other org. solvents.

GENERAL

[For study of \tilde{C} as solvent for detn. of mol. wts. by raising of b.p. (ebullioscopic const. = 55.0° per mole solute/100 g. \tilde{C}) see (23). — For study of thermal conductivity see (24). — For soly. in \tilde{C} of gaseous HCl, H₂S, or NH₃ see (11). — For study of influence of \tilde{C} upon inflammability of mixts. of air with CH₄ (25) (10) (26) (27), with CO (10) (28), with H₂ (10), or acetylene (10) see indic. refs.]

Binary systems contg. \bar{C} . [System $\bar{C}+CCl_4$: for f.p./compn. data see (18); for n_D^{25} /compn. and use in anal. of the system see (22); for vap. press. and liq./vapor compn. of system see (29). — System $\bar{C}+1,1,2,2$ -tetrachloroethane (3:5750): for f.p./compn. data see (17). — System $\bar{C}+p$ pentachloroethane (3:5880): for f.p./compn. data (eutectic, f.p. -54.8° contg. 58.4 wt. % \bar{C}) see (18). — System $\bar{C}+i$ sopropyl alc. (1:6135); for D_{23}^{25} /compn. and n_D^{25} /compn. data see (30).]

Č forms binary azeotropes with many alcohols [e.g., \bar{C} with MeOH (1:6120) forms a const.-boilg. mixt., b.p. 63.75° at 760 mm., contg. 36.5 wt. % \bar{C} (3); \bar{C} with EtOH (1:6130) forms a const.-boilg. mixt., b.p. 76.75° at 760 mm., contg. 37 wt. % \bar{C} (3); \bar{C} with n-propyl alc. (1:6150) forms a const.-boilg. mixt., b.p. 94.05° at 760 mm., contg. 52 wt. % \bar{C} (31); \bar{C} with isopropyl alc. (1:6135) forms a const.-boilg. mixt., b.p. 81.7° at 760 mm., contg. 30 wt. % \bar{C} (31); \bar{C} with n-butyl alc. (1:6180) forms a const.-boilg. mixt., b.p. 108.95° at 760 mm., contg. 71 wt. % \bar{C} (3); \bar{C} with isoamyl alc. (1:6200) forms a const.-boilg. mixt., b.p. 116.1° at 760 mm., contg. 80 wt. % \bar{C} (31); \bar{C} with ethylene glycol (1:6465) forms a const.-boilg. mixt., b.p. 119.1° at 760 mm., contg. 94 wt. % \bar{C}].

 $\bar{\mathbf{C}}$ forms binary azeotropes with many other org. cpds. [e.g., $\bar{\mathbf{C}}$ with formic acid (1:1005) forms a const.-boilg. mixt., b.p. 88.15° at 760 mm., contg. 50 wt. % $\bar{\mathbf{C}}$ (32); $\bar{\mathbf{C}}$ with \mathbf{AcOH} (1:1010) forms a const.-boilg. mixt., b.p. 107.35° at 760 mm., contg. 61.5 wt. % $\bar{\mathbf{C}}$ (218); $\bar{\mathbf{C}}$ with propionic acid (1:1025) forms a const.-boilg. mixt., b.p. 119.15° at 760 mm., contg. 91.5 wt. % $\bar{\mathbf{C}}$ (4); $\bar{\mathbf{C}}$ with isobutyric acid (1:1030) forms a const.-boilg. mixt., b.p. 120.5°, contg. 97 wt. % $\bar{\mathbf{C}}$ (33)].

Uses of \bar{C} . \bar{C} because of its solvent properties, b.p., uninflammability, and immiscibility with aq., etc., finds wide use. — [Other examples of its utility include the following: for use as dry-cleaning solvent see (34), cf. (35) (36) (222); for use with lower aliph. alcs. as solv. for cellulose ethers see (37); for use in dewaxing of lubricating oil see (38); for use in liq. HCN to diminish inflammability and explosiveness see (39); for use as a component of comml. tear-gas mixts. see (40).]

[For study of use of \bar{C} as an anesthetic (41), as fumigation agt. (with CCl₄) for grain or flour (42), for sterilization of surgical catgut (43), of antiseptic action (compared with CHCl₃ (44)) (45) see indic. refs.]

[For examples of studies of use of \bar{C} as anthelmintic especially with reference to hookworm and similar parasites see (46)–(57) incl.; for comparison of anthelmintic action of \bar{C} with that of CCl₄ (58) (59) or of chenopodium oil (60) see indic. refs.; for patent prepn. of \bar{C} for use as anthelmintic see (61).] (For toxicity see below.)

[For use of \bar{C} as the "booster" liquid in detn. of aq. by distn. especially in molasses and other sugar industry products see (62) (63) (64) (65) (66) (67). — For use of \bar{C} in prepn. of anhydrous Na₂O₂ by removal of moisture by distn. see (68).]

[For brief general surveys of \bar{C} see (69) (70).]

Physiological actn. and/or toxicity of C. [For studies from various viewpoints on toxicity of C see (57), (71)-(82) incl., also especially (219) (220) (224).]

Determination of C. C is usually detd. by some form of deen. followed by volumetric or gravimetric detn. of resultant chloride ion [e.g., for methods involving deen. of C with Na + AmOH in xylene (83) (84), with Na + ethanolamine in dioxane soln. (85) (223), or with Na in liq. NH₃ (86) (note that some cyanide forms. occurs) see indic. refs.; for methods involving thermal deen. see (87) (215)].

[For detn. of \tilde{C} by means of a recording ultra-violet photometer (the R. + H. Tri-Per Analyzer) see (88).]

PREPARATION OF C

From various polychloroethanes or polychloroethylenes. [For prepn. of $\bar{\mathbb{C}}$ from hexachloroethane (3:4835) by pyrolysis at 565° (89–94% conversion (89)), by passing over porcelain chips in hot tube (90) (note that CCl₄ (3:5100) is also formed), or by passing with H_2 over Ni at 270° (91) see indic. refs.; for prepn. of $\bar{\mathbb{C}}$ from hexachloroethane (3:4835) by treatment with granulated Zn in boilg. alc. (7), with Zn + dil. H_2 SO₄ at room temp. for several days (100% yield (5)) (92) (116), or even with Zn + aq. above 80° (93), with alc. KSH (94), with molecular Ag at 280° in s.t. (95), with SbF₃ at 300–325° under press. (96), with acetylene over activated carbon at 200–400° (97) cf. (123), with aniline at 170° at ord. press. (7), with N/10 abs. EtOH/NaOH at 25° (216), or with alc. free NaOEt in ether under press. at 140° (217) see indic. refs.]

[For prepn. of \tilde{C} from pentachloroethane (3:5880) by elimination of 1 HCl in various ways: e.g., by passing over bone char at 280° (98), or over N₁Cl₂ at 330° (99), by htg. with AlCl₃ at 70-100° (100% yield (101)) (100) or under reflux (102), with liq. NH₃ at -18 to -34° under reduced press. (103) (104), with MeOH over Al₂O₃ at 290° (MeCl (3:7005) is also formed) (105), with acetylene over cat. at 200-300° (vinyl chloride (3:7010) is also formed) (106), with alc. KOH (107) (108), or in alc. with 2 N aq. NaOH in cold (98% yield) (109) see indic. refs.]

[For prepn. of C from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) (see also below under prepn. of C from acetylene) on pyrolysis at 700° (110), with air over pumice + CuCl₂ at 430-450° (111), or with Cl₂ over activated carbon contg. 30% CuCl₂ at 300-320° (112) see indic. refs.]

[For prepn. of \tilde{C} from 1,2-dichloroethane (ethylene dichloride) (3:5130) with Cl_2 over cat. at 300-500° see (113); from ethane or its chloro derivs. with Cl_2 + fused metal chlorides such as $AlCl_3$, etc., at 250-500° see (114).]

[For formn. of \tilde{C} from trichloroethylene (3:5170) on pyrolysis at 700° (110) or with anhyd. FeCl₃ on htg. see (115).]

From various polychloromethanes. [For prepn. of \tilde{C} from CCl₄ (3:5100) through tube at 1300-1400° see (116) (117); for formn. of \tilde{C} (together with other prods.) from CCl₄ + H₂ through hot tube over pumice at low red heat (118) or through tube at 600-650° (119), or in dark electric discharge (120), see indic. refs. — Note also that \tilde{C} has been found (121) as a by-prod. of prepn. of CCl₄ (3:5100) by actn. of Cl₂ on CS₂.]

[For form. of C from CHCl₃ (3:5050) + H_2 in dark electric discharge see (120).]

From acetylene with Cl_2 (see also above under prepn. of \bar{C} from 1,1,2,2-tetrachloroethane (acetylene tetrachloride)). [For prepn. of \bar{C} from acetylene with Cl_2 + inert gas over cat. at 250-400° see (122) (123) (124) (125); from acetylene with Cl_2 at 700-900° in absence of extraneous substances (126); from acetylene with Cl_2 see (127) (128); from acetylene with Cl_2 in halogenated solv. at 175-260° + AlCl₃, etc., see (129).]

From miscellaneous sources. [For prepn. of \bar{C} from CO + HCl over cat. at 230-240° under high press. (CHCl₃ is also formed) see (130); from unsym.-heptachloropropane (3:0200) by dissociation into \bar{C} + CHCl₃ over Cu₂Cl₂ at 250° see (131); from chloral (3:5210) by long boilg, with AlCl₃ see (132) cf. (133) (134); from tetrachloroethyl chloro-

formate with AlCl₃ see (135); from trichloroacetic acid (3:1150) over ThO₂ + kaolin at 230-250° see (136); from pentachloropropionic acid (3:4895) on htg. in aq. (137), or from its ferric salt in light (139) cf. (140), or from pentachloropropionyl chloride (3:0470) with AlCl₃ (1 mole) at 60° (138) see indic. refs.]

PURIFICATION OF C

Comml. \bar{C} conts. some impurity which readily chlorinates (15); note also that \bar{C} , especially if exposed to light and air, may contain phosgene (3:5000), trichloroacetyl chloride (3:5420), trichloroacetic acid (3·1150), and other prods.; cf. below under oxidation of \bar{C} . — [For purification of \bar{C} by treatment with Cl_2 followed by illumination (15), by treatment with aq. alk. at elev. temp. (for removal of 1,1,2-trichloroethane (3:5330) or 1,1,1,2-trichloroethane (3:5555)) (141), by refluxing with finely divided metals + dil. acid (142) or with 1% Al or AlCl₃ (143), or by passing vapor over kaolin at 250° (144), see indic. refs.]

STABILIZATION OF C

To increase the resistance of $\bar{\mathbf{C}}$ to photooxidation (see below) and other changes, the addition of very small amts. of various stabilizers has been recommended. — [For example, for study of control of photooxidation of $\bar{\mathbf{C}}$ by use of inhibitors such as thymol (1:1430), ether, alcohol, thiourea, etc., see (145). — For stabilization of $\bar{\mathbf{C}}$ by addn. of small amts. of paraffin hydrocarbons (e.g., gasoline) (146), various phenols (such as hydroquinone monomethyl or monobenzyl ether) (147), oil-sol. azo dyes contg. phenolic groups (148), mercaptans (such as n-butyl mercaptan) (149), various org. tertiary amines such as triethylamine (150) or picoline (151), various phenols, amines, and aminophenols (152), or a wide variety of org. N cpds. (221) see indic. refs.]

CHEMICAL BEHAVIOR OF C

Pyrolysis. [\check{C} on pyrolysis over heated Pt wire gives (153) (154) hexachloroethane (3:4835) + hexachlorobenzene (3:4939) + Cl₂.]

Hydrogenation. [Note that \bar{C} does not add H_2 even in pres. of Ni at 300-350° (99); \bar{C} with excess H_2 over Ni at 220° dec. (163) to carbon + HCl.]

Oxidation. \bar{C} can be oxidized especially in the presence of light and moisture giving according to conditions truchloroacetyl chloride (3:5420), phosgene (3:5000), trichloroacetic acid (3:1150), or various mixtures of these prods.; for inhibition of this oxidation see above under stabilization of \bar{C}

[For extensive studies of photochem. oxidn. of $\bar{\rm C}$ giving 87% trichloroacetyl chloride accompanied by phosgene see (15) (155) (156); for oxidn. of $\bar{\rm C}$ on stdg. with aq. in light for 4 months yielding trichloroacetic acid see (157) cf. (158); for oxidn. of $\bar{\rm C}$ to trichloroacetyl chloride with O₃ (159) (160), with peracetic acid (acetyl hydrogen peroxide) (161), with conc. HNO₃ + conc. H₂SO₄ in freezing mixt. (162), with SO₃ at 150° (164), or with N₂O₅ (194) see indic. refs.; for patents on photochem. oxidn. of $\bar{\rm C}$ to trichloroacetyl chloride (3:5420) see (165) (166).]

[\bar{C} on oxidn. with $K_2Cr_2O_7/H_2SO_4$ is completely converted to $CO_2 + H_2O + HCl$ (167); \bar{C} passed with air over CuO at 450° gives only traces (168) of phosgene.]

Reaction with halogens. [\bar{C} dislyd. in dichlorodifluoromethane ("Freon") with F₂ at -80° (169), or \bar{C} with F₂ at 0° directly (170) but not in CCl₄ soln. (169) cf. (172), or \bar{C} in vapor phase at 130° with F₂ diluted with N₂ (171), gives (20% yield (171)) 1,2-difluoro-1,1,2,2-tetrachloroethane, m.p. 26.5° (96) (169), accompanied by various other prods. such as fluoropentachloroethane, m.p. 99.0-99.5° (in s.t.), b.p. 136-138° (170), and 1,4-difluoro-octachlorobutane (170) (169), m.p. 4-5° (170), b.p. 152.2° at 20 mm., $D_4^{20} = 1.9272$, $n_D^{20} = 1.5256$ (170).]

[Č with dry Cl₂ in direct sunlight (90), or Č in CCl₄ at 22° (173) or in vapor phase at 40° and low press. (155) in light and absence of O₂, or Č with SO₂Cl₂ in pres. of dibenzoyl peroxide (174) adds Cl₂ yielding hexachloroethane (3:4835) q.v.; note, however, that Č + Cl₂ + light in pres. of O₂ undergoes photooxidation to trichloroacetyl chloride (see above under oxidation of Č). — Č with Cl₂ at 700–800° (175), or Č with Cl₂ over act. carbon at 600–650° (176), undergoes cleavage of C—C bond yielding CCl₄ (3:5100); for study of this reactn. see (177).]

[Č with Br₂ in sunlight adds 1 mole Br₂ yielding (178) (179) (110) 1,2-dibromo-1,1,2,2-tetrachloroethane, m.p. 197.5° dec. (in s. cap. tube) (180), 200-205° dec. (110), 190° dec. (138). — Note, however, that this photochem. addn. is inhibited by its reactn. prod. (181), that, although accelerated by *small* amts. O₂, pres. of large amts. O₂ lead to a halogen catalyzed photooxidation (181), that in CCl₄ soln. resultant equilibrium mixt. conts. only 30% addn. prod. (182). — For extensive study of this reactn. see (181); for studies of its rate see (183) (184); for extensive study of photochem. dissoc. of prod. see (179). — For study of reactn. of C with radio-bromine see (185).]

[\bar{C} does not add I_2 . — For soly. of I_2 in \bar{C} see (186); for use of such solns. in detn. of iodine number of unsatd. oils and fats see (187) (188).]

Behavior of \tilde{C} with other inorganic materials. [\tilde{C} with Cl_2O in CCl_4 at -20° gives (189) hexachloroethane (3:4835).]

[\overline{C} with NO₂ in s.t. at 100–120° for 3 hrs. (190), or at 100–110° for 3 hrs. (5), or at 80° for 3 hrs. or 60° for 6 hrs. (191), or at 10–12 atm. press. at 60–80° for 3–6 hrs. (191), or \overline{C} with fumg. HNO₃ at ord. temp. stood several days (5) cf. (192), adds 2 moles NO₂ yielding 1,2-dinitro-1,1,2,2-tetrachloroethane [Beil. I-102, I₁-(33)], cryst. from alc., m.p. 142–143° (s. cap. tube) (5).]

[Č with nitryl chloride (ClNO₂) yields (193) 1-nitro-1,1,2,2,2-pentachloroethane, lfts. from alc., m.p. 192° (s. cap. tube) (193).]

[\bar{C} with N₂O₅ undergoes vigorous oxidn. (presumably to trichloroacetyl chloride) (194).] [\bar{C} with NH₃ at 700-800° splits off all its halogen as NH₄Cl (195) cf. (196).]

[For behavior of \bar{C} with various common metals see (197); note that \bar{C} is not attacked by molecular Ag even at 300° (95); note that \bar{C} with Na or K or their mixture may (like many other polychloro compds.) explode under certain conditions (for an extensive study see (198)).]

Behavior of \bar{C} with organic reactants. [\bar{C} (1 mole) with CHCl₃ (2 moles) + AlCl₃ (0.2 mole) refluxed 15-20 hrs. gives (85-93% yield (199)) (101) (16) (200) (201) (202) (214) unsym.-heptachloropropane (3:0200); for study of equilibrium of system \bar{C} + CHCl₃ + unsym.-heptachloropropane see (131).]

[$\ddot{\mathbf{C}}$ with 1,1,2,3,3-pentachloropropene-1 (3:6075) + AlCl₃ gives (201) cf. (214) 1,1,3,4,5,-5,6,6,6-nonachloropentene-1.]

[\bar{C} with NaOEt at 100-120° yields (203) ethyl dichloroacetate (3:5850) + Na diethoxyacetate + other prods., presumably via ethyl α,β,β -trichlorovinyl ether, α,α -dichloro- β,β -diethoxyethylene, triethyl dichloroorthoacetate, etc., cf. (204).]

[Č (1 mole) with NaSC₆H₅ (2 moles) in alc., refluxed 48 hrs., gives (yield not stated (205)) α,β -dichloro- α,β -bis-(thiophenyl)ethylene, ndls. from alc., m.p. 71-72° (205). — Č with disodium salt of dithiopyrocatechol in alc. at 110-120° in s.t. for 7 hrs. gives small

yield (206) of
$$C_6H_4$$
 C=C C_6H_4 , golden ndls., m.p. 234° (206).]

[Č with paraformaldehyde (1:0080) + conc. H₂SO₄ as directed (207) gives α,α -dichloro- β -hydroxypropionic acid, m.p. 88–89° (s. cap. tube).]

[C with dibenzoyl peroxide on refluxing either with or without AlCl₃ gives (40% yield

(208)) α,α,β -trichloro- β -phenylethylene (α,α,β -trichlorostyrene) [Beil. V-477, V₂-(367)], b.p. 87-89° at 3 mm., $D_{-}^{25} = 1.40$, $n_{D}^{25} = 1.5758$ (208), accompanied by chlorobenzene (3:7903), CO₂, and under certain conditions by hexachloroethane (3:4835).]

[Č with large excess EtMgBr in boilg. ether evolves ethylene and on subsequent treatment with aq. gives a mixt. of ethylene + acetylene; for explanation see (209). — Č with *n*-butyllithium in pet. eth. gives violent explosion (210).]

[For study of reactn. of C with pyridine or piperidine at 16-18° see (211).]

- ② Color test with NH₄OH/Cu₂Cl₂: C

 (1-2 drops) in small glass-stoppered bottle filled with conc. aq. NH₄OH, treated with powdered Cu₂Cl₂, stopper quickly inserted (to force out air and excess liquid), shaken, and allowed to stand, gives in 3 days a pale amethyst color (212); note, however, that C

 on stdg. with metallic Cu + conc. aq. NH₄OH develops rich port-wine red color in aq. layer and brown coating on the copper (213). Note also that neither of these tests should be regarded as conclusive (see (212) (213)).
- 3:5460 (1) Timmermans, Hennaut-Roland, J. chim. phys. 27, 405-407 (1930). (2) Mathews, J. Am. Chem. Soc. 48, 572 (1926). (3) Lecat, Rec. trav. chim. 47, 15, 17 (1928). (4) Lecat, Ann. soc. sci. Bruxelles 49, 110 (1929). (5) Biltz, Ber. 35, 1529-1530 (1902). (6) Mumford, Phillips, J. Chem. Soc. 1928, 159. (7) Bourgoin, Ann. chim. (5) 6, 142-144 (1875); Bull. soc. chim. (2) 23, 344 (1875). (8) Timmermans, Bull. soc. chim. Belg. 27, 334-343 (1914); Cent. 1914, I 618. (9) Thorpe, Rodger, Phil. Trans. Roy. Soc. A-185, 495 (1894). (10) Jorissen, Meuwissen, Rec. trav. chim. 44, 132-140 (1925).
- (11) Bell, J. Chem. Soc. 1931, 1373, 1376-1377. (12) Bonino, Gazz. chim. ital. 55, 342 (1925). (13) Britton, Coleman, Zemba (to Dow Chem. Co.), U.S. 2,084,937, June 22, 1937; Cent. 1937, II 3813; C.A. 31, 5817 (1937). (14) Herz, Rathmann, Chem. Zig. 36, 1417 (1912). (15) Dickinson, Leermakers, J. Am. Chem. Soc. 54, 3852-3862 (1932). (16) Prins, J. prakt. Chem. (2) 89, 414-415, 424 (1914). (17) Timmermans, Vesselovsky, Bull. soc. chim. Belg. 40, 506 (1931). (18) van de Vloed, Bull. soc. chim. Belg. 48, 260 (1939). (19) Herz, Rathmann, Chem. Zig. 37, 621 (1913). (20) Bruhl, Ann. 200, 173 (1879).
- (21) Gladstone, J. Chem. Soc. 59, 293 (1891). (22) MacMillan, McDonald, Ind. Eng. Chem., Anal. Ed. 15, 114-116 (1943). (23) Walden, Zastrow, Roudolf, Ann. Acad. Sci. Fennicae, A-29, No. 23 (Komppa Festschrift) 26 pp. (1927); Cent. 1928, I 166; C.A. 22, 1515 (1928). (24) Bates, Hazzard, Palmer, Ind. Eng. Chem. 33, 375-376 (1941). (25) Coward, Jones, Ind. Eng. Chem. 18, 970-974 (1926). (26) Jorissen, Velisek, Rec. trav. chim. 43, 80-86 (1924). (27) Jorissen, Ind. Eng. Chem. 19, 430-431 (1927). (28) Langen van der Valk, Rec. trav. chim. 48, 207 (1929). (29) McDonald, McMillan, Ind. Eng. Chem. 36, 1175-1176 (1944). (30) Bergelin, Lockhart, Brown, Trans. Am. Inst. Chem. Engrs. 39, 173-200 (1943).
- (31) Lecat, Ann. soc. sci. Bruxelles 47, I 152 (1927). (32) Lecat, Ann. soc. sci. Bruxelles 48, I 116, 121, 122 (1928). (33) Lecat, Ann. soc. sci. Bruxelles, 49, I8 (1929). (34) Brown, Dyer, Calico Printer, Bleacher, Finisher Text. Rev. 68, 568-569 (1932); Cent. 1933, I 863. (35) Brown, J. Soc. Dyers Colourists 49, 42-45 (1933). (36) Brown, J. Soc. Dyers Colourists 59, 72-76 (1934). (37) Caroll (to Eastman Kodak Co.), U.S. 1,450,714, April 3, 1923; Cent. 1923, IV 164. (38) Standard Oil Development Co., French 790,852, Nov. 28, 1935; Cent. 1936, I 2672; C.A. 39, 3223 (1936). (39) Kershbaum (to Roessler & Hasslacher Chem. Works), U.S. 1,591,842, July 6, 1926; Cent. 1926, II 2493. (40) Dow (to Dow Chem. Co.), U.S. 1,411,422, April 4, 1922; Cent. 1922, IV 126; C.A. 16, 1998 (1922).
- (41) Foot, Bishop, Apgar, Anesthiology 4, 283-292 (1943); C.A. 37, 4133 (1943). (42) Hymas, Food 12, 207-209, 215 (1943); C.A. 37, 6043 (1943). (43) Small, Med. J. Australia 28, 407-414 (1941); C.A. 36, 868 (1942). (44) Joachimoglu, Biochem. Z. 124, 130-136 (1921); Cent. 1922, I 363. (45) Gabbano, Z. Hyg. Infectionskrankh. 109, 183-193 (1928); Cent. 1928, II 2667; not in C.A. (46) Oelkers, Rathje, Arch. expt. Path. Pharmakol. 198, 317-337 (1941); Trop. Diseases Bull. 39, 767-768 (1942); C.A. 37, 1506-1507 (1943). (47) Mönnig, Ortlepp, Onderstepoort J. Vet. Sci. Animal Ind. 13, 193-197 (1939); C.A. 35, 270 (1941). (48) Ortlepp, Mönnig, Onderstepoort J. Vet. Sci. Animal Ind. 7, 399-417 (1936); Cent. 1936, II 4096; C.A. 31, 7116 (1937). (49) Maplestone, Mukerji, Indian Med. Gaz. 72, 650-652 (1937); Cent. 1939, I 2818; C.A. 32, 2223 (1939); 68, 617-620 (1933); Cent. 1934, I 567; not in C.A.; 64, 424-426 (1929). (50) Fernando, D'Silva, Stork, Sinnatamby, Indian J. Med. Research 26, 759-783 (1939); Cent. 1939, I 2015; C.A. 33, 8818 (1939).

(51) Wright, Bozicevich, Jordon, J. Am. Med. Assoc. 109, 570-573 (1937); Cent. 1938, I 1397. (52) Schlingman, J. Am. Vet. Med. Assoc. 75, 74-85 (1929); C.A. 24, 3277 (1930). (53) Hall, Augustine, Am. J. Hyg. 9, 584-628 (1929); Cent. 1929, II 452; not in C.A. (54) Hall, Cram, J. Agr. Research 30, 949-953 (1925); Cent. 1925, II 2177; not in C.A. (55) Hall, Shillinger, Am. J. Trop. Med. 5, 229-237 (1925); C.A. 19, 2710 (1925). (56) Hanson, J. Agr. Research 34, 129-136 (1927); Cent. 1927, II 457; not in C.A. (57) Lamson, Robbins, Ward, Am. J. Hyg. 9, 430-444 (1929); Cent. 1929, I 3119; C.A. 24, 3273 (1930). (58) Rawson, Indian J. Vet. Sci. 3, 294-297 (1933); Cent. 1934, I 1519; not in C.A. (59) Rawson, J. Am. Vet. Med. Assoc. 33, 600-603 (1932); C.A. 26, 3576 (1932). (60) Manson, Indian Med. Gaz. 69, 500-507 (1934); Cent. 1935, I 3444; not in C.A.

(61) Anderson (to Parke, Davis & Co.), U.S. 1,703,377, Feb. 26, 1929; Cent. 1929, I 2444; C.A. 23, 1996 (1929). (62) Thiolepape, Fulde, Z. Writschaftsgruppe Zuckerind., Tech. Teil 87, 333-342, 488-489 (1937), Cent. 1937, II 2758, 3542; C.A. 32, 4371 (1938). (63) David, Z. Writschaftsgruppe Zuckerind., Tech. Teil 87, 482-487 (1937); Cent. 1937, II 3542, and in C.A. (64) David, Centr. Zuckerind. 44, 927-931, 945-947 (1936), 45, 99-100 (1937); C.A. 31, 3318 (1937). (65) Thielpape, Fulde, Z. Ver. deut. Zucker-Ind. 81, 567-579 (1931); Cent. 1932, I 301; C.A. 26, 1470 (1932). (66) Thielpape, Fulde, Z. Ver. deut. Zucker-Ind. 82, 665-673 (1932); Cent. 1932, II 2251; C.A. 26, 5783 (1932). (67) Schimon, Chem. Zig. 55, 982-983 (1931), Cent. 1932, I 1270; C.A. 26, 940 (1932). (68) Dragerwerk H. & B. Drager, Ger. 310,671, Nov. 15, 1920; Cent. 1921, II 166; not-in C.A. (69) Converse, Chemistry & Industry 57, 1068-1072 (1938); Can. Chem. Process Ind. 22, 361-364 (1938). (70) Imperial Chem. Ind., Ltd., Chem. Age (London) 18, 606-607 (1928).

(71) Jacobs, "Analytical Chemistry of Industrial Poisons, Hazards and Solvents," Interscience Publishers, Inc., N Y. 1941, pp. 430-432, 460, 627. (72) Smyth, N. Y. State Med. J. 42, 1072-1079 (1942), C.A. 36, 4626 (1942). (73) Carpenter, J. Ind. Hyg. Toxicol. 19, 323-326 (1937); Cent. 1938, I 123; C.A. 31, 8681 (1937). (74) Figuson, Nature 137, 361-362 (1936). (75) Barsoun, Sand, Quart. J. Pharm. Pharmacol. 7, 205-214 (1934), Cent. 1934, II 2550, C.A. 23, 6194 (1934). (76) Tomb, Helmy, J. Trop. Med. 36, 265-270 (1933); Cent. 1934, I 728; not in C.A. (77) Christensen, Lynch, J. Pharmacol. 48, 311-316 (1933); Cent. 1934, I 1075, C.A. 28, 212 (1934). (78) Maplestone, Chopra, Indian Med. Gaz. 68, 554-555 (1933); Cent. 1934, I 3492; C.A. 28, 6196 (1934). (79) Sharp, J. Trop. Med. Hyg. 33, 336-339 (1930); Cent. 1931, II 741; C.A. 25, 739 (1931). (80) Lazarev, Arch. exptl. Path. Pharmakol. 141, 19-24 (1929); Cent. 1929, II 451; C.A. 25, 3074 (1931).

(81) Schlingman, Gruhzeit, J. Am. Vet. Med. Assoc. 71, 188-209 (1927); C.A. 21, 3968 (1927).
(82) Lehmann, et al., Arch. Hyg. 74, 1-60 (1911); Cent. 1911, II 885-886; C.A. 6, 3125 (1912).
(83) "Official and Tentative Methods of Analysis," Assoc Official Agr. Chem. 5th ed., 604 (1940); J. Assoc. Official Agr. Chem. 17, 78-79 (1934). (84) Johnson, J. Assoc. Official Agr. Chem. 18, 84-85, 519-520 (1935). (85) Winteringham, J. Soc. Chem. Ind. 61, 186-187 (1942); C.A. 37, 1951 (1943). (86) Dains, Brewster, J. Am. Chem. Soc. 42, 1573-1579 (1920). (87) Winteringham, J. Soc. Chem. Ind. 61, 190-192 (1942); C.A. 37, 1951 (1943). (88) Hanson, Ind. Eng. Chem., Anal. Ed. 13, 119-123 (1941). (89) McBee, Hass, Chao, Welch, Thomas, Ind. Eng. Chem. 33, 179-180 (1941). (90) Faraday, Ann. chim. (2) 18, 53-56 (1821).

(91) Sabatter, Mailhe, Compt. rend. 138, 409 (1904).
(92) Geuther, Ann. 107, 212-213 (1858).
(93) Howell & Impetial Chem. Ind., Ltd., Brit. 535,026, April 24, 1941; Cent. 1942, II 2203; C.A. 36, 1336 (1942).
(94) Regnault, Ann. 33, 324-325 (1840).
(95) Goldschmidt, Ber. 14, 929 (1881).
(96) Booth, Mong, Burchfeld, Ind. Eng. Chem. 24, 328-329 (1932).
(97) Basel, Schaeffer (to A. Wacker Soc. Chem. Ind.), U.S. 2,178,622, Nov. 7, 1939; C.A. 34, 1336 (1940).
(88) Körner, Suchy (to A. Wacker Soc. Chem. Ind.), Ger. 464,320, Aug. 21, 1928; Cent. 1929, I 1044.
(99) Mailhe, Sabrou, Bull. soc. chim. (4) 47, 350 (1930).
(100) Mouncyrat, Bull. soc. chim. (3) 17, 799 (1897); (3) 19, 182-183 (1898).

(101) Prins, Rec. trav. chim. 54, 249-252 (1935). (102) Mugdan, Wimmer (to Consortium für Elektrochem. Ind.), U.S. 2,249,512, July 15, 1941; C.A. 35, 6601 (1941): Brit. 500,176, March 2, 1939; Cent. 1939, I 3798; C.A. 33, 5417 (1939): Ger. 694,884, July 11, 1940; C.A. 35, 5134 (1941): French 841,962, June 2, 1939; Cent. 1939, II 2280; C.A. 34, 4395 (1940). (103) Mkryan, Sbornik Trudov Armyanskogo Fuicala Akad. Nauk. 1940, No. 2, 36-41; C.A. 37, 5694 (1943). (104) Pogossjan, Mkyran, Russ. 50,533, Feb. 28, 1937; Cent. 1938, II 412. (105) I.G., French 805,563, Nov. 24, 1936; Cent. 1937, I 2258. (106) A. Wacker Soc. Chem. Ind., Brit. 480,568, March 24, 1938; Cent. 1938, I 4236; C.A. 32, 5858 (1938). (107) Pierre, J. prakt. Chem. (1) 43, 301-307 (1848). (108) Sastry, J. Soc. Chem. Ind. 35, 450-452 (1916); Cent. 1916, II 306. (109) Taylor, Ward, J. Chem. Soc. 1934, 2007. (110) Nicodemus, J. prakt. Chem. (2) 83, 315-318 (1911).

(111) Kali-Chemie, A.G., Italian 383,229, June 4, 1940; Cent. 1942, I 3143. (112) A. Wacker

Soc. Chem. Ind., Brit. 468,921, Aug. 12, 1937; Cent. 1937, II 3813; C.A. 32, 596 (1938). (113) Reilly (to Dow Chem. Co.), U.S. 1,947,491, Feb. 20, 1934; Cent. 1935, I 3345; C.A. 28, 2371 (1934). (114) Grebe, Reilly, Wiley (to Dow Chem. Co.), U.S. 2,034,292, March 17, 1936; Cent. 1936, II 2611; C.A. 30, 3178 (1936). (115) Erdmann, J. prakt. Chem. (2) 85, 84 (1912). (116) Weiser, Wightman, J. Phys. Chem. 23, 415-439 (1919). (117) Strosacker, Schuegler (to Dow Chem. Co.), U.S. 1,930,350, Oct. 10, 1933; Cent. 1934, I 124; C.A. 28, 180 (1934). (118) Besson, Compt. rend. 118, 1347 (1894) (119) Schwarz, Pflugmacher, J. prakt. Chem. (2) 158, 2-7 (1941). (120) Besson, Fournier, Compt. rend. 150, 1118 (1910).

(121) Meyer, Ber. 27, 3160-3161 (1894). (122) Basel, Schaeffer (to A. Wacker Soc. Electrochem. Ind.), U.S. 2,255,752, Sept. 16, 1941, C.A. 36, 100 (1942). (123) Basel, Schaeffer (to A. Wacker Soc. Electrochem. Ind.), U.S. 2,222,931, Nov. 26, 1940; C.A. 35, 1807 (1941). (124) Basel, Schaeffer (to A. Wacker Soc. Electrochem. Ind.), Ger. 725,276, C.A. 37, 5736 (1943); French S32,750, Oct. 3, 1938, C.A. 33, 2540 (1939). (125) Hennig (to I.G.), Ger. 712,579, Oct. 22, 1941, Cent. 1942, I 1809; C.A. 37, 4407 (1943); Swiss 213,747, June 3, 1941; Cent. 1942, I 2706; not in C.A. (126) Fruhwirth (to Donau-Chemic, A.G.), Ger. 718,888, July 13, 1942; Cent. 1942, II 2086, C.A. 37, 5082 (1943). (127) Tramm (to Ruhrchemie A.G.), U.S. 2,016,658, Oct. 8, 1935; Cent. 1936, I 875, C.A. 29, 8005 (1935). (128) Klein (to Ruhrchemie A.G.), Ger. 613,307, May 23, 1935, Cent. 1935, II 1256; not in C.A. (129) Reilly (to Dow Chem. Co.), U.S. 2,140,551, Dec. 20, 1938; Cent. 1939, I 3625, C.A. 33, 2540 (1939). (130) Thurm, U.S. 1,590,265, June 29, 1926; Cent. 1926, II 1190; C.A. 20, 3015 (1926).

(131) Böeseken, van der Scheer, de Voogt, Rec. trav. chrm. 34, 78-95 (1915). (132) Böeseken, Rec. trav. chrm. 29, 104-111 (1910). (133) Boeseken, Schimmel, Rec. trav. chrm. 32, 128-133 (1913). (134) Combes, Ann. chrm. (6) 12, 269-270 (1897). (135) Müller, Ann. 258, 60-61 (1890). (136) Senderens, Compt. rend. 172, 156 (1921), Cent. 1921, 656-657 (1921). (137) Boeseken, Rec. trav. chrm. 46, 841-843 (1927). (138) Boeseken, Ilasselbach, Rec. trav. chrm. 32, 11-12 (1913). (139) Jaeger, Cent. 1912, I 1817. (140) Jaeger, Bergei, Rec. trav. chrm. 41,

71-72 (1921); Jaeger, J. Chem. Soc 119, 2071 (1921).

(141) Cass (to du Pont Co.), U.S. 2,280,794, April 28, 1942, C.A. 36, 5484 (1942). (142) Hanson (to Dow Chem. Co.), U.S. 2,120,668, June 14, 1938, Cent. 1938, II 2349; C.A. 32, 5857 (1938) (143) Coleman (to Dow Chem. Co.), U.S. 2,000,781, May 7, 1935, Cent. 1936, I 1108; C.A. 29, 4029 (1935). (144) Britton, Coleman, Zemba (to Dow Chem. Co.), U.S. 2,084,937, June 22, 1937; Cent 1937, II 3813; C.A. 31, 5817 (1937) (145) Bailey, J. Chem. Soc. 1939, 767-769 (1939). (146) Zuckermandel (to Dow Chem. Co.), U.S. 1,835,682, Dec. 8, 1931; Cent. 1932, I 1153, C.A. 26, 999 (1932). (147) Pitman (to Westvaco Chlorine Prods. Co.), U.S. 2,319,261, May 18, 1943, C.A. 37, 6372 (1943) (148) Zuckermandel (to Dow Chem. Co.), U.S. 1,819,585, Aug. 18, 1931; Cent. 1931, II 2657, C.A. 25, 5678 (1931). (149) Stewart, DePree (to Dow Chem. Co.), U.S. 1,917,073, July 4, 1933, Cent. 1933, II 1927, C.A. 27, 4539 (1933). (150) Pitman (to du Pont Co.), U.S. 1,925,602, Sept. 5, 1933; Cent. 1933, II 3192; C.A. 27, 5445 (1933) Imperial Chem. Ind., Ltd., French 744,128, March 12, 1933, Cent. 1933, II 605.

(151) Crawford, Duncan, & Imperial Chem. Ind., Ltd., Brit. 493,875, Nov. 10, 1938; Cent. 1939, I 1252; C.A. 33, 2540 (1939). (152) Roessler & Hasslacher Chem. Co., French 732,569, Sept. 22, 1932, Cent. 1932, II 3785; C.A. 27, 304 (1933); Ger. 573, 105, March 3, 1932, C.A. 27, 2901 (1933). (153) Lob, Z. Elektrochem. 7, 903-921 (1901), Cent. 1901, II 1042. (154) Joist, Lob, Z. Elektrochem. 11, 938-944 (1905); Cent. 1906, I 223. (155) Dickinson, Carrico, J. Am. Chem. Soc. 56, 1473-1480 (1934). (156) Muller, Ehrmann, Ber. 69, 2207-2210 (1936). (157) Balley, Hickson, J. Chem. Soc. 1941, 145. (158) Kobe, Ann. 54, 182 (1845). (159) Besson, Compt. rend. 118, 1347 (1894); Bull. soc. chem. (3) 11, 918-919 (1894). (160) Swarts, Bull.

acad. roy. Belg. (3) 36, 532-552 (1898), Cent. 1898, I 588-589.

(161) E. Prilezhaeva, N. Prilezhaeva, J. Gen. Chem. (U.S.S.R.), 9, 1766-1773 (1939); C.A. 34, 3672 (1939). (162) Biltz, Ber. 35, 1533-1536 (1902). (163) Sabatier, Mailhe, Compt. rend. 138, 409 (1904). (164) Prud'homme, Compt. rend. 70, 1137 (1870); Ann. 156, 342-343 (1870). (165) Kirkbride (to Imperial Chem. Ind., Ltd.), U.S. 2,321,823, June 15, 1943; C.A. 37, 6676 (1943). Brit. 534,732, March 17, 1941; C.A. 36, 1330 (1942): Belg. 439,293, Sept. 13, 1940; Cent. 1942, I. 2706. (166) Consortium fur Elektrochem. Ind., Ger. 340,872, Sept. 19, 1921; Cent. 1921, IV 1101. (167) Guyot, Simon, Compt. rend. 170, 734-736 (1920). (168) Biesalski, Z. angew. Chem. 37, 317 (1924). (169) Bockemuller, Ann. 506, 29-33, 50-52 (1933). (170) Miller, J. Am. Chem. Soc. 62, 342 (1940).

(171) Miller, Calfee, Bigelow, J. Am. Chem. Soc. 59, 198-199 (1937). (172) Humiston, J. Phys. Chem. 23, 576-577 (1919). (173) Leermakers, Dickinson, J. Am. Chem. Soc. 54, 4648-4657 (1932). (174) Kharasch, Brown, J. Am. Chem. Soc. 61, 3433 (1939). (175) Mugdan, Wimmer (to Consortium fur Elektrochem. Ind.), Ger. 680,659, Sept. 9, 1939, Cent. 1939, II 3486; C.A. 36, 1951 (1942): French 844,300, July 21, 1939; C.A. 34, 7300 (1940). (176) I.G.,

French 836,979, Jan. 31, 1939; Cent. 1939, II 226; C.A. 33, 5869 (1939). (177) Fink, Bonilla, J. Phys. Chem. 37, 1141-1145 (1933). (178) Bourgoin, Bull. soc. chim. (2) 24, 114 (1875). (179) Carrico, Dickinson, J. Am. Chem. Soc. 57, 1343-1348 (1935). (180) Yardley, Proc. Roy. Soc. (London), A-118, 463 (1928).

(181) Willard, Daniels, J. Am. Chem. Soc. 57, 2240-2245 (1935). (182) Bauer, J. prakt. Chem. (2) 73, 208-210 (1905). (183) Herz, Rathmann, Ber. 46, 2590 (1913). (184) Hofmann, Kirmreuther, Ber. 42, 4483-4484 (1909). (185) Bohlman, Willard, J. Am. Chem. Soc. 64, 1342-1346 (1942). (186) Margosches, Hinner, Friedmann, Z. anorg. allg. Chem. 137, 81-90 (1924). (187) Margosches, Hinner, Z. deut. Öl- u. Fett-Ind. 44, 97-100 (1924); Cent. 1924, I 2648; C.A. 18, 3731 (1924). (188) Margosches, Baru, J. prakt. Chem. (2) 103, 216-226 (1922/3). (189) Goldeshwitz Schüssler, Ber. 58, 588, 573 (1925). (190) (190) (190) (190) (1889)

Goldschmidt, Schussler, Ber. 58, 568, 570 (1925). (190) Kolbe, Ber. 2, 326-329 (1869). (191) Argo, James, Donnelly, J. Phys. Chem. 23, 578-585 (1919). (192) Burrows, Hunter, J. Chem. Soc. 1932, 1357-1360. (193) Steinkopf, Kühnel, Ber. 75, 1327 (1942). (194) Haines, Adkins, J. Am. Chem. Soc. 47, 1422-1423 (1925). (195) Heslinga, Rec. trav. chim. 43, 179 (1924). (196) Stähler, Ber. 47, 912 (1914). (197) Gowing-Scopes, Analyst 39, 7 (1914). (198) Lenze, Z. ges. Schiess- u. Sprengstoffw. 27, 255-258, 293-296, 337-340, 373-376 (1932); Cent. 1933, I 1716; C.A. 27, 844 (1933). (199) Farlow, Org. Syntheses, Coll. Vol. 2 (1st ed.), 312-313 (1943); 17, 58-59 (1937). (200) Henne, Ladd, J. Am. Chem. Soc. 60, 2494 (1938).

(201) Prins, Rec. trav. chim. 57, 659, 662, Note (1938). (202) Boeseken, Prins, Cent. 1911, I 466. (203) Geuther, Fischer, Jahresber. 1864, 316. (204) Geuther, Brockhoff, Jahresber. 1873, 314. (205) Cusa, McCombie, J. Chem. Soc. 1937, 770. (206) Hurtley, Smiles, J. Chem. Soc. 1926, 2269-2270. (207) Prins, Rec. trav. chim. 51, 473-474 (1932). (208) Reijnhart, Rec. trav. chim. 46, 74-76 (1927). (209) Binaghi, Gazz. chim. tal. 57, 671-672, 674 (1927); Cent. 1928, I 908; C.A. 22, 574 (1928). (210) Marvel, Hager, Coffman, J. Am. Chem. Soc. 49, 2328 (1927).

(211) Tronow, J. Russ. Phys.-Chem. Soc. 58, 1287, 1289 (1926); Cent. 1927, II 1145; C.A. 22, 2737 (1928). (212) Doughty, J. Am. Chem. Soc. 41, 1131 (1919). (213) Doughty, J. Am. Chem. Soc. 41, 1131 (1919). (213) Doughty, J. Am. Chem. Soc. 39, 2690 (1917). (214) Prins, Rec. trav. chsm. 51, 1065-1080 (1932). (215) Smyth, Ind. Eng. Chem. 8, 379 (1936). (216) Taylor, Ward, J. Chem. Soc. 1934, 2003-2010. (217) Geuther, Brockhoff, J. prakt. Chem. (2) 7, 107-111 (1873). (218) Lecat, "L'Azeotropisme," 1918, p. 68. (219) von Oettinger, J. Ind. Hyg. Toxicol. 19, 423-424 (1937). (220) Carpenter, J. Ind. Hyg. Toxicol. 19, 323-336 (1937).

(221) Missbach (to Stauffer Chem. Co.), U.S. 2,043,257-2,043,260 incl., June 9, 1936; Cent. 1936, II 3845; C.A. 30, 5240 (1936). (222) Grebe, Stoesser, Mills (to Dow Chem. Co.), U.S. 1,989,478, Jan. 29, 1935; Cent. 1935, II 3859; C.A. 29, 2000 (1935). (223) Rauscher, Ind. Eng. Chem. Anal. Ed. 9, 296-299 (1937). (224) Lehman, Schmidt-Kehl, Arch. Hyg. Bakt. 116, 131-268 (1936); C.A. 31, 477 (1937).

3:5475 1,2,2-TRICHLOROPROPANE

$$\begin{array}{ccccc} Cl & C_3H_5Cl_3 & \textbf{Beil. I - 106} \\ CH_3-C-CH_2 & \textbf{I}_1-\\ Cl & Cl & \textbf{I}_2-\\ \end{array}$$

 $D_{25}^{25}=1.318$

[For prepn. as a by-product of the chlorination of propane see (2); for formn. of \bar{C} (47%) in chlorination of 1,2-dichloropropane (3:5200) see (3).]

Č with alc. KOH splits out HCl and gives two stereoisomeric 1,2-dichloropropenes, viz., 3:5110 and 3:5150.

3:5475 (1) Hersfelder, Ber. 26, 2435 (1893). (2) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,073, June 4, 1935; Cent. 1935, I 1500. (3) Zellner (to Tide Water Associated Oil Co.), U.S. 2,370,342, Feb. 27, 1945, C.A. 39, 3534 (1945).

CHAPTER XIII

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 1. D_4^{20} greater than 1.1500

(3:5500-3:5999)

3:5500 cis-2,3-DICHLOROBUTENE-2 Cl Cl
$$C_4H_6Cl_2$$
 Beil. S.N. 11 CH_3-C-CH_3

B.P. 124-126° at 758 mm. (1) $D_4^{20} = 1.1618$ (1) $n_D^{20} = 1.4590$ (1) $D_4^{18} = 1.1620$ (1) $n_C^{18} = 1.4616$ (1)

[See also trans stereoisomer (3:7395).]

[For prepn. of \bar{C} (accompanied by its *trans* stereoisomer (3:7395)) from 2,2,3-trichlorobutane (3:5680) with solid KOH (1 mole) at 135-140° see (1).]

C on oxidn. with 3% aq. KMnO₄ yields (1) acetic acid (1:1010).

 \bar{C} in CCl₄ at -20° treated with 7% O₃, then hydrolyzed, yields (1) acetic acid (1:1010) + acetaldehyde (1:0100).

3:5500 (1) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 6, 1553-1558 (1936); Cent. 1937, I 3785; C.A. 31, 2165 (1937).

B.P.			M.P.			•	
127.5-128°	(1) cor.	(2)	-57°	$D_{21}^{21}=1.632$	2 (7)	$n_{\rm D}^{26} = 1.456$	(1)
127°	at 760 mm.	(3)					
126-127°	at 745 mm.	(4)		$D_{15}^{15} = 1.658$	5 (3)	$n_{\rm D}^{22} = 1.45664$	(8)
		(5)					
127.2°	at 725 mm.	(6)					
49°	at 50 mm.	(3)					
45°	at 26 mm.	(7)					
20°	at 10.3 mm.	(1)					
0°	at 2-4 mm.	(1)					

Colorless oily liq. with irritating and suffocating odor, but (when pure) not especially lachrymatory. — Ord. samples may cont. triphosgene (3:1915).

[For prepn. from methyl formate (1:1000) or methyl chloroformate (3:5075) by chlorination see (8) (3) (9) (2) (1); for prepn. from bis-(trichloromethyl) carbonate (triphosgene) (3:1915) see (1); for German prepn. in World War I see (10).]

 \bar{C} (when pure) boils with no decompn. (1); however, above 300° (2) or on contact with activated carbon, charcoal, or iron oxide at ord. temp. (1) \bar{C} decomposes to phospene

(3:5000). — C on contact with alumina (1), AlCl₃ (5), or FeCl₃ (3) decomposes in a different mode yielding CCl_4 (3:5100) + CO_2 .

 $\bar{ extsf{C}}$ with aq. hydrolyzes slowly in the cold but rapidly at 100° yielding only HCl + CO₂

(1) (3); C on warming with aq. Na₂CO₃ yields NaCl + CO₂ (3).

C on treatment at 20° for 5 min. with NaI in acctone evolves CO and separates I2 to 98.8% of amt. expressed by reaction: $Cl_3C.O.CO.Cl + 2NaI \rightarrow 2CO + 4NaCl + I_2$ (11) [cf. chloromethyl chloroformate (3:5275), dichloromethyl chloroformate (3:5315), and triphosgene (3:1915)].

 $\bar{\mathbf{C}}$ with aq. NH₄OH reacts vigorously yielding urea + NH₄Cl. $-\bar{\mathbf{C}}$ with excess aniline in either aq. or non.-aq. soln. is converted to N,N'-diphenylurea (carbanilide), m.p. 233°,+ aniline hydrochloride (3). [Note that with insufficient amline a mixt. of phenyl isocyanate + N-phenylcarbamyl chloride may form (3).]

Č on addn. in cold to conc. soln. of phenol (1 mole) in aq. NaOII separates an oil (which soon solidifies) of phenyl trichloromethyl carbonate [Beil. VI₁-(88)], ndls. from ether, m.p. 70.5° (12), 66° (3); this product upon warming with aq. sodium phenolate (or C warmed with excess sodium phenolate in one operation) yields diphenyl carbonate (1:2335), cryst. from alc., m.p. 78° (12). [For corresponding reactions with p-crossle (1:1410), β -naphthol (1:1540), p-chlorophenol (3:0475), and p-nitrophenol see (13).

 $\bar{\mathbf{C}}$ with pyridine yields a yel. double quaternary ammonium salt $C_5H_5N(Cl).CO(Cl)$ -

 $N.C_5H_5$ which by aq. is decomposed to pyridine hydrochloride $+ CO_2$ (14).

[For use of C in prepn. of acid chlorides of carboxylic or sulfonic acids see (15); similarly \tilde{C} htd. with anhydrous NaOAc gives $Ac_2O + NaCl + CO_2$ (2); for actn. on methyl hydrogen sulfate yielding methyl chlorosulfonate + phosgene + CO_2 see (16).]

[For use of C for introduction of a second—CO.Cl group into acid chlorides see (17).]

3:5515 (1) Hood, Murdock, J. Phys. Chem. 23, 498-514 (1919). (2) Hentschel, J. prakt. Chem. (2) 36, 99-113 (1887). (3) Kling, Florentin, Lassieur, Schmitz, Ann. chim. (9) 13, 44 49 (1920). (4) Nekrassow, Melnikow, J. prakt. Chem. (2) 126, 81-96 (1930) (5), Ramsperger, Waddington, J. Am. Chem. Soc. 55, 214-220 (1932).
 Mohler, Helv. Chim. Acta 21, 788 (1938).
 Mohler, Polya, Helv. Chim. Acta 19, 1238 (1936).
 Grignard, Rivat, Urbain, Ann. chim. (9) 13, 228-265 (1920). (9) Hentschel, J. prakt. Chem. (2) 36, 209-215 (1887). (10) Norris, Ind Eng. Chem. 11, 822-824 (1919).

(11) Perret, Biechler, Compt. rend 203, 84-87 (1936); C.A. 30, 7423 (1936). (12) Ref. 4, pp. 93-95. (13) Melnikow, J. prakt. Chem. 128, 233-235 (1930). (11) Ger. 109,933, May 27, 1898; Cent. 1900, II 460. (15) Brit. 401,643, Dec. 14, 1933; Cent. 1934, II 2133. (16) Kraft, Alekseev. J. Gen. Chem. (U.S.S.R.) 2, 726-729 (1932); C.A. 27, 2426 (1933); Cent. 1933, II 1666. (17) Kharasch, Eberly, Kleiman, J. Am. Chem. Soc. 64, 2975-2977 (1942).

3:5540
$$\alpha,\beta$$
-Dichloro- α -ethoxyethylene) CH=CH—O—CH₂CH₃ I₁-(377) I₂-(780) Cl Cl Cl Cl D45-2 I₁-(377) I₂-(780) B.P. 128.2° cor. (1) $D_4^{25} = 1.1972$ (3) $D_4^{20} = 1.2037$ (3) $D_D^{20} = 1.2037$ (3) $D_D^{20} = 1.45584$ (3)

Č has the possibility of existing in two geometrically isomeric forms, but only this one has as yet been recognized.

[For prepn. of C from trichloroethylene (3:5170) with alc. KOH (4), with alc. NaOEt (yield: 81% (5), 70% (2)), or with alc. NaOH + CaO (6) see indic. refs.; from 1.1.1.2tetrachloroethane (3:5555) with NaOEt see (1).]

[C with calcd. amt. aq. (7), or with conc. HCl (8) yields ethyl chloroacetate (3:5700);

C on boilg. with aq. to complete soln. yields (9) chloroacetic acid (3:1370); C on htg. with aq. in s.t. at 180° yields (1) glycolic acid (1:0430), EtCl (3:7015) + HCl.]

[C with HCl gas yields (10) an addn. prod. which on htg. decomposes to chloroacetyl chloride (3:5235) + EtCl (3:7015); C with monobasic org. acids yields (2) on htg. ethyl chloroacetate (3:5700) + corresp. acid chloride; with succinic acid the products are (2) ethyl chloroacetate (3:5700) + succinic anhydride (1:0710).]

[\bar{C} with alcohols yields mainly (2) (11) the corresp. alkyl chloroacetate + EtCl (some ethyl chloroacetate + alkyl chloride are also formed (2)); \bar{C} htd. with excess NaOEt yields (1) sodium salt of ethoxyacetic acid (1:1070).]

 $[\bar{C}]$ with phenols yields exclusively (2) the corresp. aryl chloroacetate + EtCl; e.g., \bar{C} with β -naphthol (1:1540) yields (2) β -naphthyl chloroacetate, m.p. 95° (2).]

Č with aniline in aq. or aq. alc. soln. yields (12) ethyl N-phenylaminoacetate (90%) [Beil. XII-470, XII₁-(263)], m.p. 58°, and phenylaminoacetanilide (10%) [Beil. XII-556, XII₁-(285)], m.p. 112°.

[\tilde{C} readily absorbs Cl₂ at ord. temp.; if moisture is carefully excluded, the prod. breaks up (13) (14) on keeping or on htg. into dichloroacetyl chloride (3:5290) + EtCl (3:7015); if, however, moisture is given access or aq. added, then on keeping or htg. the prod. breaks up (13) (14) and on distn. gives alm. theoretical yield of ethyl dichloroacetate (3:5850) + HCl.]

[\bar{C} readily absorbs Br₂; with complete exclusion of aq. the products are (13) (14) bromochloro-acctyl chloride, b.p. 138–139° (13), and EtBr; in pres. of aq. the products are ethyl chloro-bromo-acctate, b.p. 174°, $D_4^{22}=1.5890$ (13), + HCl + HBr; some bromo-chloro-acctyl bromide, b.p. 158–160°, 47–49° at 15 mm. (15), and C₂H₅Cl (3:7015) are also (15) formed. — \bar{C} on treatment with Br₂ in the cold, then immediately followed by alc. KOH, gives good yield (3) of β -bromo- α , β -dichlorovinyl ethyl ether, b.p. 177° at 754 mm., $D_4^{20}=1.6565$, $n_3^{17}=1.50427$ (3).]

[C treated with ICl, stood 30 min. (17), filtered from I₂, then htd. to 50° to expel C₂H₆Cl gives (16) (17) chloro-iodo-acetyl chloride; addn. of aq. to latter yields by hydrolysis (16) (17) chloro-iodo-acetic acid, colorless lfts. from lt. pet., m.p. 90° (16).]

3:5540 (1) Geuther, Brockhoff, J. prakt. Chem. (2) 7, 111-117 (1873). (2) Crompton, Vanderstichele, J. Chem. Soc. 117, 691-693 (1920). (3) Smith, J. Chem. Soc. 1927, 1099-1102. (4) Paterno, Oglaloro, Ber. 7, 80-81 (1874). (5) Stephens, J. Soc. Chem. Ind. 43, T313-314, 327-328 (1924); Cent. 1925, I 357. (6) Imbert, Consortium fur Elektrochem. Ind., Ger. 216,940, Dec. 13, 1909; Cent. 1910, I 308. (7) Imbert, Consortium fur Elektrochem. Ind., Ger. 209,268, April 27, 1909; Cent. 1909, I 1785. (8) Imbert, Consortium fur Elektrochem. Ind., Ger. 210,502, June 7, 1909, Cent. 1909, II 78. (9) Imbert, Consortium fur Elektrochem. Ind., Ger. 216,716; Nov. 30, 1909; Cent. 1910, I 214. (10) Consortium fur Elektrochem. Ind., Ger. 222,194, May 19, 1910; Cent. 1910, I 1999.

(11) Imbert, Consortium für Elektrochem. Ind., Ger. 212,592, Sept. 6, 1909; Cent. 1909, I 1024. (12) Imbert, Consortium für Elektrochem. Ind., Ger. 199,624, June 24, 1908; Cent. 1908, II 358. (13) Crompton, Triffitt, J. Chem.! Soc. 119, 1874-1875. (14) McKie, J. Chem. Soc. 123, 2213-2217 (1923). (15) Backer, Mook, J. Chem. Soc. 1928, 2126. (16) Crompton, Carter, J. Chem. Soc. 123, 576-577 (1923). (17) McMath, Read, J. Chem. Soc. 1927, 538-539.

3:5550 1,3-DICHLOROBUTENE-2 Cl Cl C₄H₆Cl₂ Beil. S.N. 11 (2,4-Dichlorobutene-2)
$$CH_3-C=CH-CH_2$$

B.P. 127-129° at 756 mm. (1) $D_4^{20} = 1.1591$ (1) (3) $n_{\rm D}^{20} = 1.47239$ (1) 127-128.5° at 753 mm. (2) 1.1582 (2) 1.4695 (2) 61-63° at 70 mm. (1) 56-57° at 55 mm. (3) $n_{\rm C}^{20} = 1.46988$ (1) 53-54° at 55 mm. (2) 1.4694 (3) 53-54° at 50 mm. (1)

Colorless liq. with characteristic odor (1). — \tilde{C} is formed (5–10% (4) (5) (1)) cf. (10) in synthesis of chloroprene (3:7080). — [For use in mfg. of unsatd. cellulose ethers see (6); in mfg. of unsatd. ethers of alcohols and phenols for use as solvents, disinfectants, etc., see (7) (8).]

[For prepn. of \tilde{C} readily and in quantity (1) from vinylacetylene by shaking with an excess (4 moles) of HCl contg. CuCl see (1): from methyl vinyl ketone in 33% yield (together with other products) with PCl₅ at -10° see (2), from 2-chlorobutene-2 (3:7105) (together with other products) by actn. of Cl₂ at 350° see (9); for formn. of \tilde{C} (together with other products) from trimethylethylene + Cl₂ see (11).]

Č passed over silica gel or clay at 245-275° loses HCl yielding (4) 17-18% 3-chloro-butadiene-1.3 ("Chloroprene") (3:7080).

 \bar{C} on hydrolysis with steam (12), or aq. alk. (5) (12), or aq. K_2CO_3 (2), aq. Na_2CO_3 (70-80% yield (4)) or $CaCO_3$ (3) gives 3-chlorobuten-2-ol-1 (3:8207) q.v., b.p. 161-162°. — [Note that \bar{C} with alc. alk. does not hydrolyze or lose HCl but instead gives the corresp. ethers (see details under 3-chlorobuten-2-ol-1 (3:8207)).]

Č with Cl₂ yields (13) (14) (15) a mixt. of 2,3,4-trichlorobutene-1 (3:9064), 1,2,3,3-tetrachlorobutane (3:9080), and 1,2,2,3,4-pentachlorobutane (3:9070).

35550 (1) Carothers, Berchet, Collins, J. Am. Chem. Soc. 54, 4066-4070 (1932). (2) Churbakov. J. Gen. Chem. (U.S.S.R.) 10, 977-980 (1940); C.A. 35, 2469 (1941). (3) Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 658-662 (1937); Cent. 1937, II 371; C.A. 31, 5754 (1937). (4) Klebanskii, Chevuichalova, Sintet. Kauchuk 1935, No. 6, 16-21; Cent. 1936, I 1975; C.A. 30, 1024 (1936). (5) Klebanskii, Tzyurikh, Dolgopol'skii, Bull. acad. sci. U.R.S.S. 1935, No. 2, 189-226; Cent. 1935, II 3844; C.A. 30, 1259 (1936) (full English translation in Rubber Chem. Tech. 9, 383-408 (1936). (6) du Pont Co., Brit. 429,949, June 11, 1935; Cent. 1936, I 4098; C.A. 29, 7073 (1935). (7) Berchet (to du Pont), U.S. 2,079,758, May 11, 1937; Cent. 1937, II 2597; C.A. 31, 4676 (1937). (8) Deichsel (to I.G.). Brit. 443,113, Feb. 20, 1936; Cent. 1937, I 383-384; C.A. 30, 4873 (1936). (9) N. V. de Bataafsche Petroleum Maatschappij, Brit. 468,016, June 28, 1937; French 810,112, Mar. 15, 1937; Cent. 1933, II 4102; C.A. 31, 8543 (1937). (10) du Pont Co., Brit. 395,131, Aug. 3, 1933; Cent. 1933, 2455; Brit. 387,325; Cent. 1933, I 4525; French 721,532, Mar. 4, 1932; Cent. 1932, II 2107.

(11) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, I 4223; C.A. 33, 4190 (1939). (12) Collins (to du Pont), U.S. 2,192,299, March 5, 1940; C.A. 34, 4392 (1940). (13) Carothers, Berchet, J. Am. Chem. Soc. 55, 1628-1631 (1933). (14) Coffman (to du Pont), U.S. 1,964,720, July 3, 1934, Cent. 1934, II 3180; C.A. 28, 5080 (1934). (15) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934; Cent. 1935, I 3725; C.A. 28, 5716 (1934).

3:5552	2-CHLOROETH (Ethylene chloro β-chloroethanol, β-chloroethyl alce "glycol chlorohy	hydrin, ohol,	Cl	СН₂ОН	C₂H₅OCl	Beil. I - 337 I ₁ -(170) I ₂ -(333)
B.P.			F.P.			
[132°	at 761 mm	. (1)]	-67.5° (7)	$D_4^{25}=1$	1.1972 (14)	$n_{\rm D}^{25} = 1.44123 (22)$
[132.0°		(2)]	(8)		L.19654 (8)	
[130-13	31° at 760 mm	. (3)]	-69.0°	1	1.1961 (10)	1.44012 (9)
			(21)	1	1.1947 (9)	•
129.46	s° at 761.1 m	m. (4)				
128.7-	128.8° at 764 mm	. (5)				
128.66	s° at 760 mm	. (6)				$n_{\rm D}^{24} = 1.4402 (10)$
128.60	° at 760 mm	. (7)				
128.6°	at 760 mm	. (8)		$D_4^{20}=1$	1.2022 (13)	$n_{\rm D}^{20} = 1.44212 \ (22)$
128.1-	128.2° at 752 mm	. (9)		1	1.20190 (8)	1.4421 (23)
128.05	o° at 744 mm	. (6)		1	1.20027 (6)	1.44208 (13)
128.0°	at 760 mm	. (10)		1	L.1988 (4)	(9)
128°	(1	1)(12)		1	1.1981 (22)	1.44197 (6)
127.9-	128.1° at 761 mm	. (13)				1.44189 (24)
127.9	128.1° at 741 mm	. (14)				1.44163 (25)
127.6-	128.6°	(15)				
127.1-	128.1° cor.	(16)		$D_4^{15}=1$	L. 20720 (13)	$n_{\rm D}^{15} = 1.44382(22)$
127-12	27.5°	(17)				1.44380 (8)
126.5-	126.7° at 729 mm	. (18)				
51-52°	at 22 mm	. (1)				
44°	at 20 mm	. (19)				
43°	at 3–4 mm	. (20)				

Colorless liq. — miscible with aq. (see also below) and most org. solv.

MISCELLANEOUS PHYSICAL PROPERTIES

BINARY SYSTEMS CONTAINING C

 \bar{C} + water. For values of D_4^{20} and n_D^{20} (also n_C^{20} , n_F^{20} , n_G^{20}) over whole range 0-100% \bar{C} see (6) cf. (22) (23); for thermal anal. of systems see (26). — For study of salting-out of \bar{C} from its aq. solns. (11) or its isolation by ether extraction of aq. solns. satd. with NaCl or Na₂CO₃ (27) see indic. refs. — For concn. of \bar{C} , i.e., dehydration of its aq. solns. by distn. of the water with C₆H₆ (28), with 1,2-dichloroethane (ethylene dichloride) (3:5130) (29), or with cyclohexanol (1:6415) (30) see indic. refs. — See also below under azeotropes.

Note that boilg. aq. solns. of Č undergo slow decompn., e.g., about 10% in 8 hrs. (23), 50% in 5 hrs. (107) cf. (11) (presumably by loss of HCl and evoln. of ethylene oxide (1:6105), b.p. 10.7°, and/or (38) acetaldehyde (1:0100), b.p. 20.2°.

 \ddot{C} with hydrocarbons. \ddot{C} with C_6H_6 (1:7400): for b.p., vapor-liq. equil., and n_D^{25} see (10). — \ddot{C} with toluene (1:7405): for b.p., vapor-liq. equil., and n_D^{25} see (10) (see also below under azeotropes).

 \bar{C} with alcohols. \bar{C} with butanol-1 (1:6180): for b.p., vapor-liq. equil., and n_D^{25} see (10). — \bar{C} with isobutyl alc. (1:6165): for b.p., vapor-liq. equil., and n_D^{25} see (10).

C with ethers. C with di-isopropyl ether (1:6125): for b.p., vapor-liq. equil., and

 $n_{\rm D}^{25}$ see (10). — \bar{C} with di-n-butyl ether (1:7950): for b.p., vapor-liq. equil., and $n_{\rm D}^{25}$ see (10). — \bar{C} with β,β' -dichloro-diethyl ether (3:6025): for b.p., vapor-liq. equil., and $n_{\rm D}^{25}$ see (10) (see below under azeotropes).

 $\tilde{\mathbf{C}}$ with chlorinated hydrocarbons. $\tilde{\mathbf{C}}$ with 1,2-dichloroethane (ethylene dichloride (3:5130): for b.p., vapor-liq. equil., and D see (31) (see also below under azeotropes). (For use of ethylene dichloride in dehydration of $\tilde{\mathbf{C}}$ see (30).)

AZEOTROPES CONTAINING C

Binary azeotropes. \bar{C} with water forms a const.-boilg. mixt., b.p. 97.85° at 760 mm. (26) (8), 97.8° at 760 mm. (23) (32), contg. 45.8 wt. % (8), 43.5 wt. % = 14.7 mole % (32) \bar{C} : constants for this azeotropic mixt. at other press. include the following: at 771 mm., b.p. 96-96.2° (26); at 735 mm., b.p. = 95.8° (33) (11), contg. 42.5 wt. % \bar{C} (33) (11); at 504 mm., b.p. = 86.4° (23); at 400 mm., b.p. = 80.55°, contg. 40.5 wt. % \bar{C} (23). — Note that compn. changes only slightly (23) with press. — For study of influence of NaCl (11) (23) or of HCl (11) see indic. refs.

 $\bar{\mathbf{C}}$ with toluene (1:7405) gives a const.-boilg. mixt., b.p. 106.9°, contg. 27 mole % $\bar{\mathbf{C}}$ (10). — $\bar{\mathbf{C}}$ with di-n-butyl ether (1:7950) gives a const.-boilg. mixt., b.p. 123.0°, contg. 68 mole % $\bar{\mathbf{C}}$ (10). — $\bar{\mathbf{C}}$ with β,β' -dichlorodiethyl ether (3:6025) gives a const.-boilg. mixt., b.p. 128.2°, contg. 91.8 mole % $\bar{\mathbf{C}}$ (10).

Ternary azeotropes: \bar{C} with aq. + C_6H_6 (1:7400) gives a const.-boilg. mixt., b.p. 67.0-67.3° (29). - \bar{C} with aq. + ethylene dichloride (3:5130) gives a const.-boilg. mixt., b.p. 69.6° (29). - \bar{C} with aq. + 1,1,2-trichloroethylene (3:5170) gives a const.-boilg. mixt., b.p. 70.8-71.5° (29).

MISCELLANEOUS PHYSICAL PROPERTIES OF C

[For sepn. of \bar{C} from gas mixts. by adsorption (?) on $Mg(ClO_4)_2$ or other perchlorates see (34).]

USES OF C

The manifold uses of \bar{C} , based upon both its physical and its chemical characteristics, cannot here be reviewed in detail; however, some examples include the following.

[For use in sepn. of butadiene from hydrocarbon mixts. (35), in dewaxing and removing naphthenes from mineral lubricating oils (36), in refining of rosin (37), in extraction of pine lignin (38) (39), as solv. for various resins (40), as solv. for cellulose acetate (41) or cellulose ethers (42), for addn. to rayon spinning baths (43) see indic. refs.]

PHYSIOLOGICAL AND BIOCHEM. BEHAVIOR OF C

[For study of pharmacol. of \bar{C} (or its phosphoric esters, etc.) see (44); for reports of poisoning by \bar{C} see (45) (46); for study of toxicity of vapor of \bar{C} see (403).]

[For effect of \bar{C} upon amylase (47) (48) or lipase (49) see indic. refs.; for use of \bar{C} in prod. of yeast of depressed enzymatic activity see (50).]

DETERMINATION OF C

[For colorimetric detn. of \tilde{C} by reactn. with diazotized sulfanilic acid in alk. soln. at 25° see (106) (note that method involves oxidn. of \tilde{C} by the reagt. to chloroacetaldehyde (3:7212) and color formn. with latter); for detn. of \tilde{C} in aq. solns. by refractometry see (11) (25) (6) (23).]

PREPARATION OF C

From ethylene. With hypochlorous acid, e.g., from $Cl_2 + aq$. $-\bar{C}$ is usually prepd. from ethylene by addn. of HOCl, the HOCl may be obtained by use of $Cl_2 + aq$. (sometimes in the pres. of alk. acceptors for the simultaneously formed HCl), by use of organic hypochlorites, or other org. cpds. which hydrolyze to give HOCl.

[For scientific papers discussing prepn. of \tilde{C} from ethylene + HOCl (Cl₂ + aq.) see (401) (11) (51) (52) (53) (54) (55) (56) (57) (58) (59); for very old work see (60); for examples of patents employing this method see citations (61)-(82) cf. (402), inclusive; for study of metal-corrosion problems involved in this method of prepn. of \tilde{C} see (83).]

With organic hypochlorites (e.g., ter-butyl hypochlorite (3:7165)). [For patents on prepn. of \bar{C} from ethylene + ter-butyl hypochlorite see (84) (85).]

With N-chlorourea. [For prepn. of \bar{C} from ethylene with N-chlorourea in 5% H₂SO₄ contg. CuCl₂ at 0° (yield: 60-70% \bar{C} accompanied by 2% ethylene dichloride (3:5130)) see (86).]

From ethylene glycol (1:6465). [For prepn. of \tilde{C} from ethylene glycol satd. with HCl gas and htd. in s.t. (12) (90), or treated at 160° (87) (4) or 180° (88) with stream of HCl (yields: 70-80% (88), 60% (87)), see indic. refs.; note that ethylene glycol with excess conc. HCl in s.t. at 100° gives no \tilde{C} (89) but only ethylene dichloride (3:5130), while mere distn. with conc. HCl (9 moles) gives (15) only 12% \tilde{C} .)]

[For prepn. of \bar{C} from ethylene glycol with S_2Cl_2 (2.5 wt. pts. (91)) on refluxing (yields: 82.5% (92), 72.8% (91)) (93) (94) (95) see indic. refs.: for forms. of \bar{C} from glycol with SiCl₄ see (96).]

From ethylene glycol esters. [For patents on prepn. of \tilde{C} from ethylene glycol diformate (1:3402) with HCl gas at 100° via formn. of β -chloroethyl formate and subsequent alcoholysis of latter with MeOH/HCl (97), or from ethylene glycol diacetate (1:3511) with EtOH + HCl at 125–135° under press. (EtOAc is also formed) (98), see indic. refs.]

From ethylene oxide (1:6105). [For formn of \bar{C} from ethylene oxide with liq. HCl (99) or with S_2Cl_2 (100) (other prods. are also formed) see indic. refs.]

From other miscellaneous sources. [For formn. of \tilde{C} from 1,2-dichloroethane (ethylene dichloride) (3:5130) by conversion with SO₃ below 45° to β -chloroethyl chlorosulfonate (see below) and subsequent hydrolysis to \tilde{C} (101); from bis-(β -chloroethyl) sulfate (see below) by refluxing with aq. (102); from β -chloroethyl trichloroacetate (3:6410) by shaking with aq. (103); from β -chloroethyl vinyl ether (3:7464) on distn. with aq. + trace of HCl (acetaldehyde is also formed) (104); from chloroacetaldehyde (3:7212) by reduction of carbonyl group with EtOMgBr (105) see indic. refs.]

CHEMICAL BEHAVIOR OF C

Pyrolysis of \bar{C} . $[\bar{C}$ in s.t. at 184° for 10 hrs. yields (107) 1,2-dichloroethane (ethylene dichloride) (3:5130) and acetaldehyde (1:0100) (the latter partially as aldehyde resin); for study of rate of decompn. of \bar{C} at 368° see (108).]

BEHAVIOR WITH INORGANIC REACTANTS

Reduction of C. [C with Na/Hg + aq. (109), or C in aq. soln. in pres. of alk. with H₂ at atm. press. + cat. (110), yields ethyl alcohol (1:6130); in latter method reduction is facilitated by NaOH, less so by Ca(OH)₂ or CaCO₃; using Pd/CaCO₃ yield of EtOH is 91%; using Ni yield of EtOH is 80% accompanied by 20% ethylene glycol (1:6465) (110).]

Oxidation of C. C on oxidn. with CrO₃ yields (111) chloroacetic acid (3:1370).

Behavior with H_2O . \tilde{C} on boilg. with aq. undergoes gradual decomposition: e.g., 10% in 8 hrs. (23), 50% in 5 hrs. (107) cf. (11), presumably by loss of HCl and formation of ethylene oxide (1:6105), acetaldehyde (1:0100) etc. — [Note that \tilde{C} with aq. vapor over $ZnCl_2 + ZnO$ at $250-255^\circ$ yields (112) acetaldehyde (1:0100).]

Behavior with inorganic acids. (See also below under behavior with salts of inorganic acids.)

With H_2SO_4 . \bar{C} with conc. H_2SO_4 readily dissolves and according to conditions yields either β -chloroethyl hydrogen sulfate or bis- $(\beta$ -chloroethyl) ether. (Note that \bar{C} with SO_2Cl_2 (see below) gives bis- $(\beta$ -chloroethyl) sulfate.)

[For study of rate and extent of formn. of β -chloroethyl HSO₄ with conc. or fumg. H₂SO₄ at 25° see (14); for reactn. of barium salt of this prod. with aniline see (113).]

 $\ddot{\mathbf{C}}$ with conc. $\mathrm{H}_2\mathrm{SO}_4$ (17% by wt. of $\ddot{\mathbf{C}}$) refluxed 6 hrs. gives (114) bis-(β -chloroethyl) ether (3:6025).

With HNO_3 . [\bar{C} with HNO_3/H_2SO_4 (115) (116) gives (92% yield (115)) β -chloroethyl nitrate, $ClCH_2CH_2ONO_2$, b.p. $149-150^\circ$; for use of this prod. in explosives see (115) (117); for use as ignition accelerator in Diesel engine fuels see (118) (119) (120).]

With HNO_2 . [C with HNO_2 (from $NaNO_2 + HCl$) at -5° gives (70% yield (121)) (122) (123) β -chloroethyl nitrite $ClCH_2CH_2ONO$, b.p. 90-91° (121), 89-89.5° (122), $D_2^{20} = 1.212$ (122), $n_D^{20} = 1.4125$ (122). (This prod. is not to be confused with the isomeric chloro-nitro-ethanes Beil. I-101.)]

Behavior with salts of inorganic acids. (For behavior with NaCN, anhyd. Na₂CO₃, NaSCN, etc., see further below under organic reactants; for behavior with NaSH see further below under alkali reactants.)

With alkali iodides. \bar{C} with NaI in hot alc. (124) (125) or boiling acetone (126) for 16 hrs. (127) (better 4 hrs. (20)), or with KI in alc. at room temp. for 24 hrs. (128) gives (95% yield (127)) β -iodoethanol (ethylene glycol iodohydrin), b.p. 176-177° dec. (124), 86-87° at 25 mm. (20), 85-88° at 25 mm. (127), 85° at 25 mm. (124), 61° at 7 mm. (4), $D_{4}^{20} = 2.1968$ (4), $n_{D}^{20} = 1.57134$ (24). [For study of rate of reaction of \bar{C} with KI in dry acetone at 50° and 60° see (16).]

With alkali sulfides (for alkali sulfhydrates, e.g., NaSH, see below). — $[\bar{C}$ with aq. K₂S (129) or with aq. Na₂S (11) (130) (131) (132) at 30–35° for 1 hr. (33) splits out 2 NaCl giving (yields: 90–95% (11), 79–86% (33)) bis-(β-hydroxyethyl) sulfide ("thiodiglycol") [Beil. I-470, I₁-(244), I₂-(525)], b.p. 164–166° at 20 mm. (33), 130° at 2 mm. (131), 104° at 0.005 mm. (132), f.p. = -16° (132), $D_2^{20} = 1.1821$ (132), 1.1819 (132), $n_D^{20} = 1.52031$ (132), misc. with aq., readily sol. alc., acetone, EtOAc, or CHCl₃, but spar. sol. ether, C₆H₆, or CCl₄ (131) (corresp. dibenzoate, m.p. 65° (133), di-(p-nitrobenzoate), m.p. 107.7° (134), bis-(N-phenylcarbamate), m.p. 128.5–129.5° (131)). — Note that this prod. ("thiodiglycol") with \bar{C} at 100° for 13 hrs. (131) adds to form tris-(β-hydroxyethyl)sulfonium chloride (HOCH₂CH₂)₃SCl, non-hygroscopic ndls., m.p. 126–127° (132), 125–126° (131). Note also that \bar{C} (1 mole) + Na₂S + 1-chloropropanol-2 (propylene chlorohydrin) (3:7747) yields (135) a mixed deriv., viz., β-hydroxyethyl β-hydroxy-n-propyl sulfide.]

With alkali selenide. [\bar{C} with aq. Na₂Se yields (136) bis-(β -hydroxyethyl) selenide.]

With alkali disulfide. [Č with aq. Na₂S + S gives (46% yield (137)) (138) bis-(β -hydroxyethyl) disulfide [Beil. I-471, I₂-(528)], b.p. 155° at 30 mm., $D_4^{20} = 1.3375$ (137).]

With NaHSO₃. [C with solid NaHSO₃ in s.t. at 170-180° for several hrs. gives (139) the salt of 2-hydroxyethanesulfonic acid-1 ("isethionic acid").]

With Na_3PO_4 . [Č with satd. aq. Na_4PO_4 as directed (140) cf. (3) gives (30% yield (140)) di-sodium β -hydroxyethyl phosphate, cryst. from aq. alc. as hexahydrate, m.p. 61° (140).]

With Na₂AsO₃. [\bar{C} with aq. alk. Na₃AsO₃ (from As₂O₃ in aq. alk.) as directed (141) (142) (143) cf. (144) (145) gives β -hydroxyethylarsonic acid (also known as β -hydroxyethylarsinic acid) = HOCH₂CH₂AsO(OH)₂, very sol. aq. but forming spar. sol. monohydrated calcium salt (141).]

With Na_2SnO_2 . [Č with aq. alk. Na_2SnO_2 (from $SnCl_2 + aq$. NaOH) gives (146) salt of β -hydroxyethylstannonic acid = $HOCH_2CH_2.SnO(OH)$.]

Behavior with acid halides of inorganic acids. With thionyl chloride (SOCl₂). [Č with SOCl₂ (small excess) in cold gives (83% yield (147)) β -chloroethylsulfinyl chloride = ClCH₂CH₂OS(O)Cl, b.p. 93-95° at 40 mm., 84-85° at 20 mm., $D_4^{20} = 1.5010$, which upon attempted distn. at ord. press. dec. into SO₂ + ethylene (di)chloride (3:5130) (147). — However, Č (excess) with SOCl₂ at elevated temp. (147) or Č (1 mole) with SOCl₂ (1 mole) in cold (148) gives (75% yield (148)) cf. (156) bis- (β -chloroethyl) sulfite = (ClCH₂CH₂O)₂SO, b.p. 133° at 12 mm. (148), 117.5-118° at 4 mm. (147), $D_0^{20} = 1.422$, $n_0^{20} = 1.481$ (148).]

With sulfuryl chloride (SO_2Cl_2). [Č with SO_2Cl_2 in cold gives (149) (70% yield (122)) β -chloroethyl chlorosulfonate = ClCH₂CH₂O.SO₂Cl [Beil. I₂-(336)], b.p. 101° at 23 mm., $D_-^{20.5} = 1.552$, $n_D^{18.3} = 1.4587$ (122). — However, Č with SO_2Cl_2 under reflux (121) (or β -chloroethyl chlorosulfonate + β -chloroethyl nitrite (above) (122)) gives (50% yield (121)) bis-(β -chloroethyl) sulfate = (ClCH₂CH₂O)₂SO₂ [Beil. I₂-(336)], b.p. 154-154.5° at 8 mm. (121), 130° at 3.5 mm. (122), m.p. + 11° (121), $D_4^{20} = 1.4801$ (121), $n_D^{20} = 1.4622$ (121), 1.4620 (122).]

With phosphoryl chloride (POCl₃). [\bar{C} with POCl₃ at 0° (150) or in CCl₄ at room temp. (151) gives (46–47% yield (151)) β -chloroethylphosphoryl dichloride = ClCH₂CH₂OP-(O)Cl₂ [Beil. I₂-(337)], b.p. 108–110° at 15 mm. (151). — \bar{C} with POCl₃ in pyridine at -20° gives (140) the salt of mono-(β -chloroethyl)phosphoric acid = ClCH₂CH₂OP(O)-(OH)₂ [Beil. I₁-(170), I₂-(336)]. — \bar{C} with POCl₃ in CCl₄ refluxed 16 hrs. gives (60% yield (152) cf. (140)) tri-(β -chloroethyl) phosphate = (ClCH₂CH₂O)₃PO [Beil. I₂-(337)], b.p. 180–182° at 2–3 mm., D_{20}^{20} = 1.428 (152). — For patent on reaction of \bar{C} with POCl₃ see (153).]

With boron trifluoride (BF₃). [Č with BF₃ forms a molecular compound (154) BF₃.2Č which can be distilled in vac. without decompn.; b.p. 59° at 2 mm., $D_4^{20} = 1.4009$, $n_{\rm He}^{174} = 1.40841$ (154).]

With silicon tetrachloride (SiCl₄). [\bar{C} (4 moles) with SiCl₄ (1 mole) yields (155) (96) tetra-(β -chloroethyl) orthosilicate, (ClCH₂CH₂O)₄Si [Beil. I-337, I₂-(337)], b.p. 195-200° at 15 mm. (156), 170-180° at 8 mm. (96) (also obtd. (156) from SiCl₄ + β -chloroethyl nitrite (above)).]

Behavior with alkalies. \bar{C} with alkalies (or appropriate acid acceptors) loses HCl to yield according to conditions either ethylene glycol (1:6465) or ethylene oxide (1:6105).

[E.g., \bar{C} with aq. NaOH on htg. hydrolyzes to ethylene glycol (1:6465); for general articles on this process see (54) (157) (158) (22); for studies of kinetics of the reaction see (404) (18) (159) (160) (161); for examples of patents on hydrolysis of \bar{C} to ethylene glycol by use of aq. alkali or alkaline-earth hydroxides, carbonates, or bicarbonates see (162) (163) (63) (164) (165) (166) (167).]

[\overline{C} added dropwise to 70% aq. NaOH (168) (169) or hot CaO (170) gives ethylene oxide (1:6105), b.p. +10.7°; for patents on this conversion see (171) (172) (173) (174) (175).]

Behavior with alkali sulfhydrate. [\bar{C} with NaSH (from Na₂S.9H₂O satd. with H₂S (137)) at 55-65° (137) (176) or \bar{C} with NaSH in alc. for 36 hrs. at room temp. (177) gives (yields: 55% (176), 50-55% (137), 26-30% (177)) β -hydroxyethyl mercaptan ("monothioethylene glycol") = HOCH₂CH₂SH [Beil. I-470, I₂-(523)], b.p. 157-158° dec. at 742

mm. (178), 61° at 18 mm. (179), 58° at 18 mm. (137), 55° at 13 mm. (178), 52° at 12 mm. (177); $D_4^{20} = 1.1143$ (178); $n_D^{20} = 1.4996$ (178) (corresp. bis-(N-phenyl)carbamate, m.p. 146° (178); corresp. metallic mercaptide derivs. many of which have m.p.'s (178).]

Behavior with ammonia (for amines see below under behavior with organic reactants). [Č with aq. NH₄OH gives (180) a mixt. of three hydroxyamines, viz., β-hydroxyethylamine (2-aminoethanol-1) [Beil. IV-274, IV₁-(424), IV₂-(717)]; bis-(β-hydroxyethyl)amine ("diethanolamine") [Beil. IV-283, IV₂-(729)]; and tris-(β-hydroxyethyl)amine ("triethanolamine") [Beil. IV-285, IV₂-(729)]. — Although all three of these products are now extremely important industrial compounds, they are usually manufactured from ethylene oxide with NH₃ and details lie beyond the scope of this text. — However, for a useful monograph see (181).]

Behavior with hydrazine (NH₂.NH₂). [\bar{C} with 1 mole hydrazine loses HCl yielding (182) β -hydroxyethylhydrazine + hydrazine hydrochloride; \bar{C} with 2-3 moles hydrazine yields (182) ethylene oxide accompanied by a little N,N-bis- $(\beta$ -hydroxyethyl)hydrazine.]

BEHAVIOR OF C WITH ORGANIC REACTANTS

Behavior with hydrocarbons. $[\bar{C} \text{ with } C_6H_6 + \text{AlCl}_3 \text{ (followed by aq.)} \text{ is claimed } (183) \text{ to yield } \beta\text{-phenylethyl alc. } (1:6505), \text{ but this has subsequently been denied } (184) \text{ where } 1,2\text{-diphenylethane (bibenzyl) } (1:7149) \text{ and resin were the only prods. obtd. } (See also below under behavior of <math>\bar{C}$ with organometallic cpds.)]

Behavior with organic hydroxyl compounds. With alcohols (see also below under carbohydrates). \bar{C} (anhydrous) with sodium alkoxides (from prim. or sec. aliphatic or aromales. + Na) on htg. splits out NaCl giving the corresp. mono ethers of ethylene glycol.

[E.g., $\bar{\mathbf{C}}$ with NaOMe gives (35% yield (185)) β -hydroxyethyl methyl ether (1:6405) q.v.; $\bar{\mathbf{C}}$ with NaOEt gives (60% yield (185)) β -hydroxyethyl ethyl ether (1:6410) q.v.; $\bar{\mathbf{C}}$ with NaOPr gives (40% yield (185)) β -hydroxyethyl n-propyl ether (1:6414) q.v.; $\bar{\mathbf{C}}$ with NaOisoPr gives (25% yield (185)) β -hydroxyethyl n-porpyl ether (1:6430) q.v.; $\bar{\mathbf{C}}$ with NaOBu gives (30% yield (185)) β -hydroxyethyl n-butyl ether (1:6430) q.v.; $\bar{\mathbf{C}}$ with NaOiso-Bu gives (36% yield (185)) β -hydroxyethyl n-amyl ether, b.p. 181° at 745 mm. (185).] $\bar{\mathbf{C}}$ with NaOCH₂C₆H₅ similarly gives (186) (187) ethylene glycol monobenzyl ether

(1:6533) q.v.] With carbohydrates (or their relatives). [\bar{C} with d-glucose + HCl yields (188) cf. (189)

2-chloroethyl-d-glucoside.] [\bar{C} with "acetobromglucose" + Ag₂CO₃ (190) (193) in C₆H₆ (189) (191) gives (yields: 69% (189), 45–50% (190)) tetra-acetyl- β -d-(β -chloroethyl)glucoside (tetra-acetyl- β -d-glucosido-ethylene chlorohydrin), m.p. 119–120° (192), 118.5–119.5° (189), 114° cor. (190) (191). — For isomerization of this prod. (in boilg. CHCl₃ for 6½ hrs.) to tetra-acetyl- α -d-(β -chloroethyl)glucoside, m.p. 82–83°, see (194).]

[\bar{C} with "acetobromogalactose" + Ag₂CO₃ (190) (194) in C₆H₆ (191) gives (77% yield (194)) tetra-acetyl- β -d-(β -chloroethyl)galactoside, m.p. 117° cor. (190) (191), 115.5–116.5° (194).]

[For analogous prepn. from \tilde{C} of triacetyl- β -d-(β -chloroethyl)xyloside, m.p. 137° cor., or of hepta-acetyl- β -d-(β -chloroethyl)lactoside, m.p. 78–80°, see (190) (191).]

[For condens. of \overline{C} with mannitol (1:5830) or sorbitol (1:5820) see (195).]

[For use of \bar{C} in degradation ("depolymerization") of cellulose or starch see (196) (197); for use of \bar{C} + NaOH in introduction of β -hydroxyethyl groups into cellulose see (198).]

With aliphatic mercaptans. C with salts of alkyl or alkaryl mercaptans gives the corresp. S-monoethers of monothioethylene glycol.

[E.g., C with NaSMe in abs. alc. (199) (200) or ether (201) (202) or less advantageously

 \bar{C} with KSMe in aq. alc. (201) gives (yields 74–82% (199), 78% (201), 40% (199)) β-hydroxyethyl methyl sulfide (β-methylmercaptoethanol) [Beil. I₂-(524)], b.p. 80.5–81° at 30 mm. (201), 68–70° at 20 mm. (199), $D_{20}^{20} = 1.0640$ (201), $n_{D}^{20} = 1.4867$ (201); this prod. with MeI in dry ether gives on stdg. in cold the corresp. dimethyl-β-hydroxyethylsulfonium iodide, hygroscop. cryst. from MeOH/ether, m.p. 60–62° (202). — \bar{C} with EtSH in alc./NaOEt (203), in alc. KOH (132), or even in conc. aq. KOH (204) gives (yield 70–74% (203)) β-hydroxyethyl ethyl sulfide [Beil. I-470, I₂-(525)], b.p. 184° (204) (132), 182–184° u.c. (203), $D_{4}^{20} = 1.0166$ (132), $n_{D}^{20} = 1.48669$ (132).]

[\bar{C} with n-BuSH in hot aq. NaOH refluxed 1 hr. gives (81% yield (205)) β -hydroxyethyl n-butyl sulfide [Beil. I₂-(525)], b.p. 92-93° at 3 mm., $D_{25}^{25} = 0.9693$, $n_D^{20} = 1.4800$ (205). — \bar{C} with allyl mercaptan in conc. aq. KOH gives (50% yield (206)) β -hydroxyethyl allyl sulfide [Beil. I₂-(525)], b.p. 91° at 12 mm., $D_{20}^{20} = 1.0283$ (206). — \bar{C} with NaSCH₂C₆H₅ in aq. soln. gives (100% yield (179)) β -hydroxyethyl benzyl sulfide, b.p. 169° at 18 mm.]

[C with ethylene dithioglycol (HSCH₂CH₂SH) + powdered NaOH htd. 1 hr. gives (177) ethylene dithioglycol bis-(β-hydroxyethyl ether) = HOCH₂CH₂—S—CH₂CH₂—S—CH₂CH₂OH [Beil. I₂-(533)], lfts., m.p. 62-63°.]

With phenols. [\bar{C} with phenol (1:1420) in aq. NaOH (207) or alc. NaOEt (208), or \bar{C} with NaOC₆H₅ on htg. (17) (209), or \bar{C} with KOC₆H₅ at 150° for 6 hrs. (210), or \bar{C} with phenol salt refluxed 8 hrs. (211) gives (yields: 84% (17), 79% (207), 55–62% (211), 50% (209)) β-hydroxyethyl phenyl ether (β-phenoxyethanol) (1:6518) q.v., b.p. at 80 mm. = 165° (211), 163–166° (208), 163–167° (210), b.p. 128–130° at 20 mm. (17), 134–135° at 18 mm. (209). — (Note that \bar{C} with NaOC₆H₅ in pres. of Et₃N gave only 12.5% yield (212) of β-phenoxyethanol.)]

[Similarly $\bar{\mathbb{C}}$ with aq. sodium o-nitrophenolate in s.t. at 125° for 20 hrs. gives (213) β -(o-nitrophenoxy)ethanol, oil, b.p. 180–182° at 4 mm., m.p. 35–36° (215) (corresp. acetate, oil; corresp. benzoate, m.p. 75–76° (213)); $\bar{\mathbb{C}}$ with m-nitrophenol with 40% aq. KOH at 100° for 2 hrs. (213), or with 2 N NaOH reflux d 4 hrs. (214), gives β -(m-nitrophenoxy)ethanol, m.p. 90–91° (213), 88° (214), 87–88° (215); $\bar{\mathbb{C}}$ with sodium p-nitrophenolate in 50% alc. in s.t. at 120° for 23 hrs. (213), or in boilg. AmOH (216) (217), gives β -(p-nitrophenoxy)ethanol, m.p. 101–102° (213), 94–95° (216), 92–94° (215) (corresp. acetate, m.p. 85–87°; corresp. benzoate, m.p. 116° (213).]

[Analogous condensations of \bar{C} with other monohydric phenols include the following: for \bar{C} with o-cresol (1:1400) (218), with β -naphthol (1:1540) (218), with m-methoxyphenol (1:1765) (219) (220) (221), with methyl p-hydroxybenzoate (1:1549) (222), with p-bromophenol (218), with p-acetylaminophenol (213), with m-diethylaminophenol (212), with 8-hydroxyquinoline (212) see indic. refs.]

[Analogous condensations of \bar{C} with polyhydric phenols include the following: with pyrocatechol (1:1520) (223), resorcinol (1:1530) (224) (218), 4-acetylresorcinol (219), 4-ethylresorcinol (219) see indic. refs.]

With throphenols. [\bar{C} with throphenol in alc. NaOEt (225) (203) or in 10% aq. KOH (226) gives (76% yield (203)) β -hydroxyethyl phenyl sulfide, b.p. 245° (203), 144.5° at 26 mm. (203), 134-135° at 7 mm. (225), 115-116° at 2 mm. (226), $D_4^{20} = 1.1431$ (226), $n_D^{25} = 1.5897$ (225), $n_D^{20} = 1.5917$ (226). $-\bar{C}$ with p-toly mercaptan in conc. aq. NaOH at 100° for 2 hrs. gives (83% yield (133)) (227) β -hydroxyethyl p-tolyl sulfide, b.p. 282-283° dec., 174° at 30 mm. (133).]

[For analogous condens. of \bar{C} with o-nitrophenyl mercaptan (228), m-nitrophenyl mercaptan (228), p-nitrophenylmercaptan (228) (229), o-carboxythiophenol (230), and many other thiophenols (231) see indic. refs.]

Behavior of \tilde{C} with organic ethers (or epoxy cpds.). [\tilde{C} with ethylene oxide (1:6105) + conc. H₂SO₄ gives (30-35% yield (232)) 2-(β -chloroethoxy)ethanol-1 (3:9185) accompanied

by other prods.: for behavior of \bar{C} with epichlorohydrin (3:5358) or with α -ethyl- α -methyl-ethylene oxide see (232). — \bar{C} with α,β' -dichlorodiethyl ether (3:9150) stood 24 hrs. at room temp., then htd. 1 hr., gives (27% yield (233)) acetaldehyde bis-(β -chloroethyl) acetal. (see below). — \bar{C} with bis-(α -chloroethyl) sulfide gives (234) β -trithioacetaldehyde, m.p. 125°. — For behavior of \bar{C} with 2,3-dichlorodioxane (3:9105) see (235); with 1,4-dithiane see (131).]

Behavior of \tilde{C} with carbonyl compounds. \tilde{C} with aldehydes or their polymers. [\tilde{C} with paraformaldehyde (1:0080) + dry HCl gas gives (yields: 65% (237), 55% (236)) (238) (239) chloromethyl β -chloroethyl ether [Beil. I-581, I₂-(645)], b.p. 145-147° (237), 46° at 10 mm. (236); $D_4^{20} = 1.2817$ (237), 1.2814 (236); $n_2^{20} = 1.4578$ (236), 1.4592 (237). — Note that this prod. with \tilde{C} (239), or \tilde{C} (8 wt. pts.) + paraformaldehyde (1 wt. pt.) + CaCl₂ + HCl gas refluxed 5 min. (38) gives formaldehyde bis-(β -chloroethyl)acetal [Beil. I-575], b.p. 218-219° (239), 218.1° at 760 mm. (240), b.p. 93-94° at 11 mm. (38), now an industrial prod. in U.S. because of its use in manufact. of self-sealing gasoline tanks (240).]

[$\bar{\mathbf{C}}$ with acetaldehyde (1:0100) (241) (20) (233) or paraldehyde (1:0170) (236) + HCl gas gives according to circumstances either α -chloroethyl β -chloroethyl ether (3:9150) q.v. or acetaldehyde bis-(β -chloroethyl)acetal, b.p. 194-196° dec. (233), 109-110° at 30 mm. (20), 106° at 17 mm., $D_{-}^{19} = 1.1712$, $n_{D}^{16} = 1.4532$ (233).]

[C with propional dehyde (1:0110) + HCl gas gives (51% yield (236)) β -chloroethyl α -chloro-n-propyl ether, b.p. 60° at 10 mm., $D_4^{20} = 1.1399$, $n_D^{20} = 1.4496$ (236).]

[Č with *n*-butyraldehyde (1:0130) + HCl gas gives (70% yield (236)) β -chloroethyl α -chloro-*n*-butyl ether, b.p. 71° at 10 mm., $D_4^{20} = 1.1009$, $n_D^{20} = 1.4471$ (236).]

 \bar{C} with diketene. [\bar{C} with diketene (242) gives (243) β -chloroethyl acetoacetate.]

Behavior of \bar{C} with organic acids. \bar{C} with organic acids under appropriate conditions behaves conventionally as a substituted ethyl alcohol yielding the corresponding β -chloroethyl esters. Since the number of possibilities is enormous, no attempt can be made here to list all such cases; only a few typical examples must suffice. Note, moreover, that, because during ordinary esterification hydrolysis of the chlorine atom of \bar{C} may occur, many esters of \bar{C} are best made from its reaction with acyl halides q.v.

[$\bar{\mathbf{C}}$ with anhydrous formic acid (1:1005) in pres. of anhydr. Na₂SO₄ (244) or of HCl gas (245) gives β -chloroethyl formate, b.p. 132° at 764 mm. (245), 127-129° at 768 mm. (244), $D_4^{20} = 1.2214$ (244); for study of rate of esterification of $\bar{\mathbf{C}}$ by formic acid under various circumstances see (246).]

[C with anhydr. oxalic acid (1:0535 on satn. with HCl gas and htg. at 100° gives (245) di-(β-chloroethyl) oxalate (3:0572), m.p. 45°.]

[\bar{C} with 2-hydroxy-5-methylbenzoic acid (*p*-cresotinic acid) + conc. H₂SO₄ gives β -chloroethyl *p*-cresotinate, b.p. 136-139° at 10 mm. (247).]

[$\ddot{\mathbf{C}}$ with p-aminobenzoic acid + conc. H₂SO₄ gives (248) (249) β -chloroethyl p-aminobenzoate.]

Behavior of \tilde{C} with salts of organic acids. \tilde{C} with sodium salts of organic acids on htg. eliminates NaCl yielding the corresp. β -hydroxyethyl esters; however, not infrequently secondary reactions of this product then occur or can readily be caused to occur, such as loss of water, ring closure, etc.

[\bar{C} with aq. NaCN at 45–50° for 5 hrs. (250) (251), or with alc. NaCN at 100° for 6 hrs. (88) (27), or with KCN in 50% alc. (252) or boilg. alc. (253) (254), gives (yields: 86% (27), 85–95% (251), 79–80% (250), 71% (253)) β -hydroxyethyl cyanide (β -hydroxypropionitrile = hydracrylonitrile = ethylene cyanohydrin) [Beil. III-298, III₁-(113), III₂-(213)], b.p. 116–118° at 20 mm. (250), 110° at 15 mm. (27) (253), 107–109° at 12 mm. (250).]

[C (1 mole) with NaHCO₃ (1 mole solid) or with Na₂CO₃ (½ mole solid) as directed (255) is claimed to give (80% yield) monomeric ethylene glycol carbonate (CH₂)₂O₂CO₋]

[$\ddot{\mathbf{C}}$ (1 mole) with KSCN (1 mole) in excess $\ddot{\mathbf{C}}$ (1.5 moles as solv.) on warming does not yield the expected β -hydroxyethyl thiocyanate, since this prod. spontaneously undergoes bimolecular self-condensation evolving COS and producing (45% yield (256)) 1-(β -hydroxyethyl)imidazolidthione-2, m.p. 167-168° dec.; for behavior of this prod. with ethereal HCl see (257).]

[Č with NaOBz at 145° (258) or Č with NaOBz + a little Et₂NH at 130° for 4 hrs. (259), or Č with KOBz as directed (260), gives (yields: 85% (259), 33% (260)) ethylene glycol monobenzoate (β -hydroxyethyl benzoate), m.p. 36.5-37.5° (261), 36-37° (260) cf. (259); b.p. 173° at 21 mm. (259), 156° at 14 mm. (260), 150-151° at 10 mm. (261) (corresp. p-toluenesulfonate, m.p. 74-75° (262)).]

[Č with Na p-nitrobenzoate + a little Et₂NH at 130° for 4 hrs. (259), or \tilde{C} with K p-nitrobenzoate in C₆H₆ in s.t. at 100° (263), gives (yields: 83% (259), 60% (263)) ethylene glycol mono-(p-nitrobenzoate), m.p. 77-78° (263), 77° (259).]

[For analogous behavior of \tilde{C} with sodium salicylate (259), sodium sorbate (264), sodium methylarsenite (265), sodium p-toluenesulfinate (133), or sodium naphthenate (266) see indic. refs.]

Behavior of \tilde{C} with acid chlorides of organic acids. \tilde{C} with acid chlorides of organic acids behaves as a substituted primary alcohol splitting out H from its OH with Cl from the acid chloride to yield the corresp. β -chloroethyl esters. No attempt can be made here to list all possible cases, but the following text will furnish ample illustrative examples.

With acid chlorides of aliphatic acids. [\bar{C} with acetyl chloride (3:7065) gives (yields: 90% (267), 82% (248)) (268) β -chloroethyl acetate (3:5735) q.v. — \bar{C} with trichloroacetyl chloride (3:5420) + pyridine in ether gives (45% yield (103)) (275) β -chloroethyl trichloroacetate (3:6510) q.v. — \bar{C} with sorbyl chloride (CH₃CH = CH — CH = CH — CO.Cl) [Beil. I-484, I₂-(453)] gives alm. quant. (269) β -chloroethyl sorbate, b.p. 115° at 15 mm. (269). — For studies of rate of reactn. of \bar{C} with various acyl chlorides in dioxane soln. at 15°, 25°, and 35° see (270). — \bar{C} with malonyl (di)chloride (3:9030) gives bis-(β -chloroethyl) malonate, b.p. 164° at 15 mm. (271).]

With various chloroformates. \bar{C} with carbonyl chloride (phosgene) (3:5000) at room temp. gives (272) (121) (273) (125) only (yield 82% (273), 78% (121)) β -chloroethyl chloroformate (3:5780) q.v.: note that no bis-(β -chloroethyl) carbonate (see below) is formed.]

[\bar{C} with trichloromethyl chloroformate ("diphosgene") (3:5515) gives (61% yield (274)) β -chloroethyl trichloromethyl carbonate = ClCH₂CH₂O.CO.O.CCl₃, b.p. 115° at 16 mm., 110° at 12 mm., $D_4^{20} = 1.5664$, $n_D^{20} = 1.4748$ (274).]

[\bar{C} with β -chloroethyl chloroformate (3:5780) gives (70% yield (121)) di-(β -chloroethyl) carbonate (3:6790) q.v.]

With acid chlorides of aromatic acids. [C with benzoyl chloride on htg. gives (yields: 90% (276), 84.5% (277), 55% (263)) β -chloroethyl benzoate (3:8860) q.v.]

Behavior of \tilde{C} with organic esters of inorganic acids. [\tilde{C} with Me₂SO₄ at 120° as directed gives (60% yield (126)) β -chloroethyl methyl ether (β -methoxyethyl chloride) (3:7265) q.v.]

[\bar{C} with Et₂SO₄ + solid NaOH on htg. gives (278) ethylene glycol monoethyl ether ("Cellosolve") (1:6410); note, however, that \bar{C} with EtOH + conc. H₂SO₄ at 145° gives (279) β -chloroethyl ethyl ether (3:7463).]

[$\ddot{\mathbf{C}}$ (1 mole) with ethyl metaphosphate (1 mole) stood 4 days at room temp. (280) cf. (281) gives β -chloroethyl ethyl hydrogen phosphate (isolated as barium salt); however, $\ddot{\mathbf{C}}$ + ethyl metaphosphate in CHCl₃ refluxed 3 hrs. gives (140) β -chloroethyl dihydrogen phosphate (isolated as barium salt).]

 \bar{C} with organic hypochlorites (or mixtures which yield them) gives ethers [e.g., \bar{C} with ter-butyl hypochlorite (3:7165) + ethylene gives (60.8% yield (282)) β,β' -dichlorodiethyl

ether (3:6025). — \bar{C} with N,N-dichlorobenzenesulfonamide + butene-1 in CHCl₃ at -15° gives (283) (probably via formn. and addn. of β -chloroethyl hypochlorite) 1-chloro-2-(β -chloroethoxy)butane, b.p. 195.5°, $D_4^{20}=1.1223$, $n_D^{20}=1.453$; the use of butene-2 or of 2-methylpropene (isobutylene) gives analogous products (283) cf. (284).]

Behavior of C with organometallic compounds (or their equivalents). [C with KC_6H_5 splits out KCl yielding (285) β -phenylethyl alc. (1:6505).]

 $\bar{\mathbf{C}}$ with arom. RMgX cpds. reacts in analogous fashion yielding the corresp. alcohols [e.g., $\bar{\mathbf{C}}$ with C_6H_6MgBr (287) (288) or C_6H_6MgCl (289) gives (95% yield (286)) β -phenylethyl alc. (1:6505); $\bar{\mathbf{C}}$ with o-tolyl MgBr gives (20–24% yield (290)) (287) β -(o-tolyl)ethanol; $\bar{\mathbf{C}}$ with m-tolyl MgBr gives (20–24% yield (290)) β -(m-tolyl)ethanol; $\bar{\mathbf{C}}$ with p-tolyl MgBr gives (yields: 80% (291), 20–24% (290)) (287) β -(p-tolyl) ethanol; many other analogous cases are known].

[Note that \tilde{C} with C_2H_5MgBr gives (292) ClCH₂CH₂OMgBr which may then be reacted with RMgBr types as above (292).]

[$\bar{\mathbf{C}}$ with diethyl malonate in alc. NaOEt (i.e., diethyl disodiomalonate) might be expected to yield diethyl bis- $(\beta$ -hydroxyethyl)malonate; this compd., however, is unknown since it loses 2 EtOH, ring-closing to (271) the spiro-dilactone of bis- $(\beta$ -hydroxyethyl)malonic acid [Beil. XIX₁-(680)], m.p. 109-110°.] — [Note also that $\bar{\mathbf{C}}$ (1 mole) with diethyl malonate (1 mole) + 1% HCl gas undergoes transesterification yielding (405) both β -chloroethyl ethyl malonate, b.p. 105-106° at 3 mm., and bis- $(\beta$ -chloroethyl) malonate, b.p. 142-143° at 3 mm.]

[C with ethyl acetoacetate + alc. NaOEt (i.e., ethyl sodio-acetoacetate) boiled 5 hrs. gives a prod. (probably lactone of α -(β -hydroxyethylacetoacetic acid) which with 10% HCl after 5 hrs. boiling gives (40% yield (293)) pentanone-4-ol-1 (γ-aceto-n-propyl alc.) [Beil. I-831, I_I-(422), I₂-(873)], b.p. 115-116° at 20 mm. (294), D_4^{20} = 1.0071 (295), n_D^{20} = 1.439 (294) (corresp. semicarbazone, m.p. 167-168° (296)): note that this prod. (which is an important intermediate in the prepn. of the antimalarial "Atabrine" (297)) is best prepd. from ethylene oxide + ethyl sodioacetoacetate which gives first (60% yield (294)) the lactone of α -(β -hydroxyethyl)acetoacetic acid, b.p. 142-143° at 30 mm., n_D^{20} = 1.4562, which with warm HCl ring-opens and splits off AcOH giving (96% yield (294)) desired γ-aceto-n-propyl alc. (above).]

[\bar{C} + sodium phenobarbital (Na deriv. of 5-ethyl-5-phenylbarbituric acid) gives (60% yield (298)) 1-(β -hydroxyethyl)phenobarbital, m.p. 145.0-145.5° cor. (note that this prod. is not obtd. from \bar{C} + Ag salt of phenobarbital). — \bar{C} with theobromine (3,7-dimethylxanthine) in aq. NaOH in s.t. at 125° for 6 hrs. gives (47-57% yield (366)) (367) 1-(β -hydroxyethyl)theobromine, m.p. 194° (367), 193° (366).]

Behavior of \bar{C} with amines. With primary aliphatic amines. $[\bar{C}]$ (1 mole) with aq. MeNH₂ (1 mole) at 110° for 12–24 hrs. gives (80% yield (299)), β -(methylamino)ethanol [Beil. IV-276, IV₂-(718)], b.p. 159° (300) (301), 155–156° at 760 mm. (273) (corresp. 3,5-dinitrobenzoate, m.p. 195–196.5° (302); corresp. \bar{B} .PkOH, 148° (303); corresp. reaction prod. with α -naphthyl isothiocyanate, viz., N-(β -hydroxyethyl)-N-methyl-N-(α -naphthyl) thiourea, m.p. 125° (303)). — \bar{C} with excess aq. MeNH₂ on standing in s.t. at 100° for several hrs. (304) or \bar{C} with β -(methylamino)ethanol (above) in aq. at 120° (299) gives methyl-bis-(β -hydroxyethyl)amine (N-methyl-diethanolamine) [Beil. IV-284, IV₂-(729)], b.p. 115° at 5 mm. (240) (note that this prod. is new commercial chem. in U.S. (240)).]

[Č with EtNH₂ as above should give β-(ethylamino)ethanol [Beil. IV-282, IV₂-(727)], b.p. 167-169° cor. at 751 mm., $D_4^{20} = 0.914$, $n_D^{20} = 1.444$, and (305) ethyl-bis-(β-hydroxy-ethyl)amine (N-ethyldiethanolamine) [Beil. IV-284], although both these prods. are usually prepd. from ethylene oxide.]

[For analogous reactn. of \bar{C} with *n*-heptadecylamine yielding N-(β -hydroxyethyl)-n-

heptadecylamine see (306) (307); with cyclohexylamine yielding N-(β -hydroxyethyl)-cyclohexylamine see (308).]

With primary aromatic amines. [$\bar{\mathbb{C}}$ (1 mole) with aniline (1 mole) refluxed a short time (299) (309) (310) (311) (312) (313) gives (yields: 70% (309), 40% (311)) N-(β -hydroxyethyl)amiline (β -phenylaminoethanol) [Beil. XII-182], b.p. 286° cor. (299), $n_D^{20} = 1.5749$ (317) (note that by reactn. of a second mole of $\bar{\mathbb{C}}$ some N,N-bis-(β -hydroxyethyl)aniline (see below) may also form, and that some N,N'-diphenylethylenediamine, m.p. 63.4-64.2°, may also appear (311)); note also that N-(β -hydroxyethyl)aniline on dehydration, e.g., by htg. in xylene with P_2O_5 (310), reacts bimolecularly giving in small yield N,N'-diphenylpiperazine, m.p. 160–162° (310). — $\bar{\mathbb{C}}$ (2 moles) with aniline (1 mole) especially in pres. of anhydr. Na₂CO₃ (310) or NaOH (314) or aq. at 110° (299) gives N,N-bis-(β -hydroxyethyl)aniline (N-phenyldiethanolamine) [Beil. XII-183, XII₁-(167)], m.p. 58° (315), 53.5-54° (310): note that this prod. on htg. at 200° under reduced press. (314) or htg. with P_2O_5 in xylene (310) or htg. with 70% H₂SO₄ at 160° (316) loses water and ring-closes to N-phenylmorpholine [Beil. XXVII-6], m.p. 53° (299), 52° (310).]

[Č (1 mole) with o-toluidine (2 moles) at 120–130° for several hrs. (318) (313) gives β -(o-tolylamino)ethanol, b.p. 172° at 12 mm. (318), 145–150° at 3 mm. (317), $n_D^{20} = 1.5675$ (317); note that in pres. of Na₂CO₃ the main (318) prod. (because of bimolecular condens. of this prod.) is N,N'-di-o-tolylpiperazine [Beil. XXIII-8], m.p. 174°. — Č with p-toluidine on htg. gives (319) β -(p-tolylamino)ethanol [Beil. XIII-907], b.p. 177–178° at 14 mm. (319), m.p. 42–43° (317); note, however, that analogous bimolecular ring closure of this prod. readily occurs on htg. yielding (320) N,N'-di(p-tolyl)piperazine [Beil. XXIII-9], m.p. 190°.]

[\bar{C} with o-methoxyaniline (o-anisidine) at 100° for 48 hrs. gives (75–80% yield (321)) (299) β -(o-methoxyphenylamino)ethanol [Beil. XIII-367], b.p. 305° cor. (299) (corresp. \bar{B} .HCl, m.p. 134°; \bar{B} .PkOH, m.p. 140° (321)); note that this prod. with 5 pts. conc. HCl in s.t. at 160–180° gives by a remarkable elimination of MeOH and monomolecular ring closure (38% yield (321)) (299) "phenmorpholine" [Beil. XXVII-34], b.p. 268° cor. (299), 127–128° at 12 mm. (321). — \bar{C} with p-ethoxyaniline (p-phenetidine) gives on htg. (319) β -(p-ethoxyphenylamino)ethanol, m.p. 67°, b.p. 190° at 11 mm. (319) cf. (322).]

Many other cases, analogous to the above examples, are also known but cannot be included here.

With secondary aliphatic amines. Because of the great importance of β -(dialkylamino)-ethanols in the prepn. and study of physiologically active compounds, much study has been given to their prepn. from \tilde{C} (and otherwise). From the resulting mass of data, the following examples are cited.

[\bar{C} with Me₂NH gives (323) β -(dimethylamino)ethanol [Beil. IV-276, IV₁-(425), IV₂-(719)], b.p. 135° cor. at 758 mm., $D_4^{20}=0.8866$, $n_D^{20}=1.4300$ (324) (corresp. p-nitrobenzoyl ester, m.p. 58° (325)). — \bar{C} with Et₂NH on htg. (326) under reflux for 8 hrs. (327) or in pres. of NaOH under press. at 160° for 3 hrs. (328) gives (yields: 83% (328), 68–70% (327)) β -(diethylamino)ethanol [Beil. IV-282, IV₂-(727)], b.p. 163° at 760 mm. (329), 160° at 741 mm., 100° at 80 mm., 96° at 73 mm., 55° at 10 mm. (330), 42–44° at 8 mm. (329); $D_{25}^{25}=0.8601$ (329); $n_D^{25}=1.4400$ (329), 1.4389 (330) (corresp. N-(p-nitrophenyl)carbamate, m.p. 59–60° cor. (329)).]

[\bar{C} with di-n-propylamine under reflux gives (70% yield (331)) β -(di-n-propylamino)-ethanol [Beil. IV-282], b.p. 90-92° at 22 mm. (331) (corresp. p-nitrobenzoyl ester hydrochloride, m.p. 133.5-134.5° (325)). — \bar{C} with di-n-butylamine on htg. gives (332) (333) β -(di-n-butylamino)ethanol, b.p. 225-230° at 760 mm., sl. dec. (332), 226-228° at 738 mm. (325), 90-94° at 7 mm. (333); $D_{20}^{20} = 0.8624$ (325); $n_{20}^{20} = 1.4444$ (325) (corresp. p-nitrobenzoyl ester hydrochloride, m.p. 92.5-93.5° (325) (332)). — \bar{C} with di-(isobutyl)amine

at 120° gives (60% yield (331)) β -(di-isobutylamino)ethanol [Beil. IV-283, IV₁-(430)], b.p. 203-206° (334), 96-98° at 15 mm. (331) (corresp. p-nitrobenzoyl ester hydrochloride, m.p. 160-161° (334)). — \bar{C} with di-(eec-butyl)amine gives (335) β -(di-sec-butylamino)ethanol, b.p. 225-226° cor. at 760 mm. (335), 224-226° at 745 mm. (325), $D_{20}^{20} = 0.8780$ (325), $n_{20}^{20} = 1.4475$ (325) (corresp. p-nitrobenzoyl ester, m.p. 51.0-51.5° (325)). — \bar{C} with discoamylamine on htg. gives (60% yield (331)) (334) β -(discoamylamino)ethanol [Beil. IV-283, IV₁-(430)], b.p. 126-128° at 15 mm. (331) (corresp. p-nitrobenzoyl ester hydrochloride, m.p. 123-124° (334) (325)).]

 \bar{C} with alicyclic secondary amines. $[\bar{C}$ with di-(cyclohexyl)amine gives (336) β -(dicyclohexylamino)ethanol, b.p. 145-150° at 4 mm. (336). $-\bar{C}$ with ac-tetrahydro- β -naphthylamine (2 moles) in xylene at 110-115° for 3 hrs. (under N₂) gives (80-85% yield (337)) β -(ac-tetrahydro- β -naphthylamino)ethanol hydrochloride, m.p. 183.8-184.8° cor. (337).

 \bar{C} with aromatic secondary amines. $[\bar{C}$ with N-methylaniline in s.t. at 100° for 35 hrs. gives (65% yield (338)) cf. (339) β -(N-methylanilino)ethanol [Beil. XII-182], b.p. 218–219° at 110 mm. (338), 148–150° at 13 mm. (340); note, however, the claim (341) that \bar{C} (1 mole) with N-methylaniline (1.5 moles) refluxed 10–12 hrs. gives (14% yield (341)) N,N'-diphenylpiperazine, m.p. 164–165°. — \bar{C} with N-ethylaniline on htg. without solv. (338) or in aq. (313) gives β -(N-ethylanilino)ethanol [Beil. XII-183], b.p. 269–271° at 750 mm. (340), 267–268.5° (338).]

 \bar{C} with heterocyclic secondary amines. [\bar{C} with piperidine at 100° (326), or \bar{C} with piperidine (2 moles) in acetone overnight at room temp. (342), gives β -(N-piperidine) ethanol (N-(β -hydroxyethyl)piperidine) [Beil. XX-25], b.p. 199° (326), 89-91° at 20 mm. (343), 90° at 12 mm. (342), $D_{25}^{25} = 0.9732$ (343), $n_{D_1}^{25} = 1.4749$ (343) (corresp. \bar{B} .HCl, m.p. 122-124° (343), 120° (344), 64-65° (342)) (note unexplained disagreement); \bar{B} .PkOH, m.p. 100° (345), benzoyl ester hydrochloride, m.p. 176° (346), 175-176° (347), 173-174° (348), 171-172° (345), 167-168° (342); p-nitrobenzoyl ester hydrochloride, m.p. 175-176° (342)).]

[$\bar{\mathbf{C}}$ with morpholine would be expected to yield N-(β -hydroxyethyl)morpholine (4-morpholineëthanol) although only vague reference (351) is reported; this prod. can, however, be prepd. indirectly from $\bar{\mathbf{C}}$ by ring closure of tris-(β -hydroxyethylamine)(triethanolamine) with 70% H₂SO₄ at 160-170° (349) (316), or from triethanolamine hydrochloride at 200-205° under pressure (40 mm.) for 14 hrs. (46% yield (350)); 4-morpholineëthanol [Beil. XXVII-7] is now comml. prod. in U.S. (351): b.p. 227° cor. at 757 mm. (349), 118-120° at 24 mm. (350); $D_4^{25} = 1.0681$ (350), $n_D^{25} = 1.4770$ (350) (corresp. benzoyl ester hydrochloride, m.p. 205° (346), 204.6-205.8° (350); corresp. p-nitrobenzoyl ester hydrochloride, m.p. 214.6-215.4° (350)).]

With tertiary amines. \bar{C} with tertiary amines behaves as an alkyl halide giving by addition to the tertiary amine nitrogen the corresp. quaternary ammonium salt. [E.g., \bar{C} (1 mole) with pyridine (1 mole) at 135° for 1 hr. (343) (352) cf. (344) (353) gives (100% yield (343)) β -hydroxyethyl-pyridinium chloride [Beil. XX-220, XX₁-(75)], hygroscopic flakes from abs. EtOH by addn. of dry ether, m.p. 124-125° (343).]

[$\check{\mathbf{C}}$ with 3-carbomethoxypyridine (methyl nicotinate) 1 hr. at 120° gives (343) β -hydroxyethyl-3-carbomethoxypyridinium chloride. — $\check{\mathbf{C}}$ with N,N-dimethyl-n-dodecylamine (354), or $\check{\mathbf{C}}$ with N,N-dimethyl-n-octadecylamine (354), or $\check{\mathbf{C}}$ with N-(n-heptadecylbenzimidazole) (355) gives corresp. quat. salts.]

Behavior of \tilde{C} with amides and sulfonamides. [For use of \tilde{C} as means of introduction of β -hydroxyethyl group into amides, diamides, ureas, etc., see (356).]

 $\{\bar{C} \text{ with sodium } p\text{-toluenesulfonamide at } 120^{\circ} \text{ for } 6 \text{ hrs. under press. } (357) \text{ gives } N\text{-}(\beta\text{-hydroxyethyl})-p\text{-toluenesulfonamide; this prod. on conversion to its sodio deriv. and further similar treatment with <math>\bar{C}$ (357) or \bar{C} with p-toluenesulfonamide + NaOH (358)

gives N,N-bis- $(\beta$ -hydroxyethyl)-p-toluenesulfonamide, cryst. from acetone, m.p. 101° (357); note that this last prod. upon ring closure with 100% H₂SO₄ at 160-170° gives N-(p-toluenesulfonyl)morpholine, hydrolysis of which yields (358) morpholine.]

[\bar{C} with the di-sodium deriv. of N,N' bis-(p-toluenesulfonyl)ethylenediamine at 100–110° for 10 hrs under press. gives (359) N,N'-bis-(p-toluenesulfonyl)ethylenediamine,

m.p. 144°.]

[Č (1 mole) with thiourea (1 mole) at not above 135° for 30 min. yields (360) S-(\$\beta\$-hydroxyethyl)isothiouronium chloride, m.p. 111° (360).]

Behavior of \tilde{C} with other miscellaneous nitrogen compounds (see also under \tilde{C} + organometallic cpds. above). [\tilde{C} with ethereal diazomethane undergoes conventional methylation of the hydroxyl group yielding (361) β -chloroethyl methyl ether (3:7265).]

[\bar{C} with aq. Na₂N.CN in cold (362) cf. (363) or with CaNCN on warming (362) gives a soln. of the monosodium deriv. of β -(cyanamido)ethanol, HOCH₂CH₂—NH—CN or HOCH₂CH₂—N=C=NH; although the parent cannot be isolated the soln. of its Na salt gives with acyl halides derivatives which can: e.g., with benzoyl chloride (2 moles) + aq. NaOH the soln. gives (362) the corresp. dibenzoyl deriv., m.p. 165°; with p-toluenesulfonyl chloride + [aq. NaOH the soln. gives (362) a mono-(p-toluenesulfonyl) deriv., m.p. 128° (which undoubtedly has the ring-closed structure of 3-(p-toluenesulfonyl-(1,3-oxazolidone-2)imide).]

[\bar{C} with acetyl isocyanate adds as an alcohol yielding (364) β -chloroethyl N-acetyl-carbamate, m.p. 73–74°. — \bar{C} with benzoyl isothiocyanate adds as an alc. at ord. temp. yielding (365) β -chloroethyl N-benzoylthioncarbamate, m.p. 179–180°.]

- β -Chloroethyl acetate: b.p. 145° (see 3:5735).
- —— β -Chloroethyl benzoate: b.p. 256° (see 3:8860).
- ① β -Chloroethyl p-nitrobenzoate [Beil. IX-390, IX₁-(158)]: ndls. from dil. alc., m.p. 56° (368) (369) (370), 55-56° cor. (371), 54.5-55.5° (103), 54-55° (372). [From \bar{C} with p-nitrobenzoyl chloride on warming (368) (371) (370); also from ethylene glycol (1:6465) + p-nitrobenzoic acid + HCl gas at 110° (372).]
- \oplus β -Chloroethyl 3,5-dinitrobenzoate: m.p. 92° (373). [From \bar{C} with 3,5-dinitrobenzoyl chloride on htg. (373).]
- --- β-Chloroethyl hydrogen 3-nitrophthalate: unreported.
- \bigcirc β -Chloroethyl hydrogen 4-nitrophthalate: m.p. 97-98° (374). [From $\stackrel{\circ}{C}$ with 4-nitrophthalic anhydride in C_6H_6 under reflux for 1 hr. (374).]
- β-Chloroethyl benzenesulfonate: oil, b.p. 184° u.c. at 9 mm. (375), 184° at 8-11 mm. (376), $D_4^{15} = 1.353$ (375). [From \bar{C} with benzenesulfonyl chloride under reflux for 3 hrs. (68% yield (377)) or on shaking with aq. NaOH in cold (68% yield (375)) (276); for study of decompn. into vinyl chloride (3:7010), acetaldehyde (1:0100), etc., on htg. see (378).]
- —— β-Chloroethyl p-toluenesulfonate: oil, b.p. 210° at 21 mm. (379) (380) (383), 192° at 15 mm. (386), 140° at 1.5 mm. (381), $n_D^{25} = 1.5280$ (381), m.p. +22.5° (381). [From \bar{C} with p-toluenesulfonyl chloride on refluxing 3 hrs. (87% yield (379)) (383) (382) or on shaking with aq. NaOH in cold (376); for reactions of this ester with RMgX cpds. see (384) (385) (386).]
- —— β-Chloroethyl carbamate [Beil. III-24, III₂-(21)]: m.p. 76° (125) (272) (387) (388). [Prepd. indirectly.]
- —— β-Chloroethyl N-phenylcarbamate [Beil. XII-320]: m.p. 51° (272) (389), 49.5–50.5° (103) (for data on optical props. see (389)); b.p. 133-135° at 2 mm. (390). [Note that this prod. has never been reported as prepd. by direct actn. of C with phenyl

- isocyanate but always by indirect means; note also that on short boilg. with aq. or alc. alk. it loses HCl and by ring closure yields 3-phenyloxazolidone [Beil. XXVII-136], lfts. from alc., m.p. 124° (272), 122° (309).]
- \odot β -Chloroethyl N-(p-bromophenyl)carbamate: pl. from lgr., m.p. 88–89° (400). [From \odot with p-bromobenzazide (400).]
- Φ β-Chloroethyl N-(α-naphthyl)carbamate [Beil. XII-1236]: m.p. 102-103° (373), 101° (391) (93), 100-101° (309). [From C with α-naphthyl isocyanate (391) (373); also from β-chloroethyl chloroformate (3:5780) with α-naphthylamine (309): note also that with dil. KOH (309) this prod. loses HCl ring-closing to 3-(α-naphthyl)-oxazolidone-2 [Beil. XXVII-136], m.p. 125° (309), while with conc. KOH it merely undergoes hydrolysis of chlorine yielding N-(β-hydroxyethyl)-α-naphthylamine, m.p. 52° (309).]
- —— β-Chloroethyl N-(β-naphthyl)carbamate [Beil. XII-1292]: m.p. 98° (309). [Prepd. indirectly from β-chloroethyl chloroformate (3:5780) with β-naphthylamine (309); for behavior with dil. and conc. KOH analogous to preceding case see (309).]
- β-Chloroethyl N-carbamidocarbamate (β-chloroethyl allophanate) [Beil. III₂-(56)]:
 m.p. 182.5° (392), 181–182° (388). [From C with vapors of isocyanic acid (392) or
 from β-chloroethyl chloroformate (3:5780) with urea (388).]
- --- N-(β -hydroxyethyl)phthalimide = (β -(N-phthalimido)ethanol) [Beil. XXI-469, XXI₁-(368)]: m.p. 129.5° cor. (394), 127-128° (395), 126.5-127.5° (357), 126-127° (396), 125-126° (397) (note that m.p. given by (393) is incorrect). [From \bar{C} with K phthalimide in s.t. at 150° for 4 hrs. (393): note that the m.p. of 88-89° reported by the only worker (393) using this method is not far from that (81° (395)) of N-(β -chloroethyl)phthalimide leaving some question as to which prod. was really obtd.]
- N-(β-hydroxyethyl)tetrachlorophthalimide: m.p. 208-209° (398). [From C with
 K tetrachlorophthalimide in s.t. at 200° for 6 hrs. (398).]
- —— β -Chloroethyl triphenylmethyl ether: m.p. 132° (399). [From \bar{C} with α -bromotriphenylmethane (399).]
- 3:5552 (1) Henry, Jahresber. 1889, 1321. (2) Grimm, Patrick, J. Am. Chem. Soc. 45, 2799 (1924). (3) Bailly, Gaume, Bull. soc. chim. (4) 35, 590-597 (1924); Compt. rend. 178, 1191 (1924). (4) Karvonen, Acad. Sci. Fennicae 3-A, 1-103; Cent. 1912, II 1270; C.A. 14, 2176 (1920). (5) De Laszlo. J. Am. Chem. Soc. 49, 2107 (1927). (6) Matejka, Jelinek, J. chim. phys. 34, 611-614 (1937). (7) Timmermans, Bull. soc. chim. Belg. 36, 507 (1927). (8) Timmermans, Martin, J. chim. phys. 25, 444-445 (1928). (9) Smyth, Walls, J. Am. Chem. Soc. 54, 2263, 2266 (1932). (10) Snyder, Gilbert, Ind. Eng. Chem. 34, 1519-1521 (1942).
- (11) Gomberg, J. Am. Chem. Soc. 41, 1414-1431 (1919). (12) Wurtz, Ann. 110, 125-128 (1859). (13) Mathews, J. Am. Chem. Soc. 48, 570 (1926). (14) Suter, Oberg, J. Am. Chem. Soc. 56, 677-679 (1934). (15) Norris, Mulliken, J. Am. Chem. Soc. 42, 2095 (1920). (16) Smith, Boord, Adams, Pease, J. Am. Chem. Soc. 49, 1338 (1927). (17) Kirner, J. Am. Chem. Soc. 48, 2747-2753 (1926). (18) Winstrom, Warner, J. Am. Chem. Soc. 61, 1205-1210 (1939). (19) Forster, Newman, J. Chem. Soc. 97, 2573 (1910). (20) Street, Adkins, J. Am. Chem. Soc. 59, 162-167 (1928).
- (21) Timmermans, Mataar, Bull. soc. chim. Belg. 30, 216 (1921). (22) Radulescu, Muresanu, Bull. Soc. Stirnte Cluy 7, 129-153 (1932); Cent. 1933, I 3156; C.A. 27, 2085 (1933). (23) Bozza, Gallarati, Ciorn. chim. ind. applicata 13, 163-173 (1931); Cent. 1931, II 409; C.A. 25, [3962 (1931). (24) Karvonen, Acad. Sci. Fennicae 5-A, No. 6, 1-139 (1914); Cent. 1919, III 807; C.A. 14, 2176 (1920). (25) Berry, J. Soc. Chem. Ind. 38-T, 145-150 (1909). (26) Bancelin, Rivat, Bull. soc. chim. (4) 25, 552-560 (1909). (27) Moureu, Brown, Bull. soc. chim. (4) 27, 902-903 (1920). (28) Kirst (to Dow Chem. Co.), U.S. 1,386,118, Aug. 2, 1921; Cent. 1921, IV 1065; C.A. 15, 3851 (1921). (29) Ernst, Kaufler (to A. Wacker Soc. Elektrochem. Ind.), [Ger. 486,492, Nov. 25, 1929; Cent. 1930, I 2005; C.A. 24, 1869 (1930). (30) Soc. Anon. des Distilleries des Deux Sèvres, Czechoslov. 34,718, Jan. 10, 1931; Cent. 1932, II 2107; not in C.A.; Brit. 305,528, April 4, 1929; Cent. 1929, II 485; C.A. 23, 4712 (1929).
- (31) Kaplan, Grishin, Skvortsova, J. Gen. Chem. (U.S.S.R.) 7, 538-544 (1937); Cent. 1937, II 2332; C.A. 31, 4554 (1937). (32) Kireev, Kaplan, Zlobin, J. Applied Chem. (U.S.S.R.) 7,

1333-1338 (1934); Cent. 1936, I 4286; C.A. 29, 5712 (1935). (33) Faber, Miller, Org. Syntheses, Coll. Vol. 2, 576-578 (1943); 12, 68-70 (1932). (34) Forrester, U.S. 2,049,608, Aug. 4, 1936; Cent. 1937, I 182; C.A. 30, 6245 (1936). (35) Schmidt, Grossinsky (to I.G.), U.S. 1,882,978, Oct. 18, 1932; Cent. 1933, I 2312; C.A. 27, 737 (1933); Brit. 309,025, Oct. 10, 1929; Cent. 1936, II 304; C.A. 24, 2468 (1930); French 650,972, Feb. 13, 1929; Cent. 1933, I 2312; C.A. 23, 2321 (1929). (36) Ferris (to Atlantic Refining Co.), U.S. 2,072,104, March 2, 1937; Cent. 1937, I 4719; C.A. 31, 2810 (1937). (37) Humphrey (to Hercules Powder Co.), U.S. 1,715,086, May 28, 1929; Cent. 1930, I 294; [C.A. 23, 3588 (1929)]; Canadian 284,988, Nov. 20, 1928; C.A. 23, 1001 (1929); not in Cent. (38) Freudenberg, Acker, Ber. 71, 1400-1406 (1941). (39) Schutz, Cellulosechem. 19, 33-38 (1941); C.A. 36, 5008 (1942). (40) B.A.S.F., Ger. 393,566, April 5, 1924; Cent. 1924, II 120; not in C.A.

(41) Rosenthal (to F. Bayer Co.), Ger. 383,699, Oct. 16, 1923, Cent. 1924, I 252; not in C.A. (42) Webb (to Eastman Kodak Co.), U.S. 1,444,406, Feb. 6, 1923, Cent. 1923, IV 342; C.A. 17, 1329 (1923). (43) F. Bayer Co., Brit. 209,333; Sept. 10, 1924, Cent. 1924, II 2715; not in C.A. (44) Smith, Natl. Inst. Health Bull. 165, 11-29 (1936); Cent. 1938, I 2016; C.A. 30, 4565 (1936). (45) Fratt, Nature 126, 995 (1930). (46) Koelsch, Zentr. Gewerbehyg. Unfallverhüt. 14, 316-325 (1927); Cent. 1927, II 2467. (47) Clark, Edwards, Trans Roy. Soc. Can. (3) 28, III 107-125 (1934); Cent. 1935, I 2548; C.A. 29, 1112 (1935). (48) Clark, Fowler, Black, Trans. Roy. Soc. Can. (3) 25, III 99-105 (1931); Cent. 1933, I 2708; C.A. 26, 2755 (1932). (49) Clark, Archibald, Trans. Roy. Soc. Can. (3) 26, III 87-92 (1932); Cent. 1933, I 3951, C.A. 27, 1649 (1933). (50) Schultz, Frey (to Standard Brands, Inc.), U.S. 1,893,152, Jan. 3, 1933; Cent. 1933, I 1862; C.A. 27, 2249 (1933).

(51) Mourea, Dodé, Bull. soc. chim. (5) 4, 281-295 (1937); Compt. rend. 203, 802-804 (1936). (52) Frahm, Rec. trav. chim. 50, 261-267 (1931). (53) Bozza, Mamoli, Guorn. chim. ind. applicata 12, 283-292 (1930); Cent. 1930, II 1854; C.A. 24, 5021 (1930). (54) Brooks, Chem. Met. Eng. 22, 629-633 (1920). (55) Shilov, Kanyaev, Domina, Ionina, J. Phys. Chem. (U.S.S.R.) 13, 1242-1248 (1939), C.A. 35, 371 (1941). (56) Zimakov, Gripich, Org. Chem. Ind. (U.S.S.R.) 1, 396-404 (1936), Cent. 1937, I 1012; C.A. 30, 6705 (1936) (57) Tropsch, Kassler, Mitt. Kohlenforsch. Inst. Prag. 1931, No. 1, 16-42; Cent. 1932, I 2159; C.A. 26, 1242 (1932). (58) Zapadinskii, J. Chem. Ind. (Moscow) 5, 1273-1276 (1928); C.A. 23, 3208 (1929); not in Cent. (59) Shilov, J. Chem. Ind. (Moscow) 5, 1273-1276 (1928); Cent. 1929, II 1646, C.A. 23, 2937 (1929). (60) Carius, Ann. 126, 195-199 (1865); Butlerow, Ann. 144, 40-42 (1867).

(61) Britton, Nutting, Huscher (to Dow Chem Co.), U.S. 2,130,226, Sept. 13, 1938; Cent. 1939, I 1856; C A. 32, 9096 (1938). (62) Youtz (to Standard Oil Co.), U.S. 1,875,309, Aug. 30, 1932; Cent. 1933, II 2053, C.A. 26, 5971 (1932). (63) Essex, Ward (to du Pont Co.), U.S. 1,626,398, April 26, 1927; Cent. 1928, I 410; C.A. 21, 2136 (1927). (64) Essex, Ward (to du Pont Co.), U.S. 1,594,608, Aug. 3, 1926; Cent. 1926, II 1693, C.A. 20, 3170 (1926). (65) McElroy, U.S. 1,510,790, Oct. 7, 1924, C.A. 19, 77 (1925); not in Cent. (66) Brooks, 1,498,781, 1,498,782, June 24, 1924; Cent. 1924, II 1631; C.A. 18, 2606 (1924). (67) Irvine, Haworth (to Carbide and Carbon Chem. Corpn.), U.S. 1,496,675, June 3, 1924; Cent. 1924, II 1510; C.A. 18, 2345 (1924). (68) Young, U.S. 1,456,959, May 29, 1923; C.A. 17, 2428 (1923); not in Cent. (69) Curme, Young, U.S. 1,456,916, May 29, 1923; C.A. 17, 2428; not in Cent. (70) Eldred, U.S. 1,456,900, May 29, 1923, C.A. 17, 2428; not in Cent. (70) Eldred, U.S. 1,456,900, May 29, 1923, C.A. 17, 2428; not in Cent. (70) Eldred, U.S. 1,456,900, May 29, 1923, C.A. 17, 2428; not in Cent.

(71) Brooks (to Chateloid Chem. Co.), U.S. 1,394,664, Oct. 25, 1921; Cent. 1922, IV 941; C.A. 16, 423 (1922). (72) Finkelstein (to I.G.), Canadian 285,920, Dec. 25, 1928; Cent. 1932, I 1153; C.A. 23, 1138 (1929). (73) Curme, Young, Canadian 238,729, March 18, 1924; Cent. 1925, I 1129; not in C.A. (74) Kennedy, Barker (to Shawinigan Chem., Ltd.), Brit. 552,319, April 1, 1943; C.A. 38, 3992 (1944). (75) Soc. Carbochim., Brit. 445,011, April 30, 1936; Cent. 1936, II 1244; [C.A. 30, 6390 (1936)]: French 795,804, March 23, 1936; C.A. 30, 5592 (1936); not in Cent. (76) Tropsch, Kassler, Brit. 377,595, Aug. 18, 1932; Cent. 1932, II 2724; [C.A. 27] 3944 (1933)]: French 732,106, Feb. 17, 1932; C.A. 27, 732 (1933); not in Cent. (77) Long, Willson, Wheeler, Brit. 265,269, March 3, 1927; Cent. 1927, II 2350, C.A. 22, 244 (1928). (78) Marks (to Carbide and Carbon Chem. Corpn.), Brit. 235,044, July 2, 1925; Cent. 1928, II 711; C.A. 20, 917 (1926): Ger. 527,940, June 24, 1931; Cent. 1931, II 1753; [C.A. 25, 5177 (1931)]. (79) T. Goldschmidt, A.G., Ger. 538,915, July 12, 1927, C.A. 26, 2198 (1932); not in Cent.: Belgian 352,582, Jan. 8, 1929, Cent. 1931, I 2932; not in C.A.: French 656,947, May 15, 1929; Cent. 1929, II 648; [C.A. 23, 4231 (1929)]: Brit. 293,754, July 11, 1927; C.A. 23, 1651 (1929); not in Cent. (80) Union Chem. Belg., French 829,493, June 28, 1938; Cent. 1938, II 3316; C.A. 33, 993 (1939). (81) Comp. Prod. Chim. d'Alais, etc., French 785,170, Aug. 3, 1935; Cent. 1936, I 1309; C.A. 39, 492 (1936). (82) Damiens, de Loisy, Piette, French 535,210, April 11, 1922; Cent. 1923,

II 741; not in C.A. (83) Iskra, J. Chem. Ind. (Moscow) 12, 947-953 (1935); Cent. 1936, I 2823; C.A. 30, 711 (1936). (84) Harford (to A. D. Little, Inc.), U.S. 2,107,789, Feb. 8, 1938; Cent.

1938, I 4718; C.A. 32, 2543 (1938). (85) Langedijk (to Shell Development Co.), U.S. 2,106,353, Jan. 25, 1938; C.A. 32, 2543 (1938); not in Cent.: N. V. de Bataafsche Petroleum Maatschappij, French 740,350, Jan. 24, 1933; Cent. 1933, I 2870-2871; C.A. 27, 2160 (1933). (86) Likhosherstov, Alekseev, J. Applied Chem. (U.S.S.R.), 7, 127-133 (1934); Cent. 1935, I 3915; C.A. 29, 452 (1935). (87) Ladenburg, Ber. 16, 1407-1408 (1883). (88) van der Burg, Rec. trav. chim. 41, 21-23 (1921). (89) Schorlemmer, J. Chem. Soc. 39, 143-144 (1881). (90) Dreyfus, Brit. 404, 938, Feb. 22, 1934; Cent. 1934, I 3395; C.A. 28, 4432 (1934).

(91) Fittig, Chanlaroff, Ann. 226, 325-329 (1884). (92) Fittig, Ström, Ann. 267, 191-194 (1892). (93) Bennett, Heathcoat, J. Chem. Soc. 1929, 268-270. (94) Carius, Ann. 124, 257-260 (1862). (95) Wietzel, Dierksen (to B.A.S.F.), Ger. 420,500, Oct. 24, 1925; Cent. 1926, I 2245; not in C.A. (96) Taurke, Ber. 38, 1668 (1905). (97) von Bichowsky, U.S. 1,488,571, April 1, 1924; Cent. 1925, I 896; C.A. 18, 1837 (1924). (98) Britton, Coleman, Moore (to Dow Chem. Co.), U.S. 1,987,227, Jan. 8, 1935; Cent. 1935, II 594; C.A. 29, 1432 (1935). (99) Gebauer-Fuelnegg, Moffatt, J. Am. Chem. Soc. 56, 2009 (1934). (100) Malinovskii, J. Gen. Chem.

(U.S.S.R.) 9, 832-839 (1939); C.A. 34, 375 (1940).

(101) Isham, Spring (to Doherty Research Co.), U.S. 1,918,967, July 18, 1933; Cent. 1933, II 2053; C.A. 27, 4815 (1933). (102) Suter, Evans, J. Am. Chem. Soc. 60, 536 (1938). (103) Meerwein, Sonke, Ber. 64, 2380 (1931). (104) Cretcher, Koch, Pittenger, J. Am. Chem. Soc. 47, 1176 (1925). (105) Callsen (to I.G.), Brit. 384,156, Dec. 22, 1932; Cent. 1933, I 1351; [C.A. 27, 4240 (1933)]: Ger. 565,157, Nov. 26, 1932; Cent. 1933, I 1514; C.A. 27, 992 (1933). (106) Zapadinski, Z. anal. Chem. 74, 273-275 (1928); J. Russ. Phys.-Chem. Soc. 60, 695-697 (1928), Cent. 1930, I 3583; C.A. 22, 3864 (1928). (107) Krassuski, J. Russ. Phys.-Chem. Soc. 34, 287-315 (1902); Cent. 1902, II 19-20. (108) Lessig, J. Phys. Chem. 36, 2335 (1932). (109) Lourenco, Ann. 120, 92-93 (1861). (110) Ushakov, Mikhailov, J. Gen. Chem. (U.S.S.R.) 7, 249-252 (1937); Cent. 1937, II 1546; C.A. 31, 4645 (1937).

(111) Kriwaxin, Zeit. für Chemie 1871, 265. (112) Dreyfus (to Celanese Corpn. of America), U.S. 2,340,371, Feb. 1, 1944, C.A. 38, 3991 (1944). (113) Saunders, J. Chem. Soc. 121, 2669, 2672 (1922). (114) Kamm, Waldo, J. Am. Chem. Soc. 43, 2225 (1921). (115) Trautzl, Z. ges. Schiess-u. Sprengstoffw. 37, 146-148 (1942); C.A. 37, 5591 (1943). (116) Henry, Ann. chim. (4) 27, 257-258 (1872). (117) Schweizer Sprengstoff Fabrik, A.G., Swiss 155,125, Sept. 16, 1932; Cent. 1933, I 356; C.A. 27, 1177 (1933): Swiss 156,455, Nov. 16, 1932, Cent. 1933, I 2902; not in C.A. (118) Heinze, Marder, Veidt, Oel Kohle, 37, 422-430 (1941); C.A. 36, 4993 (1942). (119) Woodbury, Lawson (to du Pont Co.), U.S. 2,066,506, Jan. 5, 1937; Cent. 1937, I 3264; C.A. 31, 1183 (1937). (120) Bristow, Buist, Brit. 461,320, March 11, 1937; Cent. 1937, I 5087; C.A. 31, 5542 (1937).

(121) Nekrassow, Komissarow, J. prakt. Chem. (2) 123, 160-168 (1929). (122) Levaillant, Compt. rend. 187, 731-732 (1928). (123) Henry, Rec. trav. chim. 22, 249 (1903). (124) Henry, Bull. acad. roy. Belg. (3) 18, 182-186 (1889); Ber. 24 Referate, 75 (1891). (125) Kuroda, J. Pharm. Soc. Japan 539, 44-47 (1927); Cent. 1927, II 243, C.A. 22, 4469 (1928). (126) Jones, Powers, J. Am. Chem. Soc. 46, 2531-2532 (1924). (127) Wieland, Sakellarios, Ber. 53, 208 (1920). (128) Butlerow, Ossokin, Ann. 144, 42-45 (1867). (129) Meyer, Ber. 19, 3259-3260 (1886). (130) Clarke, J. Chem. Soc. 101, 1585 (1912).

(131) Davies, Oxford, J. Chem. Soc. 1931, 228-229, 231. (132) Ettel, Kohlik, Collection Czechosłov. Chem. Commun. 3, 588-589 (1931). (133) Fromm, Kohn, Ber. 54, 320-323 (1921). (134) Major, Bull. soc. chim. (4) 41, 635 (1927). (135) M. L. B., Brit. 185,403, Oct. 25, 1922; Cent. 1923, II 684; C.A. 17, 110 (1923). (136) Poggi, Speroni, Gazz. chim. ital. 64, 498-499 (1934); Cent. 1934, II 3749; C.A. 29, 1060 (1935). (137) Bennett, J. Chem. Soc. 119, 423-424 (1921). (138) Thiess, Müller (to M. L. B.), Ger. 405,384, Oct. 31, 1924; Cent. 1935, I 1527; not in C.A. (139) Collmann, Ann. 148, 107-109 (1868). (140) Plimmer, Burch, J. Chem. Soc. 1929, 284-287.

(141) Gough, King, J. Chem. Soc. 1928, 2432-2433. (142) Edee, J. Am. Chem. Soc. 50, 1395-1396 (1928). (143) Scherlin, Epstein, Ber. 61, 1821-1825 (1928). (144) Quick, Adams, J. Am. Chem. Soc. 44, 811 (1922). (145) Oechslin (to Étab. Poulenc Frères), Brit. 191,028, Feb. 14, 1923; Cent. 1923, IV 721; C.A. 17, 2887 (1923); French 556,366, July 19, 1923; Cent. 1923, IV 721; not in C.A. (146) Oechslin (to Étab. Poulenc Frères), U.S. 1,573,738, Feb. 16, 1926; Cent. 1926, I 3362; C.A. 20, 1415 (1926): French 582,412, Dec. 18, 1924; Cent. 1926, I 3362; not in C.A. (147) Komissarov, J. Gen. Chem. (U.S.S.R.) 3, 309-312 (1933); Cent. 1934, II 40; C.A. 28, 2324 (1934). (148) Levaillant, Compt. rend. 189, 465-467 (1929). (149) Steinkopf, Mieg, Herold, Ber. 53, 1145 (1920). (150) Grün, Stiasny Festschrift 1937, 88-98; Cent. 1938, II 1937; C.A. 32, 8358 (1938).

(151) Renshaw, Hopkins, J. Am. Chem. Soc. 51, 953 (1929).
 (152) Jackson, J. Am. Chem.
 Soc. 57, 1904 (1935).
 (153) Schönberg, Wick (to I.G.), Ger. 571,521, March 1, 1933; Cent. 1933,

I 3243; C.A. 27, 4244 (1933). {154} Meerwein, Ber. 66, 412 (1933). {155} Dearing, Reid, J. Am. Chem. Soc. 50, 3060 (1928). {166} Bolzani (to I.G.), Ger. 459,738, May 15, 1928; Cent. 1928, II 1716; not in C.A. {157} Schrader, Z. angew. Chem. 42, 542-543 (1929). {158} Wada, Sato, J. Soc. Chem. Ind. Japan 38, Suppl. bindg. 497-500 (1935); Cent. 1936, I 1960; C.A. 39, 1028 (1936). {159} Porret, Helv. Chim. Acta 24, 80-85E (1941). {160} Smith, Z. physik. Chem. A-152, 153-156 (1930/1).

(161) Smith, Z. physik. Chem. 81, 346-349 (1912); 92, 725-726 (1917). (162) Lewis (to du Pont Co.), U.S. 1,895,517, Jan. 31, 1933; Cent. 1933, I 2870; C.A. 27, 2445 (1933). (163) Saunders, Wignall (to British Dyestuffs Corpn.), U.S. 1,737,545, Nov. 26, 1929; [Cent. 1930, I 2005]; [C.A. 24, 630 (1930)]: Brit. 286,850, April 5, 1928; Cent. 1928, I 2750; C.A. 23, 397 (1929). (164) Dunstan, Birch (to Anglo-Persian Oil Co.), Brit. 365,589, Feb. 18, 1932; Cent. 1932, II 613; C.A. 27, 1896 (1933): French 725,150, Sept. 14, 1931; C.A. 26, 4827 (1932); not in Cent. (165) Curme (to Carbide & Carbon Chem. Corpn.), Brit. 264,124, March 2, 1927; Cent. 1927, II 1077; C.A. 22, 92 (1928): French 619,190, March 28, 1927; Cent. 1927, II 1077; not in C.A. (166) Oehme (to Chem. Fabrik Kalk), French 612,825, Nov. 2, 1926; Cent. 1927, II 2571; not in C.A. (167) Soc. Anon. d'Explosifs Prod. Chim., French 458,733, Aug. 13, 1912; C.A. 8, 3099 (1914). (168) Maas, Boomer, J. Am. Chem. Soc. 44, 1710 (1922). (169) Wurtz, Ann. chim. (3) 69, 317–318 (1863). (170) Dominik, Bartkiewiczowna, Przemysl Chem. 18, 373-375 (1934); Cent. 1935, I 2810; C.A. 29, 5815 (1935).

(171) Britton, Nutting, Petrie (to Dow Chem. Co.), U.S. 1,996,638, April 2, 1935; Cent. 1935, II 3833; C.A. 29, 3350 (1935). (172) Thole, Birch, Scott (to Anglo-Persian Oil Co.), Brit. 374,864, July 14, 1932; Cent. 1932, II 2723; C.A. 27, 3952 (1933). (173) Burdick (to Carbide & Carbon Chem. Corpn.), Brit. 236,379, July 20, 1925; Cent. 1926, I 490; C.A. 20, 917 (1926): Canadian 245,153, Dec. 9, 1924; Cent. 1926, I 490; C.A. 19, 657 (1925). (174) Oehme (to Chem. Fabrik Kalk), Ger. 403,643, Sept. 20, 1924; Cent. 1925, I 1531; not in C.A. (175) B.A.S.F., Ger. 299,682, March 3, 1920; Cent. 1920, IV 16; not in C.A. (176) Rojahn, Lemme, Arch. Pharm. 263, 613-614 (1925). (177) Rosen, Reid, J. Am. Chem. Soc. 44, 634-636 (1922). (178) Bennett, J. Chem. Soc. 121, 2139-2146 (1922). (179) Fromm, Jorg, Ber. 58, 304-306 (1925). (180) Knorr, Ber. 30, 909-915 (1897).

(181) Fischer, "Triathanolamine und anderere Äthanolamine," 3rd ed., 213 pp., 1942 (republished by Edwards Brothers, Ann Arbor, Michigan, 1944). (182) Plisov, Ukrain. Khem. Zhur. 3, No. 1, Sci. Pt., 125-131 (1928); Cent. 1930, I 2867; C.A. 22, 3392 (1928). (183) I.G., French 716,604, Dec. 24, 1931; Cent. 1932, I 3226, [C.A. 26, 2198 (1932)]. (184) Ishikawa, Maeda, Science Repts. Tokyo Bunrika Daigaku A-3, 157-164 (1937); Cent. 1938, I 302; C.A. 31, 7860 (1937). (185) Cretcher, Pittenger, J. Am. Chem. Soc. 46, 1503-1504 (1924). (186) Kayser, Schranz (to Winthrop Chem. Co.), U.S. 1,651,458, Dec. 6, 1927; Cent. 1928, I 2457; C.A. 22, 845 (1928). (187) I.G., French 655,871, April 24, 1929; Cent. 1929, II 351; C.A. 23, 3931 (1929). (188) Schroeter, Strassburger, Biochem. Z. 232, 454 (1931). (189) Jackson, J. Am. Chem. Soc. 60, 722-723 (1938). (190) Coles, Dodds, Bergeim, J. Am. Chem. Soc. 60, 1020-1022 (1938).

(191) Coles, Dodds (to E. R. Squibb and Sons), U.S. 2,252,706, Aug. 19, 1941; C.A. 35, 4717 (1941). (192) Helferich, Lutzmann, Ann. 541, 8-9 (1939). (193) Schoeller, Allardt (to Schering-Kahlbaum), Ger. 527,036, June 24, 1931; Cent. 1931, II 1452; [C.A. 25, 4664 (1931)]. (194) Helferich, Werner, Ber. 75, 1449, 1451 (1942). (195) Schmidt, Meyer (to I G.), U.S. 1,922,459, Aug. 15, 1933; C.A. 27, 5082 (1933); not in Cent.: Brit. 317,770, Sept. 19, 1929; Cent. 1939, I 129; C.A. 24, 2141 (1930). (196) Lange (to I.G), U.S. 1,714,565, May 28, 1929; [Cent. 1928, II 1747]; [C.A. 23, 3543 (1929)]: Brit. 290,377, June 14, 1928; Cent. 1928, II 1818; C.A. 23, 981 (1929). (197) Leuchs (to F. Bayeer Co.), Ger. 408,714, Jan. 23, 1925; Cent. 1925, I 1820; not in C.A. (198) Dreyfus, Brit. 166,767, Aug. 18, 1921; Cent. 1921, IV 1140; C.A. 16, 830 (1922). (199) Windus, Schildneck, Org. Syntheses, Coll. Vol. 2, 345-346 (1943); 14, 54-56 (1934). (200) Windus, Marvel, J. Am. Chem. Soc. 53, 2576 (1930).

(201) Kirner, J. Am. Chem. Soc. 50, 2451-2452 (1928). (202) von Braun, Anton, Weissbach, Ber. 63, 2859 (1930). (203) Steinkopf, Herold, Stöhr, Ber. 53, 1010, 1012 (1920). (204) Demuth, Meyer, Ann. 240, 310 (1887). (205) Whitner, Reid, J. Am. Chem. Soc. 43, 637 (1921). (206) Scherlin, Wasilewsky, J. prakt. Chem. (2) 123, 174-175 (1929). (207) Peacock, Tha, J. Chem. Soc. 1928, 2304-2305. (208) Bentley, Haworth, Perkin, J. Chem. Soc. 69, 164-165 (1896). (209) Rindfusz, J. Am. Chem. Soc. 41, 669 (1919). (210) Smith, Niederl, J. Am. Chem. Soc. 53, 808 (1931).

(211) Smith, J. Am. Chem. Soc. 62, 994 (1940). (212) Butler, Renfrew, J. Am. Chem. Soc. 60, 1583-1584 (1938). (213) Katrak, J. Indian Chem. Soc. 13, 334-336 (1936). (214) Binkley, Hamilton, J. Am. Chem. Soc. 59, 1717 (1937). (215) Boyd, Marle, J. Chem. Soc. 105, 2138 (1914). (216) Boedecker, Rosenbusch, Ber. pharm. Ges. 30, 251-258; Cent. 1920, III 239. (217)
J. D. Riedel, A.G., Ger. 232,298, July 17, 1920; Cent. 1920, IV 436; not in C.A. (218) Rindfuss,

Jennings, Harnack, J. Am. Chem. Soc. 42, 161-165 (1920). (219) Motwani, Wheeler, J. Chem. Soc. 1935, 1098-1101. (220) Perkin, Ray, Robinson, J. Chem. Soc. 1926, 945-946.

(221) Sonn, Patschke, Ber. 58, 96-97 (1925). (222) Lautenschlager, Bockemuhl, Schwarz (to M. L. B.), Ger. 412,699, April 25, 1925; Cent. 1925, II 613; not in C.A. (223) Chem. Werke Grenzbach, A.G., Ger. 352,983, May 10, 1922; Cent. 1922, IV 206; not in C.A. (224) Motwani, Wheeler J. Univ. Bombay 4, 104-105 (1935); Cent. 1936, I 4560; C.A. 30, 5197 (1936). (225) Amstutz, J. Org. Chem. 9, 315 (1944). (226) Kirner, Richter, J. Am. Chem. Soc. 51, 3413-3414 (1929). (227) Thiess, Muller, Hopker (to M. L. B.), Ger. 391,007, Feb. 28, 1924; Cent. 1924, I 2012; not in C.A. (228) Bennett, Berry, J. Chem. Soc. 1927, 1666-1676. (229) Waldron, Reid, J. Am. Chem. Soc. 45, 2402 (1923). (230) Galbraith, Smiles, J. Chem. Soc. 1935, 1237.

(231) Baddeley, Bennett, J. Chem. Soc. 1933, 46-48. (232) Fourneau, Ribas, Bull. soc. chim. (4) 41, 1046-1056 (1927). (233) Grignard, Purdy, Compt. rend. 175, 201-202 (1922); Bull soc. chim. (4) 31, 982-987 (1922). (234) Bales, Nickelson, J. Chem. Soc. 123, 2489 (1923). (235) Böeseken, Tellegen, Plusje, Rec. trav. chim. 57, 77-78 (1938). (236) Lingo, Henze, J. Am. Chem. Soc. 61, 1574-1576 (1939). (237) Farren, Fife, Clark, Garland, J. Am. Chem. Soc. 47, 2421 (1925). (238) Litterscheid, Ann. 330, 120, 126 (1903). (239) Henry, Bull. soc. chim. (3) 13, 592 (1895); Ber. 28, Referate, 851 (1895). (240) McLure, Chem. & Eng. News 22, 420-421 (1944). (241) Minné, Adkins, J. Am. Chem. Soc. 55, 300 (1933). (242) Boese, Ind. Eng. Chem. 32, 16-22 (1940). (243) Boese (to Carthide & Carthon Chem. Corpn.) U.S. 2 167 168, July 25, 1939

16-22 (1940). (243) Boese (to Carbide & Carbon Chem. Corpn.), U.S. 2,167,168, July 25, 1939; Cent. 1939, II 4591; C.A. 33, 8626 (1939). (244) Palomaa, Herna, Ber. 66, 309-310 (1933). (245) Contardi, Ercoli, Atti IX congr. intern. chim. Madrid 5, 163-173 (1934); Cent. 1936, II 3904; C.A. 31, 1764 (1937). (246) Kailan, Rosenblatt, Monatch. 68, 109-170 (1936). (247) M. L. B., Ger. 360,491, Oct 3, 1922, Cent. 1923, II 479; C.A. 18, 841 (1924). (248) Blicke, Blake, J. Am. Chem. Soc. 53, 1008, 1020 (1931). (249) M.L.B., Ger. 194,748, Jan. 15, 1905, C.A. 2, 1894 (1908). (250) Kendall, McKenzie, Org. Syntheses, Coll. Vol. 1, 256-258 (1941); 3, 57-59 (1923).

(251) Bauer (to Röhm & Haas Co.), U.S. 1,388,016, Aug. 16, 1921; Cent. 1921, IV 1222; C.A. 15, 4011 (1921): Ger. 365,350, Dec. 8, 1922, [Cent. 1923, II 251], not in C.A.: French 525,539, Sept. 23, 1920; Cent. 1921, IV 1222; not in C.A.: Swiss 90,695, Sept. 16, 1921; [Cent. 1922, II 324]; not in C.A. (252) Erlenmeyer, Ann. 191, 268 (1878). (253) Jacobs, Heidelberger, J. Am. Chem. Soc. 39, 1465-1466 (1917). (254) Moureu, Bull. soc. chim. (3) 9, 426 (1893); Ann. chim. (7) 2, 191 (1894). (255) Steimmig, Witter (to I.G.), Ger. 516,281, Jan. 22, 1931; Cent. 1931, I 2114; C.A. 25, 1840 (1931). Brit. 321,894, Dec. 12, 1929; Cent. 1930, I 1368; C.A. 24, 2756 (1930). (256) Sergeev, Kolychev, Kondrat'ev, J. Gen. Chem. (U.S.S.R.) 7, 2600-2604 (1937); Cent. 1938, II 2587; C.A. 32, 2534 (1938). (257) P. C. Sergeev, B. S. Kolychev, V. S. Kolychev, J. Gen. Chem. (U.S.S.R.) 7, 2863-2867 (1937); Cent. 1938, II 2931; C.A. 32, 2940 (1938). (258) F. Baeyer & Co., Ger. 245,532, April 13, 1912, Cent. 1912, I 1407; C.A. 6, 2494 (1912). (259) Cretcher, Pittenger, J. Am. Chem. Soc. 47, 2561 (1925). (260) Halasz, Rovira, Bull. soc. chim. (5) 8, 185-198 (1941); Cent. 1942, I 1942.

(261) Verkade, Tollenaar, Posthumus, Rec. trav. chim. 61, 373-382 (1942); Cent. 1942, II 1339, C.A. 37, 5372 (1943). (262) Butler, Nelson, Renfiew, Cretcher, J. Am. Chem. Soc. 57, 577 (1935). (263) Jones, Major, J. Am. Chem. Soc. 49, 1535-1536 (1927). (264) Rosenthal (to F. Baeyer & Co.), Ger. 389,086, Jan. 25, 1924; Cent. 1924, I 1717; not in C.A. (265) Oechslin (to Étab. Poulene Frères), French 585,970, March 12, 1925; Cent. 1926, II 1583; not in C.A. (266) Zernik (to Erdol-u. Kohle-Verwertung. A.G.), Ger. 373,849, April 16, 1923; Ger. 402,992, Sept. 19, 1924; Cent. 1925, I 410; not in C.A. (267) Bogert, Slocum, J. Am. Chem. Soc. 46, 766 (1924). (268) Henry, Ber. 7, 70 (1874). (269) Wagner-Jauregg, Helmert, Ber. 71, 2538 (1938). (270) Palomaa, Leimu, Ber. 66, 813-815 (1933); Leimu, Ber. 70, 1040-1053 (1937).

(271) Bennett, J. Chem. Soc. 127, 1277-1282 (1925). (272) Nemirowsky, J. prakt. Chem. (2)
31, 173-175 (1885). (273) Schotte, Priewe, Roescheisen, Z. physiol. Chem. 174, 142 (1928).
(274) Nekrassov, Melnikov, J. prakt. Chem. (2) 127, 214 (1930). (275) Delacre, Bull. soc. chim.
(2) 48, 708 (1887). (276) Zaki, J. Chem. Soc. 1930, 2271-2272. (277) Kirner, J. Am. Chem.
Soc. 48, 2751 (1926). (278) Davidson (to Carbide & Carbon Chem. Corp.), U.S. 1,732,356,
Oct. 22, 1929; Cent. 1930, I 2005; C.A. 24, 127 (1930). (279) Swallen, Boord, J. Am. Chem. Soc.
52, 653 (1930). (280) McMeekin, J. Am. Chem. Soc. 59, 2383 (1937).

(281) Langheld, Ber. 44, 2082 (1911). (282) Irwin, Hennion, J. Am. Chem. Soc. 63, 859 (1941). (283) Likhosherstov, Zhabotinskaya, Pavlovskaya, Ponomarenko, J. Gen. Chem. (U.S.S.R.) 8, 997-1007 (1938); Cent. 1939, I 1960; C.A. 33, 3761 (1939). (284) Likhosherstov, Shalaeva, J. Gen. Chem. (U.S.S.R.) 8, 370-379 (1938); Cent. 1939, II 66-67; C.A. 32, 5369 (1938). (285) Dorrer, Hopff (to I.G.), Ger. 596,523, May 14, 1934; Cent. 1934, II 1845; C.A. 28, 5077 (1934). (286) Grignard, Compt. rend. 141, 44-45 (1905); Ann. chim. (8) 10, 23-31 (1907). (287) Grignard, Ger. 164,883, Nov. 16, 1905; Cent. 1905, II 1751-1752. (288) I.G., French

682,142, May 23, 1930; Cent. 1930, II 3082; C.A. 24, 4304 (1930). (289) Shoruigin, Isagulyantz, Guseva, Poliakov, Ossipova, French 738,277, Dec. 23, 1932; Cent. 1933, I 3630; C.A. 27, 1638 (1933). (290) Shoesmith, Connor, J. Chem. Soc. 1927, 1770.

(291) von Braun, Wirz, Ber. 60, 106 (1927). (292) Chichibabine, Elgasine, Lengold, Bull. soc. chim. (4) 43, 238-242 (1928). (293) Bennett, Phillip, J. Chem. Soc. 1928, 1937-1938. (294). Knunyantz, Chelintzev, Osetrova, Compt. rend. acad. sci. U.R.S.S. N.S. 1, 312-317 (1934); Cent. 1934, II 2381; C.A. 28, 4382-4383 (1934). (295) Filipov, J. prakt. Chem. (2) 93, 176 (1916). (296) Paul, Bull. soc. chim. (5) 2, 753 (1935). (297) Knunyantz, Chelintzev, Benevolenska, Osetrova, Kursanova, Bull. acad. sci. U.R.S.S., Classe sci. math. nat. 1934, 165-176; Cent. 1935, I 1896—1897; C.A. 28, 4837 (1934). (298) Henze, Spurlock, J. Am. Chem. Soc. 63, 3360-3361 (1941). (299) Knorr, Ber. 22, 2088-2095 (1889). (300) Slotta, Behnisch, J. prakt. Chem. (2) 135, 234 (1932).

(301) Goldberg, Whitmore, J. Am. Chem. Soc. 59, 2280-2282 (1937). (302) Schlittler, Helv. Chim. Acta 24, 327-328E (1941). (303) Blount, Openshaw, Todd, J. Chem. Soc. 1940, 289. (304) Morley, Ber. 13, 222-223 (1880). (305) Ladenburg, Ber. 14, 1878 (1881). (306) I.G., Brit. 361,261, Dec. 10, 1931; Cent. 1932, I, 1438; C.A. 27, 1112 (1933): French 716,560, Dec. 23, 1931; Cent. 1932, I 1438, C.A. 26, 2288 (1932). (307) I.G., Brit. 358,114, Oct. 29, 1931; Cent. 1932, I 449; C.A. 26, 4926 (1932). (308) I.G., Brit. 297,484, Oct. 18, 1928; Cent. 1929, I 1863; C.A. 23, 2722 (1929); French 638,023, May 14, 1928; Cent. 1928, II 834; C.A. 23, 248 (1929). (309) Otto, J. prakt. Chem. (2) 44, 17-18 (1891). (310) Rindfusz, Harnack, J. Am. Chem. Soc. 42, 1724 (1920).

(311) Shoruigin, Smirnov, J. Gen. Chem. (U.S.S.R.) 4, 830-833 (1934); Cent. 1935, II 3763; C.A. 29, 2155 (1935). (312) Bergmann, Ger. 382,693, Oct. 5, 1923; Cent. 1924, I 1594; not in C.A. (313) B.A. S.F., Ger. 163,043, Sept. 16, 1905, Cent. 1905, II 1062. (314) Adkıns, Simington, J. Am. Chem. Soc. 47, 1687-1688 (1925). (315) Gabel, Ber. 58, 577-579 (1925). (316) Knorr, Ger. 95,854, March 30, 1897; Cent. 1898, I 813. (317) Adams, Segur, J. Am. Chem. Soc. 45, 788 (1923). (318) Dains, Brewster, Blair, Thompson, J. Am. Chem. Soc. 44, 2639 (1922). (319) Muller (to J. D. Riedel, A.C.), Ger. 414,259, June 2, 1925, Cent. 1925, II 765; not in C.A. (320) Wurtz, Compt. rend. 68, 1506 (1869); Ann. Suppl. 7, 94-95 (1870).

Von Braun, Seemann, Ber. 55, 3821 (1922). (322) Bergmann, Ulpts, Camacho, Ber. 55, 2810-2812 (1922). (323) Ladenburg, Ber. 14, 2408-2409 (1881). (324) Knorr, Mathes, Ber. 34, 3482-3484 (1901). (325) Burnett, Jenkins, Peet, Dreyer, Adams, J. Am. Chem. Soc. 59, 2250 (1937). (326) Ladenburg, Ber. 14, 1877-1879 (1881). (327) Hartmann, Org. Syntheses, Coll. Vol. 2, 183-184 (1943); 14, 28-29 (1934). (328) Soderman, Johnson, J. Am. Chem. Soc. 47, 1393-1394 (1925). (329) Horne, Shriner, J. Am. Chem. Soc. 54, 2928 (1932). (330) Headlee, Collett, Lazzell, J. Am. Chem. Soc. 55, 1067 (1933).

(331) Samdahl, Weider, Bull. soc. chim. (5) 2, 2014-2016 (1935). (332) Adams, Kamm, Volwiler (to Abbott Laboratories, Inc.), U.S. 1,358,750, Nov. 16, 1920; Cenl. 1921, II 804; C.A. 15, 412 (1921). (333) Soc. Chem. Ind. Basel, Brit. 451,925, Sept. 10, 1936; Cenl. 1937, I 662; C.A. 31, 416 (1937). Brit. 448,181, July 2, 1936; Cenl. 1937, I 662; C.A. 30, 7124 (1936). (334) Einhorn, Fiedler, Ladisch, Uhlfelder, Ann. 371, 146-148 (1909). (335) Adams, Jenkins, Volwiler (to Abbott Laboratories, Inc.), U.S. 1,513,730, Nov. 4, 1924, Cenl. 1925, I 1133; C.A. 19, 153 (1925). (336) Bockmuhl, Kross, Ehrhart (to I G.), Ger. 593,192, March 8, 1934; Cent. 1934, I 3770; C.A. 28, 4540 (1934): Brit. 404,674, Feb. 15, 1934; Cent. 1934, I 3770; C.A. 28, 4178 (1934): Swiss 161,737, + 161,738, July 17, 1933; Cenl. 1933, II 3597; not in C.A. (337) Coles, Lott, J. Am. Chem. Soc. 58, 1989 (1936). (338) Laun, Ber 17, 676-677 (1884). (339) Slotta, Behnisch, Ann. 497, 174 (1932). (340) Gabel, Bull. soc. chim (4) 41, 936-940 (1927).

(341) Wedekind, Bruch, Ann. 471, 76-77, 88-89 (1929). (342) Vassiliades, Bull. soc. chim. (5) 4, 1132-1133 (1937). (343) Barnes, Adams, J. Am. Chem. Soc. 49, 1310-1312 (1927). (344) Roithner, Monatsh. 15, 667-668 (1894). (345) von Braun, Braunsdorff, Rath, Ber. 55, 1674 (1922). (346) Leffler, Brill, J. Am. Chem. Soc. 55, 367 (1931). (347) Pyman, J. Chem. Soc. 97, 1801 (1908). (348) D'Ianni, Adkins, J. Am. Chem. Soc. 61, 1679 (1939). (349) Knorr. Ann. 301, 9 (1898). (350) Gardner, Maenni, J. Am. Chem. Soc. 53, 2765-2766 (1931).

(351) Wilson, Ind. Eng. Chem. 27, 871 (1935). (352) Litterscheid. Arch. Pharm. 249, 78 (1902). (353) Coppola, Gazz. chim. ital. 15, 331-332 (1885). (354) du Poñt Co., Brit. 477,981, Feb. 10, 1938; Cent. 1938, II 183; not in C.A. (355) Soc. Chem. Ind. Basel, French 784,869, July 27, 1935; Cent. 1935, II 3864; [C.A. 30, 487 (1936)]; Swiss 175,026, April 16, 1935; Cent. 1935, II 2156; C.A. 30, 304 (1936). (356) Dreyfus, Brit. 482,126, April 21, 1938; Cent. 1938, II 1484; C.A. 32, 6258 (1938). (357) Peacock, Dutta, J. Chem. Soc. 1934, 1303-1304. (358) Payman, Piggott (to Imperial Chem. Ind.), U.S. 1,859,527, May 24, 1932; C.A. 26, 3808 (1932); not in Cent.: Brit. 298,336, Nov. 1, 1928, Cent. 1929, I 1616; C.A. 23, 2723 (1929). (359) Peacock, Givan, J. Chem. Soc. 1937, 1470. (360) Olin, Dains, J. Am. Chem. Soc. 52, 3322 (1930).

(361) Meerwein, Hinz, Ann. 484, 17, 22-23 (1930). (362) Fromm, Honold, Ber. 55, 906-909 (1922). (363) Fromm, Ann. 442, 139-140 (1925). (364) Ercoli, Ann. chim. applicata 25, 263-273 (1935); Cent. 1935, II 3090; C.A. 30, 1028 (1936). (365) Yang, Johnson, J. Am. Chem. Soc. 54, 2071 (1932). (366) Rojahn, Fegeler, Arch. Pharm. 268, 568-569 (1930). (367) Béhal (to Étab. Poulenc Frères), French 569,463, April 12, 1924; 27,349, June 6, 1924; Cent. 1925, I 1537; not in C.A. (368) Einhorn, Uhlfelder, Ann. 371, 133 (1910). (369) Altwegg, Landrivon, U.S. 1,393,191, Nov. 11, 1921; Cent. 1922, IV 947; C.A. 16, 422 (1922). (370) M.L.B., Ger. 194,748, Jan. 21, 1908; Cent. 1908, I 1004; [C.A. 2, 1894 (1908)]; Ger. 179,627, Dec. 11, 1906; Cent. 1907. I 1364; [C.A. 1, 2056 (1907)].

(371) Cope, McElvain, J. Am. Chem. Soc. 53, 1590 (1931). (372) Rosenzeneig, Legerlotz, Austrian 101,671, Nov. 25, 1925; Cent. 1926, II 1585; not in C.A. (373) Jones, Burns, J. Am. Chem. Soc. 47, 2973 (1925). (374) Blicke, Castro, J. Am. Chem. Soc. 63, 2438 (1941). (375) Földi, Ber. 53, 1837 (1920). (376) von Kereszty, Wolf, Ger. 353,195, May 12, 1922; Cent. 1922, IV 156; C.A. 17, 1243 (1923). (377) Gilman, Perkins, J. Am. Chem. Soc. 47, 251 (1925). (378) Földi, Ber. 60, 659 (1927). (379) Clemo, Perkin, J. Chem. Soc. 121, 644 (1922). (380) Clemo,

Tenniswood, J. Chem. Soc. 1931, 2550.

(381) Tipson, Cretcher, J. Am. Chem. Soc. 64, 1162 (1942). (382) Gilman, Beaber, J. Am. Chem. Soc. 45, 841 (1923). (383) Perkin, Clemo (to British Dyestuffs Corp.), Brit. 193,618, March 22, 1923; Cent. 1925, I 899; C.A. 17, 3510 (1923). (384) Ashworth, Burkhardt, J. Chem. Soc. 1928, 1798. (385) Johnson, Schwartz, Jacobs, J. Am. Chem. Soc. 60, 1883 (1938). (386) Bert, Compt. rend. 213, 1015-1016 (1941); C.A. 37, 4049 (1943). (387) Puyal, Montagne, Bull. soc. chim. (4) 27, 862 (1924). (388) von Kereszty, Wolf, Ger. 387,963, Jan. 7, 1924, Cent. 1924, Il 403; not in C.A. (389) Dewey, Witt, Ind. Eng. Chem., Anal. Ed. 14, 648 (1942). (390) Sprinson, J. Am. Chem. Soc. 63, 2250 (1941).

(391) Bickel, French, J. Am. Chem. Soc. 48, 749 (1926). (392) Grandière, Bull. soc. chim. (4) 35, 189 (1924). (393) Dersin, Ber. 54, 3158 (1921). (394) Smith, Platon, Ber. 55, 3151 (1922). (395) Wenker, J. Am. Chem. Soc. 59, 422 (1937). (396) Billman, Parker, J. Am. Chem. Soc. 65, 762 (1943). (397) Garelli, Racciu, Atti accad. scr. Torino, Classe scr. fis. mat. nat. 69, I 358-363 (1934); Cent. 1934, II 2823; [C.A. 29, 6223 (1934)]. (398) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934). (399) Bennett, Reynolds, J. Chem. Soc. 1935, 140-141. (400) Sah, Tao, Rec. trav. chim. 58, 14-15 (1939).

(401) Murray, J. Council Sci. Ind. Research 17, 213-221 (1944); C.A. 39, 2283 (1945).
(402) Reed (to C. L. Horn) U.S. 2,378,104, June 12, 1945; C.A. 39, 4088 (1945).
(403) Goldblatt, Chiesman, Brit. J. Ind. Med. 1, 207-213 (1944): Goldblatt, Brit. J. Ind. Med. 1, 213-223 (1944): C.A. 39, 5359 (1945).
(404) Porret, Helv. Chim. Acta, 27, 1321-1328 (1944); C.A. 39, 4789 (1945).
(405) Michael, Weiner, J. Am. Chem. Soc. 58, 1003 (1936).

B.P. F.P. 129.2° cor. at 760 mm. (1) (2) -68.1° (1) $D_4^{20} = 1.5532$ (1) $n_D^{20} = 1.48211$ (1) 129–129.7° at 760 mm. (3) 1.4828 (2) 129–130° (4) (5) 35–36° at 20 mm. (3)

Volatile with steam. — [Earlier b.p.'s around 135° were probably on impure material.] [For use of \tilde{C} as dry cleaning fluid see (6); in manufacture of low-luster rayon see (7).]

[For prepn. of \bar{C} from 1,1,1-trichloroethane (3:5085) by actn. of Cl_2 in sunlight (8) (45% yield (1)) or by chlorination of ethyl chloride (3:7015) (1), ethylene dichloride (3:5130) (9), 1,1-dichloroethylene (3:5005) (10), or 1,1-diiodoethylene (11) see indic. refs.: for formn. of \bar{C} from 1,1,2,2-tetrachloroethane (3:5750) + AlCl₃ (12) (13) or with aq. Ca(OCl)₂ (13) see (12) (13): from trichloroethylene (3:5170) over pumice at 700° (5) or by cat. addn. of HCl (2) see (5) (2): from 1,2-dichloroethylene (3:5030) + HCl + AlCl₃ see (14).]

[For formation of \bar{C} together with other products by actn. of Cl_2 on β,β' -dichlorodiethyl sulfide (" mustard gas") see (3) (4).]

[For reactn. of \tilde{C} with acetylene + cat. to yield 1,2-dichloroethylene (3:5030) with 1,1,2-trichloroethylene as by-product see (15); for reactn. of \tilde{C} with 1,2-dichloroethylene + AlCl₃ to yield a pentachlorobutane, b.p. 76-77.9° at 10 mm., $D_{22}^{22} = 1.611$, $n_{D}^{22} = 1.5548$, see (16); for reactn. of \tilde{C} with C_6H_5MgBr in toluene see (17).]

3:5555 (1) Henne, Hubbard, J. Am. Chem. Soc. 58, 404-406 (1936). (2) Kharasch, Norton, Mayo, J. Org. Chem. 3, 48-54 (1938). (3) Phillips, Davies, Mumford, J. Chem. Soc. 1929, 548. (4) Mann, Pope, J. Chem. Soc. 121, 597 (1922). (5) Nicodemus, J. prakt. Chem. (2) 83, 318 (1911). (6) Parkhurst (to Stand. Oil Cal.), U.S. 1,948,045, Feb. 20, 1934; Cent. 1934, II 863; C.A. 28, 2924 (1934). (7) Kline (to du Pont Rayon), U.S. 2,042,944, June 2, 1936; Cent. 1937, I 478; C.A. 30, 5038 (1936). (8) Regnault, Ann. chim. (2) 69, 162 (1838). (9) Laurent, Ann. 22, 292-305 (1857). (10) I.G., Ger. 530,649, July 31, 1931; Cent. 1931, II 1920.

(11) Kaufmann, Ber. 55, 258 (1922). (12) Mouneyrat, Bull. soc. chim. (3) 19, 499-500 (1898). (13) Kokatnur, J. Am. Chem. Soc. 41, 122-123 (1919). (14) Prins, Rec. trav. chim. 45, 80-81 (1926). (15) Wiegand (to Chem. Fabrik von Heyden), Ger. 566,034, Dec. 14, 1932; Cent. 1933, I 1350: Ger. 567,272, Dec. 30, 1932; Cent. 1933, I 1842. (16) Prins, Rec. trav. chim. 56, 123-124

(1937). (17) Bert, Bull. soc. chim. (4) 41, 1173-1174 (1927).

3:5570
$$d$$
, l - α -CHLORO- n -BUTYRYL CHLORIDE $C_4H_6OCl_2$ Beil. II - 277 CH₃.CH₂.CH.C=O II₁-(123) II₂--

B.P. 129–132° (1) $D_-^{17} = 1.257$ (1) 62–63° at 70 mm. (2) 51–52° at 41 mm. (2)

[For prepn. of \bar{C} from α -chloro-n-butyric acid (3:9130) with SOCl₂ see (2); for formn. of \bar{C} from n-butyryl chloride (3:7370) with SO₂Cl₂ + dibenzoyl peroxide in CCl₄ (15% \bar{C} + 55% β - and 30% γ -isomers) see (3).]

 \bar{C} on hydrolysis with aq. yields α -chloro-n-butyric acid (3:9130) q.v.

3:5570 (1) Markownikow, Ann. 153, 241 (1870). (2) Blaise, Bull. soc. chim. (4) 15, 668 (1914). (3) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940).

3:5576
$$\beta$$
-CHLOROPROPIONALDEHYDE C₃H₅OCl Beil. I - 632 (3-Chloropropanal-1; CH₂.CH₂.CHO I₁— I₂-(690)

B.P. 130–131° (1) $D_{-}^{15} = 1.268$ (1) $n_{-}^{15} = 1.475$ (1) 125–130° (2) 50° at 60 mm. (3) 40–44° at 18 mm. (4) 40° at 19 mm. (1) 40–50° at 10 mm. (2)

Liquid; insol. aq.; sol. alc. or ether. — C readily polymerizes (see below).

PREPARATION OF C

[For prepn. of \bar{C} from acrolein (1:0115) with dry HCl gas at -10 to -15° (yields: 87% (5), 65% (4)) (6) (7) (8) (9) (10) see indic. refs.; note that since HCl is present much of the prod. may appear as the trimer (see below); for prepn. of \bar{C} from its trimer (see below) by distillation at ord. press. see (1); for prepn. of \bar{C} from 1,3-dichloropropene-1 (3:5280) by cat. vapor-phase hydration see (20).]

CHEMICAL BEHAVIOR OF C

Polymerization. \bar{C} in the pres. of even traces of HCl readily polymerizes to a trimer (2), white cryst. from abs. EtOH (6) or MeOH at -10° (1), very sol. in ether, acetone, AcOH, CHCl₃, pet. ether, or C₆H₆ (1); m.p. 36° (1), 35.5° (6), 34.5-35.5° (11), 33.5° (2), 32° (10); b.p. (without depolymerization) 170-175° at 12-15 mm. (2); note that this trimer on distillation at ord. press. depolymerizes into \bar{C} (1).

Oxidation. \tilde{C} on oxidn. with fumg. HNO₃ (5) (6) (7) (8) (9) (12) or with conc. HNO₃ (13) gives (yields: 65-70% (7), 60-65% (8), 50% (6)) β -chloropropionic acid (3:0460). — \tilde{C} readily reduces AgNO₃ or Fehling's soln.

Behavior with other inorganic reactants. \bar{C} adds NaHSO₃, but the resultant compd. with dil. H₂SO₄ does *not* regenerate \bar{C} [for formn. of the KHSO₃ epd. of \bar{C} from β -chloropropionaldehyde diethylacetal (3:9490) see {14}].

[C with solid KOH on htg. gives (10) a polymer of acrolein (metaacrolein).]

[C with PCl₅ gives (15) (16) 1,1,3-trichloropropane (3:5660).]

Behavior with organic reactants. Acetal formation. [\bar{C} in MeOH with HCl gas presumably would yield β -chloropropionaldehyde dimethylacetal [Beil. I₁-335, I₂-(690)], b.p. 86° at 100 mm. (17), 51° at 19 mm. (1), 45° at 12 mm (18), $D_{-}^{20} = 1.059$ (18), $D_{-}^{15} = 1.064$ (1), $n_{-}^{20} = 1.41631$ (18), $n_{-}^{15} = 1.427$ (1), although such direct prepin. has not actually been reported; the prod. is usually obtd. from acrolem (1:0115) in MeOH with dry HCl gas (1) (17) (18) cf. (19). — Note, however, that in this process there is also formed some α,γ -dichloro-n-propyl methyl ether [Beil. I₂-(690)] (1), b.p. 55° at 19 mm. (1), 45° at 12 mm. (18), $D_{-}^{15} = 1.186$ (1), $n_{-}^{20} = 1.4478$ (18), $n_{-}^{15} = 1.450$ (1).]

[C in EtOH with HCl gas presumably would yield similarly β-chloropropionaldehyde diethylacetal (3:9490) q.v., although such direct forms. has not actually been reported.] Behavior with NaOAc/AcOH. [C with NaOAc/AcOH on htg. ppts. NaCl and gives (1) (by loss of HCl) some acrolein (1:0115) and (as a result of the HCl) some trimer (see above).

Behavior with acetic anhydride. [C with Ac₂O (1:1015) refluxed several hrs. gives (1) a mixt. of prods. including α -chloroallyl acetate, allylidene diacetate, β -chloropropylidene diacetate, m.p. 43°, and the trimer of \tilde{C} .]

Behavior with RMgX reactants. [C with RMgX cpds. in ether, followed by hydrolysis, reacts normally by addn. to the aldehyde group; e.g., C with EtMgBr gives (3) 1-chloropentanol-3 [Beil. I₁-(184), I₂-(421)], b.p. 173° at 760 mm., C with excess n-AmMgBr gives (43% yield (4)) 1-chloro-octanol-3, b.p. 110-115° at 14 mm. (4)

3:5576 (1) Kirrmann, Goudard, Chahidzadeh, Bull. soc chim. (5) 2, 2147-2150 (1935). (2) Grimaux, Adam, Bull. soc. chim. (2) 36, 22-24 (1881). (3) Fourneau, Ramart-Lucas, Bull. soc. chim. (4) 25, 366 (1919). (4) Shriner, Rendleman, Berger, J. Org. Chem 4, 104 (1939). (5) Moureu, Bull. soc. chim. (3) 9, 387-388 (1893); Ann. chim. (7) 2, 156-158 (1894). (6) Moureu, Murat, Tampier, Ann. chim. (9) 15, 222-224 (1921); Compt. rend. 172, 1267 (1921). (7) Moureu, Chaux, Bull. soc. chim. (4) 35, 1362-1364 (1924). (8) Moureu, Chaux, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 166-168 (1941), (1st Ed.) 160-162 (1932); 8, 54-56 (1928). (9) Wohlk, J. prakt. Chem. (2) 61, 205-209 (1900). (10) Geuther, Cartmell, Ann. 112, 3-6 (1859).

(11) Krestownikoff, J. Russ. Phys.-Chem. Soc. 11, 248 (1879); Jahresber. 1879, 552. (12) Arndt, Ber. 56, 1276-1277, Note (1923). (13) Rohm & Haas Co., Brit. 526,122, Sept. 11, 1940; C.A. 35, 6981 (1940). (14) Crawford, Kenyon, J. Chem. Soc. 1927, 399-400. (15) van Romburgh, Bull. soc. chim. (2) 37, 103 (1882). (16) Geuther, Zeit. für Chemie 1865, 29. (17) Wohl, Momber, Ber. 47, 3348-3349 (1914). (18) Dulière, Bull. soc. chim. (4) 33, 1651 (1923). (19) Voet, Bull. soc. chim. (4) 41, 1308-1314 (1927). (20) Anderson, Stager, McAllister (to Shell Development Co.) U.S. 2,359,459, Oct. 3, 1944; C.A. 39, 708 (1945).

3:5585 METHYL CHLOROACETATE CH₂.COOCH₃ C₃H₅O₂Cl Beil. II - 197
$$H_{1-}$$
(88) H_{2-} (191) B.P. F.P. 131.5° (1) -32.65 ° (1) $D_{4}^{20} = 1.2358$ (6); $n_{D}^{20} = 1.42207$ (6) 131° (2) 1.2340 (8) (8) 130.8° (3) 130.0° at 760 mm. (4) 130.0° at 740 mm. (5) 129.6–129.8° at 756 mm. (6) 129° (7)

[For prepn. of \bar{C} from chloroacetic acid (3:1370) with MeOH (43-45% yield (2)), with MeOH + HCl (68.5% yield (2)) (5) (9), with MeOH + BF₃.Et₂O (65% yield (2)), or with Me₂SO₄ in s.t. at 200° (10) see indic. refs.; from chloroacetyl chloride (3:5235) + MeOH see (7); from chloroacetamide + MeOH +BF₃ (64% yield) see (2); from α,β -dichlorovinyl ethyl ether (3:5540) with MeOH see (11) (12).]

[For constant-boilg. mixts. of \bar{C} with various org. cpds. see Beil. II₂-(191) or (13) (14).] \bar{C} on shaking with 2 vols. cold conc. NH₄OH yields (7) (16) (more readily (15) than ethyl chloroacetate (3:5700)) chloroacetamide, m.p. 121° (16). — \bar{C} on htg. with 2 moles aniline at 100°, extracted with aq. to remove aniline hydrochloride, yields an oil which on steam distillation gives in the distillate (7) methyl anilinoacetate (phenylglycine methyl ester) [Beil. XII-470, XII₁-(263)], m.p. 48° (7). [This prod. on boilg. with excess aniline yields (7) anilinoacetanilide (phenylglycine anilide) [Beil. XII-556], m.p. 110-111° (7).

 \bar{C} on hydrolysis (probably best with N/10 Ba(OH)₂ cf. (17)) yields methyl alc. (1:6120) and chloroacetic acid (3:1370). [For studies of hydrolysis under various conditions see (18) (19); for study of alcoholysis of \bar{C} with EtOH + HCl see (20).]

3:5585 (1) Timmermans, Bull. soc. chim. Belg. 31, 392 (1922). (2) Toole, Sowa, J. Am. Chem. Soc. 59, 1971-1973 (1937). (3) Cheng, Z. physik. Chem. B-24, 305 (1934). (4) Lecat, Ann. soc. sci. Bruxelles 47, I 112 (1927). (5) Schreiner, Ann. 197, 7-8 (1879). (6) Karvonen, Ann. Acad. Sci. Fennicae A-10, No. 4, 20 (1916); Cent. 1919, III, 808. (7) Meyer, Ber. 8, 1152-1158 (1875). (8) Schjanberg, Z. physik. Chem. A-172, 228 (1935). (9) Henry, Ber. 6, 742 (1873). (10) Simon, Compt. rend. 176, 585 (1923).

(11) Crompton, Vanderstichele, J. Chem. Soc. 117, 692 (1920). (12) Imbert, Consortium für Elektrochem. Ind., Ger. 212,592, Sept. 6, 1909; Cent. 1909, II 1024. (13) Lecat, Rec. trav. chim. 45, 622 (1926), 46, 243 (1927). (14) Lecat, Ann. soc sci. Rruxelles 47, I 25, I12 (1927). (15) Henry, Rec. trav. chim. 24, 165 Note 3 (1905). (16) Steinkopf, Malinowski, Ber. 44, 2901 (1911). (17) Newitt, Linstead, Sapiro, Boorman, J. Chem. Soc. 1937, 882. (18) Drushel, Hill, Am. J. Sci. (4) 30, 72-78 (1910), Cent. 1916, II 967; C.A. 4, 2438 (1910). (19) Palomaa, Ber. 74, 1866-1870 (1941). (20) Kolhatkar, J. Chem. Soc. 107, 931 (1915).

3:5590 1,3-DICHLORO-2-METHYLPROPENE-1
$$C_4H_6Cl_2$$
 Beil. I -209 $(\alpha,\gamma$ -Dichloroisobutylene) Cl CH_3 Cl I_1 — I_2 — CH_2 — CH I_3 — I_4 — I_4 — I_5

Note: \bar{C} by virtue of allylic transposition may frequently yield derivatives of its synionic isomer, 1,1-dichloro-2-methylpropene-2 (3:7480) q.v. The products (and/or their deriva-

tives) formerly (4) regarded as cis and trans stereoisomers of C may very probably be C and its synionic isomer (3:7480).

[For prepn. of \bar{C} from 1,2,3-trichloro-2-methylpropane (3:5885) by dehydrochlorination with quinoline (73-85% yield) see (7).]

[For prepn. of \tilde{C} from 1,1-dichloro-2-methylpropene-2 (3:7480) by htg. under reflux see (2): for formn. of \tilde{C} (together with other products) from 2-methylpropene-1 (isobutylene) (60% yield (5)) (1) + Cl₂, or from 3-chloro-2-methylpropene-1 (isobutenyl chloride) (3:7145) with Cl₂ (1 mole) + NaHCO₃ (1.5 moles) at 0° (2) see indic. refs.; for formn. of \tilde{C} (20% yield (6)) (together with other products) from 1,3-dichloro-2-methylpropanol-2 (3:5977) + strong oxygen acids see (6); for formn. of \tilde{C} (46% yield (3)) from 1,3-dichloro-2-methylpropanol-2 (3:5977) by htg. with P₂O₅ for 2 hrs. at 110-115° see (3).]

 \bar{C} on hydrolysis with aq. + CaCO₃ (2) (4) or aq. + MgO (4) gives (2) (3) (46% yield (4)) 1-chloro-2-methylpropen-1-ol-3 (3-chloro-2-methylallyl alc.) (3:8340) q.v.

C with O₃ followed by hydrolysis yields (2) (3) (5) chloroacetone (3:5425).

C treated with Cl₂ in the dark at 0° for 37 hrs. yields (4) 1,1,2,3-tetrachloro-2-methyl-propane (3:6165) + other products.

 \bar{C} with cuprous cyanide refluxed 9-10 hrs. gives (67% yield (7)) 4-chloro-3-methylbuten-3-nitrile-1, b.p. 70-73° at 10 mm., $D_4^{20}=1.0856$, $n_D^{20}=1.4643$ (7); this product on hydrolysis with hot conc. HCl for 2 hrs. gives (7) 4-chloro-3-methylbuten-3-oic acid-1, m.p. 35° (corresp. phenylhydrazide, m.p. 147-148°).

3:5590 (1) Pogorshelski, J. Russ. Phys.-Chem. Soc. 36, 1129-1184 (1904); Cent. 1905, I 668, (2) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4223; C.A. 33, 4190 (1939). (3) D'yakonov, J. Gen. Chem. (U.S.S.R.) 10, 402-413 (1940); C.A. 34, 7861 (1940). (4) Rogers, Nelson, J. Am. Chem. Soc. 58, 1029-1031 (1936). (5) D'yakonov, Tishchenko, J. Gen. Chem. (U.S.S.R.) 9, 1258-1264 (1939); C.A. 34, 710 (1940). (6) Groll, Burgin (to Shell Development Co.), U.S. 2,042,223, 2,042,222, May 26, 1936; Cent. 1937, 1274; C.A. 30, 4875 (1936). (7) Mooradian, Cloke, J. Am. Chem. Soc. 68, 785-789 (1946).

3:5605 3,3,3-TRICHLORO-2-METHYLPROPENE-1 $C_4H_5Cl_3$ Beil. S.N. 11 (1,1,1-Trichloro-2-methylpropene-2) $H_2C=C-CCl_3$

B.P. 132° (1) $D_{-}^{20} = 1.293$ (1) $n_{-}^{20} = 1.479$ (1)

Note: \tilde{C} readily undergoes allylic transposition so that in reactns. of \tilde{C} products derived from the isomeric 1,1,3-trichloro-2-methylpropene-1 (3:5025) may be expected (1) (2) (3) (4).

[For prepn. of $\bar{\rm C}$ (yield: 30–43% (4), 15% (1)) from β,β,β -trichloro-ter-butyl alc. ("Chlore-tone") (3:2662) by htg. to 200° with P₂O₅ and dimethylaniline (1) or quinoline (4) see indic. refs.] [A 57% yield of the isomeric 1,1,3-trichloro-2-methylpropene-1 (3:5025) together with some α -chloroisobutyric acid (3:0235) is separated from $\bar{\rm C}$ by redistillation (1).]

 \bar{C} on hydrolysis by boilg. 1 day with aq. Na₃PO₄ gives (60% yield (2)) 3,3-dichloro-2-methylpropen-2-ol-1, b.p. 78-79°, $D_{-}^{20}=1.298, n_{-}^{20}=1.493$ (p-nitrobenzoate, m.p. 91°, N-phenylcarbamate, m.p. 64° (2)).

 \bar{C} on htg. with NaOAc + AcOH gives (2) 3,3-dichloro-2-methylpropen-2-yl acetate, b.p. 79° at 12 mm., D_{-}^{20} = 1.257, n_{-}^{20} = 1.4718 (2). [With boilg. NaOH this regenerates the corresp. alc. (2).]

Č with NaOEt gives in the cold 70% yield (2) of 3,3-dichloro-2-methylpropen-2-yl ethyl ether, b.p. 56° at 12 mm., $D_{-}^{20} = 1.1285$, $n_{-}^{20} = 1.4610$ (2).

 \bar{C} in AcOH treated with O₃, then hydrolyzed, gives (70% yield) α,α,α -trichloroscetone (3:5620), b.p. 133-134⁵ (1).

[For behavior of C with PCl₅, with HF, or with HF + anisole see (4).]

- ② 2,3-Dibromo-1,1,1-trichloro-2-methylpropane: m.p. 34° (1). [From $\ddot{C} + Br_2$ without solvent; crude prod. recrystd. from alc. at -10° (1); cf., however, (4).]
- 3,3-Dichloro-2-methylpropen-2-yl p-nitrobenzoate: m.p. 91° (2). [From C on boilg. with dil. alc. soln. of K p-nitrobenzoate (2).]
- 3:5605 (1) Jacob, Bull. soc. chim. (5) 7, 581-586 (1940). (2) Kirrmann, Jacob, Bull. soc. chim. (5) 7, 586-593 (1940). (3) Kirrmann, Jacob, Compt. rend. 203, 1528-1529 (1936). (4) Price, Marshall, J. Org. Chem. 8, 532-535 (1943).

3:5615 1,2-DICHLOROBUTENE-2 Cl Cl
$$C_4H_6Cl_2$$
 Beil. S.N. 11 (high-boilg stereoisomer) CH_3 — CH = C — CH_2

B.P. 132-134° at 752 mm. (1)
$$D_4^{20} = 1.1597$$
 (2) $n_D^{20} = 1.4590$ (2) $125-127^{\circ}$ (2) $D_4^{18} = 1.1601$ (2) $n_C^{18} = 1.4635$ (2) $D_4^{16} = 1.1771$ (1) $n_C^{16} = 1.4710$ (1)

[See also low-boilg. stereoisomer (3:5360).]

[For prepn. of \tilde{C} (together with its stereoisomer (3:5360)) from 1,2,3-trichlorobutane (3:5935) with KOH at 150° (2), or from 2,2-dichlorobutane (3:7415) or 2,3-dichlorobutane (3:7615) with alc. KOH (5), see indic. refs.; for formn. of \tilde{C} (together with its stereoisomer and also 2,4-dichlorobutene-2 (3:5550)) from 2-chlorobutene-2 (3:7105) by actn. of Cl₂ at 350° see (3).]

 \ddot{C} with 1 mole Cl₂ + 1.5 moles NaHCO₅ at 0° gives (100% yield (4)) 1,2,2,3-tetrachlorobutane (3:9078).

C on hydrolysis by htg. with 2 pts aq. + 1 mole powdered CaCO₃ at 70° for 4 hrs. gives (1) a mixt. of about equal parts of 2-chlorobuten-2-ol-1 (3:8240) and (by allylic transposition) 3-chlorobuten-3-ol-2 (3:9115).

 $\bar{\rm C}$ on oxidn. with KMnO₄ in acetone gives (1) chloroacetic acid (3:1370) + AcOH (1:1010) + HCl. — $\bar{\rm C}$ in CCl₄ at -17° treated with O₃ followed by aq. gives acetaldehyde (1:0100).

3:5615 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 658-662 (1937); Cent. 1937, II 371; C.A. 31, 5754 (1937). (2) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 6, 1553-1558 (1936); Cent. 1937, I 3786; C.A. 31, 2165 (1937). (3) N. V. Bataafsche Petroleum Maatschappi, Brit. 468,016, July 22, 1937; French 810,112, Mar. 15, 1937, Cent. 1937, II 4102. (4) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4222; C.A. 33, 4190 (1939). (5) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 663-666 (1937); Cent. 1937, II 371; C.A. 31, 5754 (1937).

3:5620 1,1,1-TRICHLOROPROPANONE-2
$$C_3H_3OCl_3$$
 Beil. I - 655 $(\alpha,\alpha,\alpha$ -Trichloroacetone; CH_3 -C-CCl₃ I_1 -(344) methyl trichloromethyl ketone) I_2 -(719)

B.P.
$$134^{\circ}$$
 (1) (3) $D_4^{20} = 1.435$ (3) $n_{\alpha}^{20} = 1.4592$ (3) 60° at 54 mm. (1) $D_4^{17.1} = 1.4389$ (3) $D_4^{17.1} = 1.4389$ (3)

Limpid colorless liq. with faintly camphoraceous odor. — Insol. aq., but volatile with steam (3). — \bar{C} is not lachrymatory.

[For prepn. from 1,1,1-trichloro-2-methylpropene-2 (3:5605) with O₃ in AcOH, followed by hydrolysis (70% yield) see (2); from corresp. alc., 1,1,1-trichloropropanol-2 (3:0846), by oxidn. with K₂Cr₂O₇/H₂SO₄ see (3); from 2-trichloromethyl-2,4,4-trimethyl-1,3-dioxolone-5 [Beil. XIX₁-(656)] by hydrolytic cleavage with AcOH/HCl (60% yield) see (1): for formn. of C (together with other prods.) from propanol-2 (1:6135) with Cl₂ (4), from chloroacetone (3:5425) with Cl₂ at 30-40° (5), or from trichloroacetyl chloride (3:5420) with MeZnI (1) see indic. refs. - Note that the prod. from chloral + diazomethane, formerly supposed (6) to have been C, has since been shown (7) (8) to be 3,3,3-trichloro-1,2-epoxypropane (3:5760) (" γ,γ,γ -trichloropropylene oxide").]

 $(\bar{C} \text{ on reduction with } Al(C_2H_5)_3.Et_2O \text{ in ether (9) or with fused } Al(OEt)_3 \text{ in abs. alc.}$ under H₂ or N₂ (10) gives (yields: 67% (10), 65% (9)) 1,1,1-trichloropropanol-2 (3:0846).]

[C resists further chlorination; e.g., C with SO₂Cl₂ (1 mole) on protracted htg. at 180° yields (3) 1,1,1,3-tetrachloropropanone-2 (3:6085), b.p. 71-72° at 13 mm., hydrate, m.p. 65° (3).]

[C with diazomethane in dry ether gives (83% yield (3)) 1,1,1-trichloro-2-methyl-2,3epoxypropane, b.p. 51° at 10 mm., m.p. 53-54° (3).]

- (2) (P) Cleavage with aq. alkali: C with aq. alk. even in cold splits almost instantly into chloroform (3:5050) and acetic acid (1:1010).
- (1) 1,1,1-Trichloropropanone-2 semicarbazone: m.p. 140° dec. (on Hg bath) (1) (11). [From C with semicarbazide HCl in pres. of NaOAc, or with free semicarbazide (11).]

3:5620 (1) Blaise, Bull. soc. chim. (4) 15, 734-737 (1914); Compt. rend. 155, 1253 (1912). (2) Jacob, Bull. soc. chim. (5) 7, 581-586 (1940); C.A. 36, 3508 (1942). (3) Arndt, Amende, Ender, Monatsh. 59, 214-216 (1932). (4) Buc (to Standard Oil Co.), U.S. 1,391,757, Sept. 27, 1921; Cent. 1922, IV 942. (5) I.G., French 816,956, Aug. 21, 1937; Cent. 1938, I 2216. (6) Schlotterbeck, Ber. 42, 2561-2562 (1909). (7) Arndt, Eistert, Ber. 51, 1118-1122 (1928). (8) Arndt, Z. angew. Chem. 40, 1099-1100 (1927). (9) Meerwein, Hinz, Majert, Sonke, J. prakt. Chem. (2) 147, 236-237 (1936). (10) Meerwein, Schmidt, Ann. 444, 233-234 (1925).

(11) Blaise, Bull. soc. chim. (4) 17, 428 (1915); Compt. rend. 156, 1551 (1913)

B.P. 134–135° at 742 mm. (1)
$$D_{20}^{20} = 1.3932$$
 (1) $n_D^{25} = 1.4920$ (1)

[For prepn. of C from 1,1,1-trichlorobutanol-2 (3:5955) with conc. HCl + ZnCl₂ on stdg. at room temp. 1 hr. (yield not stated) see (1).]

3:5622 (1) Gilman, Abbott, J. Org. Chem. 8, 228 (1943).

at 10 mm. (2)

3:5625 ETHOXALYL CHLORIDE
$$\begin{array}{c} \text{CO.OC}_2\text{H}_5 \\ \text{CO.Cl} \end{array}$$
 $\begin{array}{c} \text{C}_4\text{H}_5\text{O}_3\text{Cl} \\ \text{II}_1\text{-}(234) \\ \text{II}_2\text{-}(508) \end{array}$ B.P. 136–138° (1) $D_4^{20} = 1.2234$ (2) 1.35–136° (2) 1.2226 (3) 1.34–135° (4) 1.33–135° at 760 mm. (14) 30° at 10 mm. (2)

Colorless mobile liq. with penetrating odor. — C fumes in air and gradually deposits hydrated oxalic acid (1:0445) (17). — C as such is insol. in aq. but rapidly hydrolyzes with formn. of HCl and ethyl hydrogen oxalate, the latter in turn being converted to oxalic acid (1:0445) + EtOH.

[For prepn. of C from diethyl oxalate (1:1055) with PCl₅ (yields: 80–90% (5), 84% (6), 80% (7)) (8) (9) (10) (11) (34) see indic. refs.; note that this mode of prepn. has been shown (4) to comprise two distinct and successive reactions: first the formn. of ethyl α,α -dichloro- α -ethoxyacetate, Cl₂C (OEt).COOEt [Beil. II-543, II₁-(236)], b.p. abt. 85° at 10 mm., $D_4^{20} = 1.23155$ (2); and second, the pyrolysis of this product by repeated distillation (13) or increased temp. (especially in the pres. of catalysts such as salts of Fe or Pt (5) (12)) yielding \tilde{C} + ethyl chloride (3:7015).]

[For prepn. of \bar{C} from ethyl hydrogen oxalate [Beil. II-535, II₁-(232), II₂-(504)] with SOCl₂ (yields: 78% (14), 72% (15)) or with PCl₅ (3) see indic. refs. (note that the initial ethyl hydrogen oxalate is readily obtd. from anhydrous oxalic acid (1:0535) with diethyl oxalate (1:1055) by htg. 3 hrs. (32% yield (15)) (18) or by distn. with EtOH and CCl₄ as directed (61% yield (16))); for prepn. of \bar{C} from K ethyl oxalate with POCl₅ or PCl₅ (17) (3) or with SOCl₂ (60-70% yield (24)) see indic. refs. (note that K ethyl oxalate can readily be prepd. in 95-97% yield from diethyl oxalate (1:1055) by digestion with aq. KOAc (24).)

[For prepn. of \tilde{C} from oxalyl (di)chloride (3:5060) with EtOH (1:6130) by reactn. of one acid chloride group but not the other (60% yield) see (25).]

[\bar{C} on passing through tube at 200° loses CO yielding (19) ethyl chloroformate (3:7295).] [\bar{C} with EtOH (1:6130) reacts normally yielding (17) diethyl oxalate (1:1055); for reactn. of \bar{C} with cellulose see (25).]

[C with diethyl sodiomalonate in ether gives (20) (12) a mixt. of triethyl oxalomalonate [Beil. III-850, III₁-(292)] and tetraethyl dioxalomalonate [Beil. III₂-(199)]; C with ethyl sodio-cyanoacetate in ether gives (21) (22) diethyl oxalo-cyanoacetate [Beil. III-850], m.p. 98° (22), 96° (21); C with diethyl methyl sodio-malonate gives (23) diethyl oxalomethyl-malonate; many other analogous condensations cannot be included here.]

 $|\bar{C}|$ with aromatic hydrocarbons in the pres. of AlCl₃ undergoes reactn. of the Friedel-Crafts type, and this procedure has been widely studied as a means of introduction of the —CO.COOEt group: e.g., \bar{C} with C_6H_6 + AlCl₃ in nitrobenzene + CS₂ gives (26) ethyl benzoylformate (ethyl phenylglyoxylate) [Beil. X-657, X₁-(314)], b.p. 256-257°; for corresp. analogous reactn. with toluene (1:7405) (27), m-xylene (1:7420) (27), cumene (1:7440) (9), pseudocumene (1:7470) (27), or mesitylene (1:7455) (27) (1) see indic. refs.]

Č with NH₃ in alc. gives (17) ethyl oxamate, NH₂.CO.CO.OC₂H₅ [Beil. II-544, II₁-(236), II₂-(509)], lfts. from hot alc., m.p. 114°. — Similarly Č with aniline should yield ethyl oxanilate, C₆H₅.NH.CO.CO.OC₂H₅ [Beil. XII-282, XII₁-(206)], tbls. or pr. from alc., ndls. from hot aq., m.p. 66-67°; Č with phenylhydrazine should yield β-(ethoxalyl)-phenylhydrazine, C₆H₅.NH.NH.CO.CO.OC₂H₅ [Beil. XV-264], lfts. from alc., m.p. 119°.

Č with urea (2 moles) reacts vigorously at room temp. as a normal acid chloride yielding (28) ethyl oxalurate, NH₂·CO.NH.CO.CO.OC₂H₅ [Beil. III-65, III₂-(54)], ndls. from ether, m.p. 184–185°.— Note, however, that Č with N-phenylurea on htg. evolves CO + C₂H₅Cl (3:7015) and yields (29) a mixt. of ethyl ω-phenylallophanate, C₆H₅·NH.CO.NH.-COOC₂H₅ [Beil. XII-359, XII₁-(234)], ndls. from boilg. alc., m.p. 106° (30), and N-phenyl-parabanic acid (oxalyl N-phenylurea) [Beil. XXIV-454, XXIV₁-(405)], lfts. from alc., m.p. 208° (29).— Č with N,N'-diphenylurea in C₆H₆ on htg. evolves C₂H₅Cl (3:7015) and yields (29) N,N'-diphenylparabanic acid (oxalyl N,N'-diphenylurea) [Beil. XXIV-455, XXIV₁-(405)], ndls. from alc., m.p. 204°.— Č with N,N'-dimethylurea (2 moles)

reacts vigorously giving (80% yield (31)) N,N'-dimethylparabanic acid [Beil. XXIV-453, XXIV₁-(404)], m,p. 154°.

[Č with RMgX cpds. gives (32) disubstituted glycolic acids ($R_2C(OH)COOH$) and/or ethoxalyl esters of disubstituted ethyl glycolates, $R_2C(O.CO.COOC_2H_5)$; similarly \bar{C} with diethylcadmium gives (63% yields (33)) ethyl α -ethyl- α -hydroxy-n-butyrate (ethyl α , α -diethylglycolate).]

3:5625 (1) Wenzel, Monatsh. 35, 948 (1914). (2) Anschutz, Ann. 254, 20, 27 (1889). (3) Mol, Rec. trav. chim. 26, 381-384 (1907). (4) Anschutz, Ber. 19, 2158-2160 (1886). (5) Blaise, Bull. soc. chim. (4) 19, 12 (1916). (6) Barré, Bull. soc. chim. (4) 41, 47-49 (1927). (7) Bert, Bull. soc. chim. (4) 41, 1165-1166 (1927). (8) Anschutz, Ber. 19, 2158-2160 (1886). (9) Bert, Bull. soc. chim. (4) 37, 1401-1405 (1925). (10) Kurrein, Monatsh. 26, 373-378 (1905).

(11) Peratoner, Struzzeri, Gazz. chim. ital. 21, 301-302 (1891). (12) Scholl, Egerer, Ann. 397, 318-320, 345-355 (1913). (13) van Alphen, Rec. trav. chim. 47, 678 (1928). (14) Diels, Nawiasky, Ber. 37, 3678-3679 (1904). (15) Fourneau, Sabetay, Bull. soc. chim. (4) 41, 537-540 (1927). (16) Contzen-Crewet, Bull. soc. chim. Belg. 35, 167-170 (1926). (17) Henry, Ber. 4, 599-601 (1871). (18) Fourneau, Sabetay, Bull. soc. chim. (4) 43, 860 (1928). (19) Grassi, Gazz. chim. ital. 27, I 31-32 (1897). (20) von Auwers, Auffenberg, Ber. 51, 1103-1106 (1918).

(21) Trimbach, Bull. soc. chim. (3) 33, 372-375 (1905). (22) Bertini, Gazz. chim. ital. 31, I 586-588 (1901). (23) Farmer, Ghosal, Kon, J. Chem. Soc. 1936, 1809. (24) Adickos, Brunnert, Lücker, J. prakt. Chem. (2) 130, 168-170 (1931). (25) von Frank, Caro, Ber. 63, 1532-1543 (1930). (26) Bouveault, Bull. soc. chim. (3) 15, 1017 (1897); (3) 17, 363-366 (1897). (27) Bouveault, Bull. soc. chim. (3) 17, 366-372 (1897). (28) Henry, Ber. 4, 644-646 (1871). (29) von Stojentin, J. prakt. Chem. (2) 32, 18-23 (1885). (30) Folin, Am. Chem. J. 19, 345-346 (1897). (31) Biltz, Topp, Ber. 46, 1396 (1913). (32) Grignard, Bull. soc. chim. (3) 29, 948-953 (1903). (33) Gilman, Nelson, Rec. trav. chim. 55, 521, 527 (1936). (34) Kindler, Ger. 728,532, Oct. 29, 1942; C.A. 38, 378 (1944).

3:5630 1,1,2-TRICHLOROPROPANE
$$CH_3.CH(Cl).CHCl_2$$
 $C_3H_5Cl_3$ Beil. I-106 (α -Chloropropylidene (di)-chloride) I₁—I₂—

B.P. 135–137° (1) cf. (2)
$$D_{-}^{16} = 1.353$$
 (1) 132° (3)

[For prepn. from 1,2-dichloropropane (propylene dichloride) (3:5200) by chlorination in presence of iron and ultra-violet light at $10-40^{\circ}$, or without ultra-violet light above 50°, see (4), or with SO_2Cl_2 in pres. of organic peroxides see (6) (7).]

Č htd. with aq. or alc. alk. splits out HCl yielding (5) 1,1-dichloropropene-1 (3:5120), b.p. 78°.

3:5630 (1) Mouneyrat, Bull. soc. chim. (3) 21, 620 (1899). (2) Van Arkel, Rec. trav. chim. 51, 1101 (1932). (3) Herzfelder, Ber. 26, 1258 (1893). (4) Levine, Cass (to du Pont), Brit. 471,188, Sept. 30, 1937; Cent. 1938, I 1218. (5) Levine, Cass (to du Pont), Brit. 471,186, Sept. 30, 1937; Cent. 1938, I 3110. (6) Kharasch, Brown, J. Am. Chem. Soc. 61, 2145 (1939). (7) Zellner (to Tide Water Associated Oil Co.) U.S. 2,370,342, Feb. 27, 1945; C.A. 39, 3535 (1945).

3:5633 3-CHLORO-2-(CHLOROMETHYL)-
$$C_4H_6Cl_2$$
 Beil. I — PROPENE-1 Cl CH₂Cl I_1 — I_1 — I_2 —(1-Chloro-2-(chloromethyl)propene-2; I_2 — I_2 — I_2 — I_2 —(181)

B.P. M.P. 138-138.3° (9)
$$-15^{\circ}$$
 to -13° (9) $D_4^{20} = 1.1782$ (9) $n_D^{20} = 1.4754$ (9) 30-31° at 9 mm. (1)

Colorless oil with faintly halogen-like odor (1).

[For prepn. of Č from tris-(chloromethyl)acetic acid (itself obtd. in quant. yield by conc. HNO₃ oxidn. (9) of 3-chloro-2,2-bis-(chloromethyl)propanol-1 = pentaerythrityl trichlorohydrin (9)) by combine decarboxylation and dehydrochlorination in boilg. quinoline (75-85% yield) see (9).]

[For formn. of \bar{C} (40% yield (2) together with other products (2) (3)) from 2-methyl-propene-1 (isobutylene) with Cl₂ (2) (3) or from 3-chloro-2-methylpropene-1 (isobutenyl chloride) (3:7145) with Cl₂ (1 mole) + NaHCO₃ (1.5 moles) at 0° see (2) (4) see indic. refs.; for formn. of \bar{C} (together with other products) from 1,2,3-trichloro-2-methylpropane (3:5885) by pyrolysis at 450-550° see (5); for formn. of \bar{C} (together with 1,3-dichloro-2-(chloromethyl)propene-1 (3:9066)) from 1,3-dichloro-2-nitro-2-(chloromethyl)propane with Na/Hg see (1); for prepn. of \bar{C} (80% yield (6) together with 20% yield 1,3-dichloro-2-methylpropene-1 (3:5590)) from 1,3-dichloro-2-methylpropanol-2 (3:5977) by actn. of strong oxygen acids see (6).]

 \bar{C} on cat. hydrogenation using Pt black yields (1) 1,3-dichloro-2-methylpropane (3:7960), but \bar{C} in alc. on boilg, with Zn dust gives (75% yield (3)) isobutylene, b.p. -6° .

 \bar{C} with O_3 gives (2) α, α' -dichloroacetone (3:0563).

 \bar{C} treated with Cl_2 in the dark at 0° yields (5) 1,2,3-trichloro-2-chloromethylpropane (3:6335). — \bar{C} treated with Br_2 in CHCl₃ yields (1) 1,2-dibromo-3-chloro-2-(chloromethyl)-propane, colorless odorless oil, b.p. 140° at 10 mm. (1); note, however, failure to react with Br_2 recorded later (9).

Č with aq. alk. as specified (7) yields 2,3-epoxy-2-chloromethylpropanol-1, b.p. 85° at 1 mm. (7). [For similar reactns. cf. (8).]

 \tilde{C} on hydrolysis with aq. CaCO₃ refluxed 2 hrs. gives (36% yield (9)) 2-(hydroxymethyl) propen-2-ol-1, b.p. 125-126° at 18 mm., $D_4^{20} = 1.0791$, $n_D^{20} = 1.4758$ (9).

3:5633 (1) Kleinfeller, Ber. 62, 1595 (1929). (2) D'yakonov, Tishchenko, J. Gen. Chem. (U.S.S.R.) 9, 1258-1264 (1939); C.A. 34, 710 (1940). (3) D'yakonov, J. Gen. Chem. (U.S.S.R.) 10, 402-413 (1940); C.A. 34, 7861 (1940). (4) Engs, Groll, Fairbairn (to Shell Development Co.), U.S. 2,189,890, Feb. 13, 1940; C.A. 34, 4079 (1940). (5) Rogers, Nelson, J. Am. Chem. Soc. 58, 1029-1031 (1936). (6) Groll, Burgin (to Shell Development Co.), U.S. 2,042,223, U.S. 2,042,222, May 26, 1936; Cent. 1937, I 1274; C.A. 30, 4875 (1936). (7) Groll, Hearne (to Shell Development Co.), U.S. 2,070,990, Feb. 16, 1937; Cent. 1937, II 2433; C.A. 31, 2612 (1937). (8) Hearne, de Jong, Ind. Eng. Chem. 33, 940-943 (1941). (9) Mooradian, Cloke, J. Am. Chem. Soc. 67, 942-944 (1945).

3:5635 2-CHLOROPROPEN-2-OL-1
$$CH_2 = C - CH_2$$
 C_8H_5OCl Beil. I-439 (2-Chloropropen-1-ol-3; Cl OH $I_1 - I_2$

B.P. 136-140° cor. (1) $D_-^{-} = 1.164$ (2)

Note that \bar{C} is the true β -chloroallyl alcohol; care must be taken to avoid confusion with 3-chloropropen-2-ol-1 (γ -chloroallyl alcohol) (3:5820) whose derivatives have often been designated in the literature as β -chloroallyl derivatives; see also the warning note under γ -chloroallyl chloride (3:5280).

[For prepn. of \bar{C} from 2,3-dichloropropene-1 (3:5190) by hydrolysis of the reactive halogen atom with hot dil. aq. alk. see (2); from 2-chloro-3-iodopropene-1 by hydrolysis of the iodine atom with hot dil. aq. KOH or with silver oxide see (1); from butadiene-1,2-(allene) with HOCl see (3).]

Colorless liq. with faint odor; \bar{C} does not have the violent vesicant action on skin shown by the isomeric γ -chloroallyl alc. (3:5820).

 \tilde{C} readily dissolves in conc. H_2SO_4 with evolution of HCl gas; after pouring onto ice and distilling acetol (hydroxyacetone) (1:5455) is obtd. (2).

[\bar{C} with PBr₃ yields (2) 3-bromo-2-chloropropene-1 (β -chloroallyl bromide) [Beil. I-201, I₁-(171)], b.p. 121° (2), 119-120° (4).]

[\overline{C} yields by suitable treatment (no details (2)) β -chloroallyl acetate [Beil. II-136], b.p. 145° (2). — For esters of \overline{C} with monocarboxylic acids (5), saturated polycarboxylic acids (6), and halogenated acids (7), and for copolymerization of certain esters of \overline{C} with styrene (8) see indic. refs.]

3:5635 (1) van Romburgh, Rec. trav. chim. 1, 238 (1882). (2) Henry, Bull. soc. chim. (2) 39, 526 (1883). (3) Smirnov, J. Russ. Phys.-Chem. Soc. 35, 854-872 (1903); Cent. 1904, I 576. (4) von Braun, Kühn, Weismantel, Ann. 449, 256 (1926). (5) Coleman, Hadler (to Dow Chem. Co.), U.S. 2,208,960, July 23, 1940; C.A. 35, 136 (1941). (6) Coleman, Hadler (to Dow Chem. Co., U.S. 2,159,008, May 23, 1939; Cent. 1939, II 2163; C.A. 33, 6876 (1939). (7) Taylor (to Dow Chem. Co.), U.S. 2,221,275, Nov. 12, 1940; C.A. 35, 1802 (1941). (8) Britton, Coleman, Zemba (to Dow Chem. Co.), U.S. 2,025,390, June 25, 1940, C.A. 34, 7039 (1940).

3:5640 α,β -Dichloroethyl ethyl ether) $C_4H_8OCl_2$ Beil. I - 612 I_1 -(328) I_2 -(676)

B.P.
$$140-145^{\circ}$$
 (1) (2) $D_{23}^{23} = 1.174$ (1) $132-133^{\circ}$ at 725 mm. (3) $66-69^{\circ}$ at 45 mm. (4) $36-37^{\circ}$ at 15 mm. (3)

Colorless liq. with sharp odor.

[For prepn. from diethyl ether (1:6110) by chlorination see (4) (1).]

Č with cold aq. rapidly hydrolyzes yielding chloroacetaldehyde hydrate (3:7212), ethyl alc. (1:6130), and HCl; for study of rate at 20° see (6).

 \tilde{C} in dil. alc. htd. some hrs. at 60° with NH₂OH.HCl (3 moles) + KOH (5 moles) soln. evapd., acidified with dil. H₂SO₄, extracted with ether, ether soln. dried with CaCl₂, evapd. gives (40% yield (5)) glyoxal dioxime (glyoxime) [Beil. I-761], sepd. from oil, recrystallized from hot aq., m.p. 178° (5).

3:5640 (1) Lieben, Ann. 146, 181-186 (1868). (2) Natterer, Monatsh. 5, 496-497 (1884). (3) Mohler, Sorge, Helv. Chim. Acta 23, 1209 (1940). (4) Wildman, Gray, J. Am. Chem. Soc. 41, 1122-1123 (1919). (5) Hantzsch, Wild, Ann. 289, 293 (1896). (6) Mohler, Hartnagel, Helv. Chim. Acta 25, 859-863 (1942); C.A. 37, 1799 (1943).

3:5650 1,2,3-TRICHLOROPROPENE-1 Cl C₃H₃Cl₃ Beil. I - 200
$$I_1$$
—ClCH₂—C=CHCl I_2 — I_2 —B.P. 142° (1) $D_{20}^{20} = 1.414$ (1)

Liq., insol. aq., eas. sol. alc., ether. [Two geom. stereoisomers are possible but unrecorded.]

[For prepn. of C from 1,2,2,3-tetrachloropropane (3:5895) with alc. alk. see (1).]

[For use in prepn. of unsatd. cellulose ethers see (2); for use in dewaxing mineral oils see (3).]

3:5650 (1) Pfeffer, Fittig, Ann. 135, 361-363 (1865). (2) du Pont Co., Brit. 429,949, June 11, 1935; Cent. 1936, I 4098; C.A. 29, 7073 (1935). (3) Standard Oil Development Co., French 790,852, Nov. 28, 1935; Cent. 1936, I 2672; C.A. 30, 3223 (1936).

3:5655 METHYL DICHLOROACETATE $C_3H_4O_2Cl_2$ Beil. II - 203 $II_1- II_{2-}(196)$

B.P. 143.3° at 764.5 mm. (1)
$$D_{19.2}^{19.2} = 1.3808$$
 (6) 143.2° (2) 143° (3) (8) 142-144° (4) 49.8-50° at 20 mm. (5)

[For prepn. of \bar{C} from dichloroacetic acid (3:6208) with MeOH + HCl gas (72% yield (3)) (7), with MeOH + $Et_2O.BF_3$ complex (70% yield (3)), with MeOH + H_2SO_4 (71.3% yield (3)), or with MeOH itself without any cat. (47-61% yield (3)), or with Me₂SO₄ in s.t. at 200° (8) see indic. refs.; for prepn. of \bar{C} from dichloroacetamide with BF₃ in MeOH (57% yield) see (3); for prepn. of \bar{C} from chloral (3:5210) (84% yield (9)), chloral hydrate (3:1270) (4), or chloral hydrate diacetate (76% yield (9)) with KCN in MeOH see indic. refs.]

[For reactn. of \bar{C} with dimethyl sodio-malonate in MeOH yielding (10) 1,1,2,3,3-penta-(carbomethoxy)propane [Beil. II-880], tbls. from MeOH + aq., m.p. 85-86° see (10).]

 $\ddot{\mathbf{C}}$ on hydrolysis yields dichloroacetic acid (3:6208) q.v. + MeOH (1:6120). [For studies of rate of hydrolysis under various circumstances see (5) (11).]

3:5655 (1) Schiff, Z. physik. Chem. 1, 378 (1887). (2) Cheng, Z. physik. Chem. B-24, 305 (1934). (3) Toole, Sowa, J. Am. Chem. Soc. 59, 1971-1973 (1937). (4) Wallach, Ann. 173, 299 (1874). (5) Skrabal, Monatsh. 71, 298-308 (1938). (6) Henry, Compt. rend. 101, 251 (1885). (7) Müller, Ann. 133, 160 (1865). (8) Simon, Compt. rend. 176, 585 (1923). (9) Chattaway, Irving, J. Chem. Soc. 1929, 1042, 1047. (10) Anschutz, Deschauer, Ann. 347, 6-7 (1906). (11) Skrabal, Ruckert, Monatsh. 50, 369-384 (1928).

3:5660 1,1,3-TRICHLOROPROPANE $ClCH_2.CH_2.CHCl_2$ $C_3H_5Cl_3$ Beil. I - 106 (\$\beta-Chloropropylidene (di)-chloride) I_1—I_2—

B.P. 143-144° (1)
$$D_{-1}^{18} = 1.351$$
 (1) $n_{-}^{18} = 1.474$ (1) $146-148$ ° (2) (3) $D_{15}^{15} = 1.362$ (3)

Č with alc. KOH splits out HCl yielding (2) (3) 3,3-dichloropropene-1 (3:5140), b.p. 84°, together with a little 1,3-dichloropropene-1 (3:5280), b.p. 107°.

3:5660 (1) Kirrmann, Pacaud, Dosque, Bull. soc. chim. (5) 1, 866 (1934). (2) Gustavson, J. prakt. Chem. (2) 50, 381-382 (1894) (3) van Romburgh, Bull. soc. chim. (2) 37, 100-102 (1882).

3: 5670
$$d$$
, l - α -CHLORO- α -METHYL- n - CH₃ C₅H₈OCl₂ Beil. II -307 BUTYRYL CHLORIDE CH₃. CH₂—C=O II₁— II₂— II₂— B.P. 143–144° at 749 mm. (1) $D_{-}^{14} = 1.187$ (1)

[For prepn. of \tilde{C} from α -chloro- α -methyl-n-butyric acid (3:8718) with PCl₃ see (1).] \tilde{C} on hydrolysis with aq. yields (1) α -chloro- α -methyl-n-butyric acid (3:8718) q.v.

3:5670 (1) Servais, Rec. trav. chim. 20, 59 (1901).

B.P. 143-145° (2)
$$D_4^{20} = 1.2699$$
 (1) $n_D^{20} = 1.4645$ (1) 141-143° (1) $D_4^{18} = 1.2630$ (2) $n_C^{18} = 1.4637$ (2) 77-84° at 15 mm. (2) $D_4^{12} = 1.33$ (2) $n_C^{12} = 1.4975$ (2)

[For prepn. of C (45% yield (2)) from 2-chlorobutene-2 (3:7105) (together with 55% 2,3-dichlorobutene-1 (3:9074)) with Cl₂ + NaHCO₃ at 0° (2) (3) or with Cl₂ + SnCl₄ in dark (4) see indic. refs.; for formn. of \bar{C} (28% yield (1)) from 1,2-dichlorobutane (3:7680) + sl. excess Cl₂ in dark at -17° (together with 19% 1,2,3-trichlorobutane) (3:5935) see (1); for formn. of C (18% yield (1)) from 2,3-dichlorobutane (3:7615) + sl. excess Cl₂ in dark at -17° (together with 36.5% 1,2,3-trichlorobutane (3:5935)) see (1).]

Č with solid KOH at 140° loses HCl yielding (1) mixt. of crs-2,3-dichlorobutene-2(3:5500), and trans 2,3-dichlorobutene-2 (3:7395).

3:5680 (1) Tishchenko, Churbakov. J. Gen. Chem. (U.S.S.R.) 6, 1553-1558 (1936); C.A. 31, 2165 (1937); Cent. 1937, I 3786. (2) Tishchenko, J. Gen Chem. (U.S.S.R.) 8, 1232-1246 (1938); C.A. 33, 4190 (1939); Cent. 1939, II 4222. (3) du Pont Co., Brit. 535,586, April 15, 1941; C.A. 36, 1337 (1942). (4) Levine, Cass (to du Pont Co.) U.S. 2,323,227, June 29, 1943; C.A. 38, 119 (1944).

B.P. 144.5° (1)
$$D_{-}^{13} = 1.3307$$
 (3) 144° (2) 143–145° at 763 mm. (3) 82–82.5° cor. at 102 mm. (4) 87° at 95 mm. (5) 53° at 23 mm. (5)

Pale yel, liq. with pungent odor, sol. alc., ether, acetone, CHCl₃ (1).

[For prepn. from β -chloropropionic ac. (3:0460) with PCl₃ (3) or SOCl₂ (96% yield (5)) see (3) (2) (5); from propional chloride (3:7170) + Cl_2 see (4) (9); from phosgene (3:5000) + ethylene + AlCl₃ see (1) (this method questioned by (6) (7)).

 \overline{C} over Al₂O₃ at 250° loses 1 HCl giving (35% yield (10)) (11) acryloyl chloride (3:7153).

- D β-Chloropropionic acid (3:0460): Ifts. from lgr. or pet. ether, m.p. 42°. [From C on boilg, with aq. (1).]
- \mathfrak{D} β -Chloropropionamide: unrecorded.
- \bigcirc β -Chloropropionanilide: cryst. from aq. or MeOH, m.p. 119° (8). [From \overline{C} + aniline in acetone; 90% yield (8).]
- **Φ** β-Chloropropion-p-toluidide: cryst. from MeOH, m.p. 121° (8) (2).

3:5690 (1) Pace, Gazz. chim. ital. 59, 580-582 (1929). (2) Wolffenstein, Rolle, Ber. 41, 736 (1908). (3) Henry, Compt. rend. 100, 115 (1885); J. prakt. Chem. (2) 31, 127 (1885). (4) Michael, Ber. 34, 4047-4048 (1901). (5) Fieser, Seligman, J. Am. Chem. Soc. 58, 2484 (1936). (6) Frolich, Wiezevich, Ind. Eng. Chem. 24, 16 (1932). (7) Varshavskii, Doroganyevskaya, Gazz. chim. ital. 64, 53-59 (1934). (8) Mayer, van Zütphen, Philipps, Ber. 58, 860 (1927); Mayer, Ger. 415,096, June 13, 1925; Cent. 1925, II 1094. (9) Schmidt, Schloffer (to I.G.) Ger. 738,398, July 15, 1943; C.A. 38, 3992 (1944). (10) Mowry, J. Am. Chem. Soc. 66, 371 (1944).

(11) Fikentscher (to I.G.), U.S. 2,050,752, Aug. 11, 1936; C.A. 30, 6762 (1936); Brit. 333,079,

Aug. 28, 1930; Cent. 1930, II 2830; C.A. 25, 524 (1931).

```
3:5700 ETHYL CHLOROACETATE CH<sub>2</sub>.COOC<sub>2</sub>H<sub>5</sub> C<sub>4</sub>H<sub>7</sub>O<sub>2</sub>Cl Beil. II - 197
II<sub>1</sub>-(88)
II<sub>2</sub>-(191)
```

							,
B.P.			F.P.				
144.5-144.9°	at 754.2 mm.	(1)	-26° (13)	$D_4^{20} = 1.1561 (11$	$n_{\rm D}^{20} =$	1.42162	(8)
143.8-144.2°		(2)		1.1520 (8)	1.4205	(14)
143.7-144.2°	cor.	(3)		1.1498 (14	1)	1.4203	(11)
143.6°	at 760 mm.	(4)					
143.5°	at 758 mm.	(5)		$D_{20}^{20} = 1.1573 (3)$	3)		
143°	at 756 mm.	(6)					
142.8°		(7)					
142.6-143.0°	at 750 mm.	(8)					
142.0-142.3°	at 743 mm.	(9)					
141-142.5°	at 738 mm.	(10)					
140-142°	at 735 mm.	(11)					
52°	at 20 mm.	(12)					

Colorless liq.; for constant-boilg. mixt. of \bar{C} with various org. cpds. see Beil. II₂-(191) or (4) (15) (16). — [For insecticidal actn. see (17); for use in refining of mineral oil see (18).]

[For prepn. of \bar{C} from chloroacetic acid (3:1370) with EtOH + dry HCl gas (10) cf. (72.5% yield '(22)) or H₂SO₄ (70% yield (23)) (19) or anhydrous MgCl₂ (20) see indic. refs.; from chloroacetyl chloride (3:5235) with EtOH (5) or with triethyl orthoformate (1:3241) at 100-110° (90% yield (21)) see indic. refs.; from α,β -dichlorovinyl ethyl ether (3:5540) with org. acids see (24) (25).]

[For formn. of \bar{C} from ethyl hydroxyacetate (ethyl glycolate) with PCl₅ see (26); from ethyl ammoacetate hydrochloride with NaNO₂ + excess HCl see (27); from ethyl diazoacetate with HCl (27) (28) or with HgCl₂ (70% yield (11)) see indic. refs.; from dichloroacetaldehyde monoethyl hemiacetal (3:5310) with alc. KCN at 20° (38% yield) see (29); from ethyl α -chloroacetoacetate (3:6207) with diethyl sodiomalonate see (30).]

 \bar{C} refluxed with KF yields KCl + ethyl hydroxyacetate (+ some ethyl fluoroacetate) (31); \bar{C} with MgI₂ in ether (32) or KI in alc. (3) (34) or in acetone at ord. temp. (35) yields ethyl iodoacetate, b.p. 180°. [For studies on rate of reactn. of \bar{C} with KI in acetone see (36) (37) (38); with NaI or LiI in acetone see (38).]

[\tilde{C} with Al/Hg + a trace of alc. (39) or with Mg + trace of I₂ in ether (40) or \tilde{C} with Mg + trace HgCl₂ in ether (41) yields ethyl γ -chloroacetoacetate (3:6375), b.p. 205°; \tilde{C} with NaCN (25) or KCN (42) yields ethyl cyanoacetate; \tilde{C} with ethyl sodioacetoacetate gives (56-62% yield (23)) diethyl acetosuccinate.]

[Č with 2 moles MeMgBr (but not MeMgI) in ether gives (yield: 60% (43), 38% (44)) 1-chloro-2-methylpropanol-2 (3:7752) (note, however, that Č with a large excess MeMgBr (4 moles) gives (40% yield (45)) 2-methylbutanol-3 (1:6170) (3,5-dinitrobenzoate, m.p. 74-75°)): for reactn. of Č with EtMgBr yielding (46) 3-(chloromethyl)-pentanol-3 [Beil. I-412], with isopropyl MgCl (47), or with phenyl MgBr (3 moles) yielding (48) chloromethyl-diphenyl-carbinol [Beil. VI-685] see indic. refs.]

[For use of \tilde{C} with Zn (or Zn + Cu (49)) + ketones to give by Reformatsky reactn. (50) β -hydroxy-esters see indic. refs.]

 \tilde{C} treated with aq. benzenediazonium chloride + NaOAc gives (15% yield (6)) ethyl γ -chloro- β -phenylhydrazono-acetoacetate, m.p. 92-93° (6).

Č with Me₃N in abs. alc. followed by treatment with 100% hydrazine hydrate as directed (51) (52) gives 83–89% yield (51) betaine hydrazide hydrochloride, (CH₃)₃N(Cl).CH₃--

CO.NH.NH₂ (Girard's reagent for ketones), m.p. 192°. [For corresp. reactn. using pyridine instead of Me₂N see (52).]

Č shaken in cold with 2 vols. conc. aq. NH₄OH gives (53) (54) (28) (29) (78-84% yield (55)) chloroacetamide, cryst. from aq., m.p. 119-120° (55), 120° (28). — Č htd. at 100° for ½ hr. with 2 moles aniline, cooled, aniline hydrochloride extracted with aq. gives (100% yield (56)) (57) (58) ethyl anilinoacetate (phenylglycine ethyl ester) [Beil. XII-470, XII₁-(263)], cryst. from dil. alc. (56) (57) or lgr. (58), m.p. 58° (58), 57-58° (57), 57° (56). [This prod. on boilg. with excess aniline yields (57) anilinoacetanilide (phenylglycine anilide) [Beil. XII-556], m.p. 110-111° (57).] — Č htd. with aq. benzylamine yields (59) chloroacet-N-benzylamide, m.p. 93.0-93.6° cor. (59).

[Č with ethyl carbamate ("urethane") + Na in dry ether as directed gives (51-57% yield (66)) triethyl N-tricarboxylate = N(COOC₂H₅)₃ [Beil. III-28], b.p. 146-147° at 12 mm. (66).]

C h.d. as directed (60) with K tetrachlorophthalimide yields N-(carbethoxymethyl)-tetrachlorophthalimide, ndls. from CHCl₃ on pouring into 2 vols. MeOH, m.p. 180-181° (60); C with Na phthalimide yields (61) N-(carbethoxymethyl)phthalimide, m.p. 112-113° (61); C with K 3-nitrophthalimide yields (62) N-(carbethoxymethyl)-3-nitrophthalimide, ndls. from alc., m.p. 79-80° (62).

 \bar{C} on hydrolysis (e.g., by boilg. 10 min. with N/10 aq. Ba(OH)₂ (14)) yields ethyl alcohol (1:6130) and chloroacetic acid (3:1370). [For studies on the kinetics of hydrolysis of \bar{C} under various conditions see Beil. II₂-(191-192) and (2) (14) (63) (64) (65).]

3:5700 (1) Schiff, Ann. 220, 108 (1883). (2) Timm, Hinshelwood, J. Chem. Soc. 1938, 862-869. (3) Perkin, J. Chem. Soc. 65, 423 (1894). (4) Lecat, Ann. soc. sci. Bruxelles 45, I 175, 291 (1926). (5) Willm, Ann. 102, 109-111 (1857). (6) Favrel, Bull. soc. chim. (4) 41, 1601-1603 (1927). (7) Cheng, Z. physik. Chem. B-24, 306 (1934). (8) Karvonen, Ann. Acad. Sci. Fennicae, A-10, No. 4, 20 (1916). (9) Oddo, Casalino, Gazz. chim. ital. 57, 61 (1927). (10) Pribham, Handl, Monatsh. 2, 696 (1881).

(11) Nesmeyanov, Powch, Ber. 67, 971-974 (1934). (12) Forster, Newman, J. Chem. Soc. 97, 2573 (1910). (13) Timmermans, Bull. soc. chim. Belg. 36, 507 (1927). (14) Newitt, Linstead, Sapiro, Boorman, J. Chem. Soc. 1937, 876-883. (15) Lecat, Rec. trav. chim. 45, 622 (1926). (16) Lecat, Ann. soc. sci. Bruxelles 47, I 152 (1927). (17) Roark, Cotton, Ind. Eng. Chem. 20, 512-514 (1928). (18) Ferris (to Atlantic Refining Co.), U.S. 2,062,872, Dec. 1, 1936; Cent. 1937, I 3578; C.A. 31, 849 (1937). (19) Conrad, Ann. 188, 218 (1877). (20) Petyanin, J. Gen. Chem. (U.S.S.R.) 10, 35-38 (1940); C.A. 34, 4726 (1940).

(21) Levaillant, Compt. rend. 195, 882 (1932). (22) Toole, Sowa, J. Am. Chem. Soc. 59, 1972 (1937). (23) Adkins, Isbell, Wojick, Org. Syntheses Coll. Vol. 2, (1st ed.), 262-263 (1943); 14, 38-39 (1934). (24) Crompton, Vanderstichele, J. Chem. Soc. 117, 691-693 (1920). (25) Stephens, J. Soc. Chem. Ind. 43, 313-314T, 327-328T (1924). (26) Henry, Ann. 156, 176 (1870). (27) Skinner, J. Am. Chem. Soc. 46, 736-738 (1924). (28) Curtius, J. prakt. Chem. (2) 38, 429 (1888). (29) Chattaway, Irving, J. Chem. Soc. 1929, 1042-1043. (30) Gault. Klees, Bull. soc. chim. (4) 39, 891 (1926).

(31) Swarts, Cent. 1903, I 14. (32) Bodroux, Bull. soc. chim. (3) 33, 833 (1905). (33) Kekulé, Ann. 131, 223 (1864). (34) Tiemann, Ber. 31, 825 (1898). (35) Knoll & Co., Ger. 230,172, Jan. 16, 1911; Cent. 1911, I 359. (36) Conant, Kirner, J. Am. Chem. Soc. 46, 249 (1924). (37) Conant, Kirner, Hussey, J. Am. Chem. Soc. 47, 489, 588 (1925). (38) Conant, Hussey, J. Am. Chem. Soc. 47, 482, 486 (1925). (39) Picka, Doht, Weisl, Monatsh. 27, 1245-1249 (1906). (40) Alexandrow, Ber. 46, 1022 (1913).

(41) Hamel, Bull. soc. chim. (4) 29, 396-400 (1921). (42) Henry, Bull. soc. chim. (2) 46, 62 (1886); Muller, Ann. 131, 351 (1864). (43) Henry, Compt. rend. 142, 944 (1906); Rec. trav. chim. 26, 149 (1907). (44) Dersin, Ber. 54, 3158-3159 (1921). (45) Huston, Jackson, Spero, J. Am. Chem. Soc. 63, 1459-1460 (1941). (46) Susskind, Ber. 39, 225-226 (1906). (47) Ivanov, Spassov, Bull. soc. chim. (5) 1, 1419-1424 (1934). (48) Klages, Kessler, Ber. 39, 1754 (1906). (49) Nieuwland, Daly, J. Am. Chem. Soc. 53, 1842-1846 (1931). (50) Shriner, Org. Reactions, I, 1-38 (1942).

(51) Girard, Org. Syntheses, Coll. Vol. 2 (1st ed.), 85-86 (1943); 18, 10-12 (1938). (52) Girard, Sandulesco, Helv. Chim. Acta 19, 1095-1107 (1936). (53) Scholl, Ber. 29, 2417 Note (1896).

(54) Tröger, Hille, J. prakt. Chem. (2) 71, 204 Note (1905).
(55) Jacobs, Heidelberger, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 153-154 (1941); (1st ed.), 147-148 (1932); 7, 16-17 (1927)
(56) Gault, Bull. soc. chim. (4) 3, 370 (1908).
(57) Meyer, Ber. 8, 1156-1158 (1875).
(58) Bischoff, Hausdorfer, Ber. 25, 2270 (1892).
(59) Buehler, Mackenzie, J. Am. Chem. Soc. 59, 421-422 (1937).
(60) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934).

(61) Weisz, Lanyi, Magyar Chem. Folyoirat, 39, 153-155 (1933); Cent. 1934, I 2746; C.A. 28, 5815 (1934). (62) Sah, Ma, Ber. 65, 1630-1633 (1932). (63) Sapazhinikova, J. Phys. Chem. (U.S.S.R.) 13, 174-185 (1939); C.A. 34, 311 (1940). (64) Anantakrishnan, Krishnamurti, Proc. Indian Acad. Sci. 14-A, 270-278, 279-288 (1941); C.A. 36, 1837 (1942). (65) Newling, Hinshelwood, J. Chem. Soc. 1936, 1357-1361. (66) Allen, Bell, Org. Syntheses, 24, 60-61 (1944).

3:5710 1,1,2-TRICHLORO-2-METHYLPROPANE CH₃
$$C_4H_7Cl_3$$
 Beil. I - 126 CH_3 CH_5 CH_5 CH_5 CH_5 CH_7 CH_7

B.P. M.P.
$$-6.5$$
 to -6.0° (1) $D_4^{25} = 1.2712$ (1) $145-146^{\circ}$ at 762 mm. (2) $n_D^{20} = 1.4666$ (1) $n_D^{20} = 1.4666$ (1)

[For prepn. (together with other products) from ter-butyl chloride (3:7045) + Cl_2 see (1); for formn. (32%) (together with 68% 3,3-dichloro-2-methylpropene-1) from 1-chloro-2-methylpropene-1 (3:7120) with Cl_2 + NaHCO₄ at 0° see (2).] [The product described in Beil. I-126 was very impure (1).]

Č on further chlorination yields (1) 1,1,1,2-tetrachloro-2-methylpropane (3:4725), m.p. 179°.

Č on prolonged refluxing with dil. NaOH loses ½ of its chlorine (1) but the reactn. products were not characterized.

3:5710 (1) Rogers, Nelson, J. Am. Chem. Soc. 58, 1027-1029 (1936). (2) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); C.A. 33, 4190 (1939); Cent. 1939, II 4222.

3:5725 1,4-DICHLOROBUTENE-2 Cl Cl C₄H₆Cl₂ Beil. S.N. 12 H₂C—CH=CH—CH₂
B.P. 145° (1)
$$n_{\rm D}^{30.5} = 1.4745$$
 (1) 75-76° at 40 mm. (1)

For this structure two geom, stereoisomers are theoretically possible but only Č (configuration undetermined) is known.

[For prepn. of \bar{C} together with other products) from butadiene-1,3 with Cl_2 , either directly or in CHCl₃, CS_2 , or lgr. soln. see (1) (2); the process can be controlled so as to yield little or no 1,2,3,4-tetrachlorobutane but rather a mixt. of \bar{C} and 1,2-dichlorobutene-3 (3:5350) in the ratio 1:2 (1) (2): for prepn. of \bar{C} from 1,2-dichlorobutene-3 (3:5350) via allylic transposition in pres. of metal halide cat. (3) such as AlCl₃ (4) see (3) (4).]

Č does not (1) rearr. to 1,2-dichlorobutene-3 (3:5350) even on htg. at 90° in a s.t.

C on htg. at 90° with 2 pts. solid KOH loses HCl yielding (1) 1-chlorobutadiene-1,3 (3:7210), b.p. 85° (1).

C on htg. in alc. with Zn dust yields (1) butadiene-1,3.

 \bar{C} with Cl_2 yields mainly (1) the solid form (m.p. 72°) of 1,2,3,4-tetrachlorobutane (3:1760).

 \ddot{C} on oxidn. with dil. alc. KMnO₄ or with O₃ followed by aq. gives (1) chloroacetic acid (3:1370).

3:5725 (1) Muskat, Northrup, J. Am. Chem. Soc. 52, 4043-4055 (1930). (2) Muskat (to du Pont), U.S. 2,038,593, Apr. 28, 1936; Cent. 1936, II 3358; C.A. 30, 3912 (1936). (3) I. G. Farbenindustrie, Brit. 505,573, May 12, 1939; Cent. 1939, II 1572; C.A. 33, 7822 (1939); Nicodemus, Schmidt (to I.G.), Ger. 716,961, Jan. 15, 1942; [C.A. 38, 2350 (1944)]. (4) Nicodemus (to I.G.), U.S. 2,242,084, May 13, 1941; C.A. 35, 5134 (1941).

B.P. 145° (1)
$$D_{27}^{27} = 1.1455$$
 (2) $n_D^{20} = 1.4234$ (2) (3) 142-144° at 743 mm. (2) 142.4-143.8° at 733 mm. (3)

Colorless oil, insol. aq.

140-145° (2)

[For prepn. from β -chloroethanol (3:5552) by actn. of AcCl (90% yield (4), 82% yield (5)) see (4) (5) (6); by actn. of Ac₂O at 110° see (7); for prepn. from ethylene oxide (1:6105) + AcCl see (3) (8); for prepn. from ethylene glycol diacetate (1:3511) + HCl + ht. + pressure see (9); for prepn. from ethylene + Cl₂ + Ac₂O see (2) (10); for prepn. (95.5% yield (11)) from di-(β -chloroethyl) sulfate + NaOAc + AcOH see (11); for still other misc. methods see Beil. II-128.]

[For study of reactivity toward KI in acetone at 50° and 60° see (12); for study of pyrolysis (to vinyl chloride) see (13); for conversion to ethylene oxide (1:6105) by treatment with alk. see (14) (15).]

 \overline{C} htd. at 100° for 5 hrs. with thiourea (1 mole) gives 100% yield of S-(β -acetoxyethyl)-isothiourea hydrochloride, cryst. from mixt. of alc. + acetone, m.p. 136-137° (17).

Č on hydrolysis yields β -chloroethanol (3:5552) + AcOH. [For study of hydrolysis by N/10 HCl see (16).]

N-(β-Acetoxyethyl)tetrachlorophthalimide: pl. from CHCl₃ poured into 2 vols.
 MeOH, m.p. 168-169° (18). [From C + K tetrachlorophthalimide (18).]

3:5735 (1) Simpson, Ann. 112, 149 (1859). (2) Baum, Vogt, Hennion, J. Am. Chem. Soc. 61, 1458 (1939). (3) Gustus, Stevens, J. Am. Chem. Soc. 55, 383 (1933). (4) Bogert, Slocum, J. Am. Chem. Soc. 46, 766 (1924). (5) Blicke, Blake, J. Am. Chem. Soc. 53, 1018 (1931). (6) Henry, Ber. 7, 70 (1874). (7) Ladenburg, Demole, Ber. 6, 1024 (1873). (8) Altwegg, Landrivon, U.S. 1,393, 191, Nov. 11, 1921; Cent. 1922, IV 947. (9) Britton, Coleman (to Dow Chem. Co.), U.S. 2,038,074, April 21, 1936; C.A. 30, 3837 (1936). (10) Brit. 460,720, Feb. 3, 1937; C.A. 31, 4675 (1937).

Suter, Evans, J. Am. Chem. Soc. 60, 537 (1938).
 Conant, Kirner, Hussey, J. Am. Chem. Soc. 47, 498 (1925).
 Bilger, Hibbert, J. Am. Chem. Soc. 58, 825 (1936).
 Britton, Coleman, Mate (to Dow Chem. Co.), U.S. 2,022,182, Nov. 26, 1935; C.A. 30, 737 (1936); Cent. 1936, I 3015.
 Simpson, Ann. 113, 116 (1860).
 Drushel, Bancroft, Am. J. Sci. (4) 44, 371-380 (1917); C.A. 12, 148 (1918).
 Sprague, Johnson, J. Am. Chem. Soc. 59, 2440 (1937).
 Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934).

Colorless liq.; sparingly sol. aq., sol. alc. or ether; volatile with steam.

80.0°

62.0°

55°

at 89 mm. (12)

at 45 mm. (12)

at 17 mm. (12)

55.5-56.3° at 31 mm. (16)

[For prepn. of \bar{C} from β,β -dichloroacetaldehyde (3:5180) with Al(OEt)₃ in abs. alc. (2) or with diethylzinc followed by aq. (1) see indic. refs.]

 \tilde{C} reduces NH₄OH/AgNO₃ (1) (2).

C on oxidn. with HNO3 yields (1) dichloroacetic acid (3:6208).

3:5745 (1) Delacre, Jahresber. 1887, 1247. (2) Böeseken, Tellegen, Plusje, Rec. trav. chim. 57, 75-76 (1938).

```
1,1,2,2-TETRACHLOROETHANE Cl<sub>2</sub>CH—CHCl<sub>2</sub> C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>
3:5750
                                                                                     Beil. I - 86
            (Acetylene tetrachloride;
                                                                                           I_{1}-(25)
           sym.-tetrachloroethane)
                                                                                           I_{2}-(55)
  B.P.
                                   F.P.
                                    -44^{\circ} (17) D_4^{25} = 1.5881 (12)
  147° cor.
                                   -43.8^{\circ} (4)
  146.2-146.8°
                                                          1.5869 (19)
               at 760 mm.
                              (2)
                                              (5)
                                                                    (20)
                                   -43.5° (18)
                              (3)
  146.35°
                                                          1.58658 (5)
                                    -42.5° (6)
                                                                           n_{\rm D}^{24} = 1.501
  146.3°
               at 758 mm. (17)
                                                                                               (21)
  146.25°
                                            (18)
                             \langle 4 \rangle
                                                                           n_{\rm D}^{20} = 1.49509
  146.2-146.7° cor.
                                                       = 1.5966 (2)
                                                                                              (22)
               at 756 mm. (20)
                                                          1.59457 (5)
                                                                                  1.4947
                                                                                              (13)
  146.20°
               at 760 mm. (5) (6)
                                                          1.5943
                                                                   (9)
                                                                                  1.49419
                                                                                                (8)
  145.6°
                             (7)
                                                                                  1.49415
                                                                                                (2)
  145.2°
               at 748 mm.
                             (8)
                                                                                  1.4940
                                                                                                (9)
  145.2°
               at 737 mm.
                            (9)
                                                                           n_D^{18.5} = 1.49490 (23)
  145-146°
               at 753 mm. (10)
  145.0°
                            (11)
  144.7°
                                                                           n_{\rm D}^{17} = 1.49559 \quad (24)
               at 751 mm. (12)
  144.5°
                            (13)
                                                  D_4^{15} = 1.60255 (5)
                                                                           n_{\rm D}^{15} = 1.49678
  144.0-144.8°
                            (14)
                                                                                               (5)
  143.5-144°
                            (15)
                                                          1.6015 (12)
  140.6°
               at 675 mm. (12)
                                                  For D_4^l from -21^\circ
                                                                           For n_{\alpha}^{l} from 13-25°
  136.0°
               at 594 mm. (12)
                                                  to 128° see (17).
               at 502 mm (12)
  130.0°
                                                                           see (11).
  125.3°
               at 435 mm. (12)
  120.5°
               at 372 mm. (12)
  115.0°
               at 313 mm. (12)
  108.0°
               at 252 mm. (12)
               at 203 mm. (12)
  102.0°
  90.0°
               at 132 mm. (12)
```

Note: Care must be taken not to confuse \bar{C} with tetrachloroethylene (3:5460) or with 1,1,1,2-tetrachloroethane (unsym.-acetylene tetrachloride (3:5555)).

Colorless liq. with odor similar to that of chloroform. — [For vapor press. of C at intervals over range 20–145° see (25); for study of thermal conductivity see (26).]

 \tilde{C} is very spar. sol. aq.: e.g., 100 g. H_2O at 20° dis. 0.288 g. \tilde{C} ; at 55-56° dis. 0.336 g. \tilde{C} (27); 1 g. \tilde{C} is sol. at 25° in 350 g. aq. (101); for soly. of H_2O in \tilde{C} at 0°, 25°, and 30° as

detd. by Karl Fischer reagt. see (28). — \bar{C} is easily volatile with steam (for use in detn. of H₂O see below).

MISCELLANEOUS PHYSICAL PROPERTIES

[For soly. in \bar{C} of dry gaseous HCl (14) (15), H₂S (14), or O₂ (29) see indic. refs.; for soly. in \bar{C} at 11-25° of I₂ (30) and use of such solns. in detn. of iodine number (31) see indic. refs.; for adsorption by activated carbon of I₂ from solns. in \bar{C} see (32).]

[For study of influence of vapors of \bar{C} on the explosion limits of mixtures of air with hydrogen (33), acetylene (33), methane (33) (34) (35), or carbon monoxide (33) (36) see indic. refs.]

[For prepn. of and comparison with \bar{C} of sym.-dideuteroiotetrachloroethane, $Cl_2C(D)$.- $C(D)Cl_2$, see {9}.]

Binary systems contg. $\bar{\mathbb{C}}$. [For f.p./compn. data and/or diagrams on systems $\bar{\mathbb{C}}$ + 1,2-dichloroethane (ethylene dichloride) (3:5130) (18); $\bar{\mathbb{C}}$ + 1,1,2-trichloroethane (3:5330) (18); $\bar{\mathbb{C}}$ + pentachloroethane (3:5880), eutectic, f.p. -73°, contg. 40.1% $\bar{\mathbb{C}}$ (18); $\bar{\mathbb{C}}$ + cis-dichloroethylene (3:5042) (37); $\bar{\mathbb{C}}$ + trans-dichloroethylene (3:5028) (37); $\bar{\mathbb{C}}$ + p-dichlorobenzene (3:0980) (38); $\bar{\mathbb{C}}$ + 1,2-dibromoethane (ethylene dibromide) (18); $\bar{\mathbb{C}}$ + 1,1,2,2-tetrabromoethane (acetylene tetrabromide) (18); $\bar{\mathbb{C}}$ + succinonitrile (18); or $\bar{\mathbb{C}}$ + succinic acid (1:0530) (18) see indic. refs. — For study of system $\bar{\mathbb{C}}$ + naphthalene (1:7200) at 30° under press. up to 1000 atm. see (39).]

 \bar{C} with various org. cpds. forms binary azeotropes [e.g., \bar{C} with anhydrous formic acid (1:1005) forms a const.-boilg. mixt., b.p. 99.25° at 760 mm., contg. 32 wt. % \bar{C} (40): note that \bar{C} with AcOH (1:1010) does not form a const.-boilg. mixt. (41) (the data listed by "Int. Crit. Tables" for such an azeotrope is actually for the mixt. AcOH + tetrachloroethylene); \bar{C} with propionic acid (1:1025) forms a const.-boilg. mixt., b.p. 140.4° at 760 mm., contg. abt. 40 wt. % \bar{C} (12); for other azeotropes see Beil. II₂-(56). — Note that no record of forms. of azeotropes of \bar{C} with MeOH or EtOH can be found.]

Ternary systems contg. \tilde{C} . [For soly. data and diagrams of system \tilde{C} + acetone (1:5400) + aq. see (43).]

USES OF C

Č is widely used in industry as a solvent and as an intermediate in the manufacture of various other chlorinated solvents, notably trichloroethylene (3:5170); for additional examples of special uses see also below.

 $\bar{\mathbf{C}}$ is frequently employed as solvent in certain types of Friedel-Crafts reactions or phthalic anhydride condensations [for study of use of $\bar{\mathbf{C}}$ as solvent in Friedel-Crafts condensation of phenol with high-mol.-wt. acyl chlorides see (44)].

[For use of \tilde{C} as swelling agent for rubber (45), in prod. of films from rubber hydrochloride (46), in prod. of cellulose acetate by pptn. from \tilde{C} with hydrocarbons (47) (note that acetylcelluloses give with \tilde{C} crystalline addition prods. (48)), together with aliphatic monohydric alcs. as solv. for cellulose alkyl ethers (49), in prepn. of transparent cellulose acetate plastics (50) see indic. refs. — For soly. of various polymers in \tilde{C} see (56).]

[For use of \bar{C} as catalyst in condensation of phenol with formaldehyde (51) or furfural (52) see indic. refs.]

[For use of \bar{C} with petroleum naphtha as a dry-cleaning fluid (53), for use of \bar{C} as a rust remover (54), as means of removing mud barriers in oil wells (55), or as an immersion fluid in opt. crystallog. (21) see indic. refs.]

[For use of \bar{C} (57) (58) or stable aq. emulsions of \bar{C} (59) as weed killers see indic. refs.] [For studies of use of \bar{C} in detn. of the observation in cacao see (60) (61) (62) (63).] [For use of \bar{C} as anti-moth prod. (64), as a component of insecticides (65), together with

CS₂ and chlorobenzene (3:7903) as insecticide (66), or together with 20% trichloroethylene (3:5170) as a fumigant and insecticide (67) see indic. refs.]

[For studies on antiseptic, bactericidal, and disinfectant action of C see (68) (69) (70).]

 \bar{C} is also employed for the detn. of H_2O by distillation; note that besides being non-inflammable \bar{C} is also much denser than water which for some applications of this method is advantageous. — [For general discussion and examples of this procedure see (226) (70) (71) (72) (73) (74) (75); for comparison of results with those obtd. by oven drying see (76); for application to detn. of H_2O in liquid and solid fuels (77) (78), in glycerol (79) (80), in liquid glue (81), in cereal (82), in dried apples (83), in cooking salt (84) see indic. refs.]

TOXICITY AND PHYSIOLOGICAL ACTION OF C

 \bar{C} is the most toxic of the group of chlorinated hydrocarbons (85) and produces marked pathological alterations in gastrointestinal tract, liver, and kidneys. — [Detailed discussion of this aspect of \bar{C} is beyond the scope of this treatment except to cite references (229) (227) (232) and (85)-(99), incl. (note that articles on this topic prior to 1930 are omitted).] [For discussion of fate of \bar{C} in body see (100). — Note also that \bar{C} (in sharp contrast to

the closely related tetrachloroethylene (3:5460)) has no efficacy as anthelmintic for hook-worms (101).]

[For actn. of C on alc. fermentation see (102) (103); for actn. on invertase see (104).]

DETERMINATION OF C

Some methods for the detn. of \bar{C} involve conversion of all of its halogen to chloride ion and subsequent volumetric or gravimetric detn. of the latter; e.g., for methods based on initial pyrolytic decomposition see (105) (89) (106) (107); for methods based on dehalogenation of \bar{C} with Na + ethanolamine in dioxane see (108) (230) (note that use of Na in liq. NH₃ causes some cyanide formn. (109)). — For detn. of \bar{C} by means of elimination of 1 HCl with cold alc. KOH see (110). — For detn. of \bar{C} by means of the Fujiwara color reactn. with NaOH/pyridine see (111). — Note that \bar{C} does not respond to the R + H "Tri-Per-Analyzer" (a recording ultra-violet photometer) (112). — For further comments on detection of \bar{C} see below under color tests.

PREPARATION OF C

 $\bar{\mathbf{C}}$ is one of a large family of "chlorinated solvents" now available from industrial sources. — The most-studied method of prepn. is that from acetylene by controlled addition of chlorine, although variants of this method are employed and other starting prods. (see below) are sometimes used. — $\bar{\mathbf{C}}$ is also obtained as a by-prod. of the manufacture of the comml. mixt. (3:5030) of the two stereoisomeric 1,2-dichloroethylenes, cis (3:5042) and trans (3:5028), 1,1,2-trichloroethane (3:5330), etc.

From acetylene by addition of chlorine. Under suitable controls to avoid explosion and with the assistance of a wide variety of catalysts \bar{C} is manufactured from acetylene by reaction with Cl₂. — [For a concise review of the general nature and difficulties of this general method see (113).]

[For important general articles on this synthesis see (114)-(122) incl. — For examples of patents employing this method see refs. (123)-(138) incl.; for special test of Ger. 204,833 (131) see (118) (120); for test of Ger. 154,677 (133) see (119) (120).]

From acetylene by other means. [For prepn. of \bar{C} from acetylene with excess SbCl₅ (139) (234) with SbCl₃ + SbCl₅ (140), with NOCl (4 moles) at 350° (141), with aq. NaOCl soln. (142), with S₂Cl₂ + Fe powder in cold (143) (144) see indic. refs.]

From ethylene. [For formn. of \bar{C} from ethylene + Cl₂ (as by-prod. of prepn. of ethylene chlorohydrin (3:5552)) (145), from ethylene + Cl₂ (as by-product of prepn. of 1,1,2-trichloroethane (3:5330)) (146) (147), from ethylene + Cl₂ (as by-prod. of a three-part process for combined prepn. of \bar{C} + ethyl chloride) (198) see indic. refs.

From dichloroethylenes. [For prepn. of C from cis-dichloroethylene (3:5042) in vapor phase at 95° in light of 4360 Å with Cl₂ (in absence of O₂) (149), or in liq. phase with SO₂Cl₂ (1½ moles) in pres. of trace of dibenzoyl peroxide refluxed 3 hrs. in dark (85% yield (150)), see indic. refs.]

[For prepn. of \bar{C} from trans-dichloroethylene (3:5028) in vapor phase at 80-95° in light of 4358 Å with Cl₂ see (151).]

[For prepn. of \bar{C} from ord. mixt. (3:5030) of both stereoisomeric dichloroethylenes with Cl₂ (13) in light of 4360 Å (152) see indic. refs.]

From trichloroethylene. [For formn. of \bar{C} (together with other prods.) from trichloroethylene (3:5170) + AlCl₃ + HCl gas at 50° see (153).]

From 1,2-dichloroethane (ethylene (di)chloride). [For prepn. of \bar{C} from ethylene (di)chloride (3:5130) with Cl₂ (148) in u.v. light see (154).]

From miscellaneous starting points. [For formn. of \bar{C} usually together with other prods. from dichloroacetaldehyde (3:5180) with PCl₅ (1), from " β -chlorovinyl iodochloride" (ClCH—CH.ICl₂) on warming (16), from 1,1,2-trichloro-2-iodoethane on distn. at ord. press. (155), from 1,2-di-iodoethylene with Cl₂ (156), or from 1,1,2-trichloroethane (3:5330) with Cl₂ + AlCl₃ at 70-80° (231) see indic. refs.]

STABILIZATION OF C

[For patents on stabilization of \bar{C} by addition of small amts. of phenols, aminophenols, etc. (157), or by addn. of less than 0.1% alkylamines (158) see indic. refs.]

CHEMICAL BEHAVIOR OF C

Pyrolysis without catalyst. \bar{C} on protracted reflux (20 days (159)) or techn. \bar{C} on repeated distn. (160) leaves a residual high-boilg. fraction ("Tetranachlauf") consistings mainly of 1,1,2,3,4,4-hexachlorobutane (3:3155), ndls. from alc., m.p. 107° (159) (160), presumably formed by elimination of 1 Cl atom from each of 2 moles of \bar{C} .— $[\bar{C}$ htd. in s.t. at 300° for 15 hrs. yields (139) trichloroethylene (3:5170); \bar{C} in s.t. at 360° for 100 hrs. yields (139) hexachlorobenzene (3:4939).]

Pyrolysis in pres. of various catalysts or HCl acceptors. \bar{C} on suitable htg. particularly in the pres. of dehydrohalogenating catalysts or acceptors of the hydrogen chloride formed loses 1 mole HCl yielding trichloroethylene (3:5170). (For elimination of HCl by chemical means such as alk., NH₃, etc., see below.)

[E.g., \bar{C} over pumice at 700° (161), over pumice contg. Cu₂(PO₄)₃ at 450-500° (162), over ThO₂ below 390° (163) cf. (164), over BaCl₂ at 300° (165), over bone char at 300-310° (166), over activated carbon at 200-300° (167), 260° (168) (note yield diminishes with increasing temp. (233)) or 500° (169), or over suitable cat. (148) loses HCl yielding trichloroethylene (3:5170). — Note also that pure \bar{C} on long exposure to u.v. light loses HCl bimolecularly yielding (159) 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), m.p. 80°.]

[\bar{C} + acetylene over cat. at 250° loses HCl yielding (167) trichloroethylene (3:5170) + vinyl chloride (3:7010); \bar{C} with MeOH over Al₂O₃ at 280° loses HCl yielding (170) trichloroethylene (3:5170) + methyl chloride (3:7005).]

Dehydrogenation. [C with air over pumice contg. CuCl₂ at 430-450° (171), or with Cl₂ over activated carbon contg. CuCl₂ at 300-320° (172), or with hexachloroethane (3:4835) over cat. at 200-400° (173) loses its two hydrogenations yielding tetrachloroethylene (3:5460).]

(Partial) dehalogenation. [\tilde{C} with H_2 over Ni at 300-320° (174), or \tilde{C} with Fe or Al + aq. (175) (176) or Zn + aq. (176) (177), or \tilde{C} with acetylene over hydrogenating cat. (such as Ni) on activated carbon at 350° (178) preferably in pres. of aq. vapor (179) or on electrolytic reductn. in pres. of ZnCl₂ (235) (236) loses 1 chlorine from each carbon atom yielding a mixt. (3:5030) of the two stereoisomeric 1,2-dichloroethylenes. — Note that \tilde{C} with Zn in alc. yields (180) acetylene.]

Oxidation. [C with air in ultra-violet light yields (181) (182) dichloroacetyl chloride (3:5290) (or in pres. of aq. dichloroacetic acid (3:6208)), accompanied by small amts. of oxalic acid and an octachlorobutane, m.p. 81°. (Note also that pure C on long exposure to u.v. light loses HCl bimolecularly yielding (159) 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), m.p. 80°.)]

[For behavior of C with CrO₃/H₂SO₄ (183) or over hot CuO (184) see indic. refs.]

BEHAVIOR WITH HALOGENS

Fluorination. [$\bar{\mathbf{C}}$ with F₂ gas at 50° for 14 hrs. gives (185) 1-fluoro-1,1,2,2-tetrachloro-ethane, b.p. 115.5-116.5°, $D_4^{20}=1.6218$, $D_D^{20}=1.4487$, and 1,2-difluoro-1,1,2,2-tetrachloro-ethane, b.p. 92-93°, m.p. 24-25°, together with various other prods. — For fluorination of $\bar{\mathbf{C}}$ with SbF₃ + SbCl₅ see (186)).]

Chlorination. [\bar{C} with Cl₂ (139) in CCl₄ soln. (187), in u.v. light (188) or X-radiation (189), or over activated carbon at 300-400° (190) (191), or in liq. phase at 60-70° (192), or with Fe at 20-80° (192), or with AlCl₃ at 20-100° (192), or under reflux at 120° (80% yield (193)), or \bar{C} with anhydr. FeCl₃ on htg. in s.t. (194), or even \bar{C} with aq. bleaching powder (192) yields hexachloroethane (3:4835).]

BEHAVIOR WITH H2SO4

Č with fumg. H₂SO₄ (65% SO₃) in pres. of H₂SO₄ at 50-60° readily gives (198) (yields: 70-73% (195), 32% (196), 30% (197)) glyoxal sulfate, O₂SO₂CH—CHO₂SO₂, [Beil. I₂-(818)], ndls. from ClSO₃H, m.p. 176-177° (198), ndls. with 1 AcOH, m.p. 121-122° from AcOH, the solv. of crystn. being lost completely in vac. over NaOH (199).

BEHAVIOR WITH ALKALINE REACTANTS

 \bar{C} under influence of many alk. reactants loses 1 mole HCl; this reacta. is used for the manufacture of trichloroethylene (3:5170) (see also above under pyrolysis of \bar{C}) and also by titration of the HCl or estimation of chloride ion formed as a diagnostic test for \bar{C} (see below).

Č on htg. with aq. alk. or alk. carbonates (200) in pres. of tetraethylene glycol as promoter (228) or with aq. Ca(OH)₂ or alk. carbonates (200) (201) (234) (114) (for test of Ger. 171,900 (200) see (202) (120)), or Č with alc. KOH (203) cf. (122) or alc. NaOEt (203), loses 1 mole HCl yielding trichloroethylene (3:5170); note that in use of alc. alkali, distn. gives the const.-boilg. mixt. of EtOH with trichloroethylene, b.p. 70-71°, from which latter is separated by washing with aq. and subsequent drying over CaCl₂ (203).

Č with EtOH/NaOH or EtOH/NaOEt (204) cf. (205), or Č with 1 N EtOH/KOH in xylene (110), instantly and quant. splits out 1 HCl at room temp.; note that this does not occur with cis-dichloroethylene (3:5042), trans-dichloroethylene (3:5028), trichloroethylene (3:5170) or tetrachloroethylene (3:5460), chloroform (3:5050), or carbon tetrachloride (3:5100), but does occur in analogous fashion with pentachloroethane (3:5880) (110).—
[For rate of reactn. of Č with KOH in 95% EtOH at 90° see (206).]

Note, however, that C in acetone with excess standard alk. refluxed 3 hrs., then residual alk. titrated back, uses 5 equivalents of alk. (207); this surprising result is presumably to

be attributed to hydrolysis of \bar{C} to glyoxal followed by disproportionation of latter to sodium glycolate: cf. (208).

Č with solid KOH on htg. yields (203) dichloroethylene (3:5030), trichloroethylene (3:5170), tetrachloroethylene (3:5460), together with a spontaneously inflammable gas which may be chloroacetylene (3:7000). — Č with anhyd. KOH in xylene at 80° under N₂ gives (209) a little dichloroacetylene (3:5010) (may be carried out as a lecture experiment (209)).

BEHAVIOR OF C WITH NH3 AND AMINES

[\overline{C} with excess NH₃ gas in pres. of aq. (210), or with aq. NH₄OH htd. under press. (210) (120), or with liq. NH₃ at -40° (211) (212), or with dry pyridine on reflux (182) loses HCl giving (yields: 92% (211) 92-96% (210)) trichloroethylene (3:5170).]

[\bar{C} htd. with aniline + aq. Ca(OH)₂ at 140-190° under press. yields (213) a mixt. of the calcium salt of N-phenylglycine and N-phenylglycine anilide, cf. (122); since this reaction really involves conversion of \bar{C} by loss of HCl to 1,1,2-trichloroethylene (3:5170) and reactn. of latter with aniline see 3:5170 for details.]

 \bar{C} with excess phenylhydrazine on stdg. at ord. temp. evolves N₂, ppts. phenylhydrazine hydrochloride, and yields C₆H₆ (110); the full mechanism of this behavior seems never to have been established, but the same three prods. are also similarly obtd. from pentachloroethane (3:5880) and hexachloroethane (3:4835).

[For rate of reactn. of Č with piperidine in 95% EtOH at 90° see (206).]

BEHAVIOR OF C WITH METALS

[For survey of action of \bar{C} on various common metals (214) (215) in pres. of moisture (223) see indic. refs.]

Č with Na or K or their alloys may (like many other polychloro compounds) explode under certain conditions [for extensive studies of this behavior including sensitivity to mechanical shock see (216) (217)].

BEHAVIOR OF C WITH METAL SALTS

[C with AlCl₃ at 110° undergoes partial rearr. (218) to the isomeric 1,1,1,2-tetrachloroethane (3:5555). — C with freshly prepared anhyd. AlBr₃ on htg. below b.p. of C yields (219) 1,1,2,2-tetrabromoethane (acetylene tetrabromide) [Beil. I-94, I₁-(30), I₂-(66)].

C with N/15 AgNO₃ in 95% EtOH shows no reactn. even after 12 hrs. at 90° (206) cf. (80).

MISCELLANEOUS

[\bar{C} does not react with excess Hg di-p-tolyl (220). — \bar{C} with excess C_6H_5MgBr yields 1,1,2,2-tetraphenylethane [Beil. V-739, V_1 -(371), V_2 -(673)] (221) cf. (222).]

COLOR REACTIONS OF C

With cyclopentanol (1:6412). Č (1 drop) with cyclopentanol (2 ml.) + trace solid NaOH, boiled 25 secs., cooled, acidified with AcOH or 85% H₂SO₄, stood 1 min., shaken gives (224) green color. [Note that this same response is also shown by 1,1,2-trichloroethylene (3:5170) but not by methylene dichloride (3:5020), CHCl₃ (3:5050), CCl₄ (3:5100), ethylene dichloride (3:5130), pentachloroethane (3:5880), cis-(3:5042) or trans- (3:5028) 1,2-dichloroethylene, or tetrachloroethylene (3:5460); for sensitivity for C see (224).]

With pyridine + NaOH (Fujiwara reagt.) [For detn. of \bar{C} with Fujiwara reagt. see (111); for relative sensitivity of Fujiwara reagt. to \bar{C} as compared to CHCl₃ (3:5050),

CCl₄ (3:5100), 1,1,2-trichloroethane (3:5330), trichloroethylene (3:5170), and tetrachloroethylene (3:5460) see (100).

With NH₄OH/CuCl. Note that C with NH₄OH/CuCl does not give blue color within 5 min. (225) (dif. from pentachloroethane (3:5880) q.v.).

3:5750 (1) Paterno, Pisati, Gazz. chim. ital. 1, 463-464 (1871); J. prakt. Chem. (2) 4, 175-178 (1871). (2) Mathews, J. Am. Chem. Soc. 48, 569 (1926). (3) Lecat, Rec. trav. chim. 45, 624. 625, Note 28 (1926). (4) Timmermans, Bull. soc. chim. Belg. 27, 334-343 (1914); Cent. 1914, I 618. (5) Timmermans, Martin, J. chim. phys. 23, 773-774 (1926). (6) Timmermans, Bull. soc. chim. Belg. 36, 504 (1927). (7) Walden, Werner, Z. physik. Chem. 111, 469 (1924). (8) Smyth, McAlpine, J. Am. Chem. Soc. 57, 979 (1935). (9) Breuer, J. Am. Chem. Soc. 58, 1290 (1936). (10) Bonino, Gazz. chim. ital. 55, 342 (1925).

(11) Hamai, Bull. Chem. Soc. Japan 8, 297-306 (1933). (12) Herz, Rathmann. Chem. Ztg. 36, 1417 (1912). (13) Kharasch, Norton, Mayo, J. Org. Chem. 3, 53 (1938). (14) Bell. J. Chem. Soc. 1931, 1373-1377. (15) Hamai, Bull. Chem. Soc. Japan 10, 5-16 (1935). (16) Howell. J. Am. Chem. Soc. 45, 185-187 (1923). (17) Jaeger, Z. anorg. allgem. Chem. 161, 59 (1917). (18) Timmermans, Vesselovsky, Bull. soc. chim. Belg. 40, 506-507 (1931). (19) Walden, Gloy, physik. Chem. A-144, 406 (1929). (20) Walden, Swinne, Z. physik. Chem. 82, 281 (1913).
 Emmons, Am. Mineral. 14, 482-483 (1929). (22) Eckart, Brennstoff-Chem. 4, 24-25

(1923); C.A. 17, 2356 (1923). (23) Cotton, Mouton, Ann. chim. (8) 28, 236 (1913). (24) Veley, Proc. Roy. Soc. London, B-82, 217-225 (1910). (25) Nelson, Ind. Eng. Chem. 22, 971 (1930). (26) Bates, Hazzard, Palmer, Ind. Eng. Chem. 33, 375-376 (1941). (27) van Arkel, Vles, Rec. trav. chim. 55, 410 (1936). (28) Staverman, Rec. trav. chim. 60, 836-841 (1941); Cent. 1942, I 1352; C.A. 37, 2638 (1943). (29) Fischer, Pfleiderer, Z. anorg. allgem. Chem. 124, 68 (1922). (30) Margosches, Hinner, Friedmann, Z. anorg. allgem. Chem. 137, 87-90 (1924).

(31) Margosches, Baru, J. prakt. Chem. (2) 103, 219 (1921/2). (32) Trividic, Rev. gén. collordes 7, 67-73 (1929); Cent. 1929, I 2862. (33) Jorissen, Meuwissen, Rec. trav. chim. 44, 132-140 (1925). (34) Coward, Jones, Ind. Eng. Chem. 18, 970-974 (1926). (35) Jorissen, Velisek, Rec. trav. chim. 43, 85-86 (1924). (36) Langen van der Valk. Rec. trav. chim. 48, 201-219 (1929). (37) Timmermans, Bull. soc. chim. Belg. 36, 187 (1927). (38) Timmermans, Bull. soc. chim. Belg. 43, 633 (1934). (39) Cohen, deMeester, Moesveld, Z. physik. Chem. 114, 321-333 (1924); 108, 104-107 (1924); Rec. trav. chim. 42, 779-783 (1923). (40) Lecat, Ann. soc. sci. Bruxelles 48, I, 119, 122 (1928).

(41) Lecat, "L'Azeotropism," 1918, p. 68. (42) Lecat, Ann. soc. sci. Bruxelles 49, 21 (1929). (43) Othmer, White, Trueger, Ind. Eng. Chem. 33, 1242-1247 (1911). (44) Ralston, Ingle, McCorkle, J. Org. Chem. 7, 457-461 (1942). (45) Dubosc, Caoutchouc & gutta-percha 16, 9815-9819, 9999-10003 (1919); Cent. 1919, IV 413-414; C.A. 14, 868 (1920). (46) Bradley, Mc-Gavack (to Naugatuck Chem. Co.), U.S. 1,519,659, Dec. 16, 1924; Cent. 1925, I 1459; C.A. 19, 446 (1925). (47) Mork, Coffin (to Lustron Co), U.S. 1,551,112, Aug. 25, 1925; Cent. 1925, II 2331; C.A. 20, 115 (1926). (48) Hess, Z. angew. Chem. 37, 998-999 (1924). (49) Stinchfield (to Eastman Kodak Co.), U.S. 1,432,364, Oct. 17, 1922; Cent. 1923, II 358; C.A. 17, 341 (1923). (50) Malone, Carroll (to Eastman Kodak Co.), U.S. 1,575,778, March 9, 1926; Cent. 1926. II 137; C.A. 20, 1522 (1926).

(51) Steindorff, Balle (to M.L.B.), Ger. 365,286, Dec. 14, 1922; Cent. 1923, II 922; not in C.A. (52) Bakelite Gesellschaft, Austrian 86,764, Dec. 27, 1921; Cent. 1922, IV 714; not in C.A. (53) Youtz (to Standard Oil Co.), U.S. 2,031,145, Feb. 18, 1936; Cent. 1936, II 898; C.A. 30, 2408 (1936). (54) Boynton, U.S. 1,715,589, June 4, 1929; C.A. 23, 3783 (1929): French 675,567, Feb. 12, 1930; Cent. 1930, I 2967; [C.A. 24, 2849 (1930)]. (55) Bertness, Johnston, Newton (to Socony-Vacuum Oil Co.), U.S. 2,278,909, April 7, 1942; C.A. 36, 5997 (1942). (56) Marvel, Dietz, Copley, J. Am. Chem. Soc. 62, 2273-2275 (1940). (57) Ressler (to du Pont Co.). U.S. 2,110,842, March 8, 1938; Cent. 1938, I 4710; C.A. 32, 3546 (1938). (58) Bakke, J. Am. Chem. Soc. Agron. 33, 759-761 (1941); C.A. 35, 7637 (1941). (59) Elston (to du Pont Co.), U.S. 2,140,519, Dec. 20, 1938; Cent. 1939, I 3247; C.A. 33, 2648 (1939). (60) Humphries, Ann. Rept. Cacao Research 8, 38-39 (1938); Cent. 1939, II 3355; C.A. 34, 588 (1940).

(61) McDonald, 6th Ann. Rept. Cacao Research 1936, 43-44; Cent. 1937, II 3253; C.A. 32, 969 (1938). (62) Wadsworth, Analyst 47, 152-163 (1922); Cent. 1922, IV 174; C.A. 16, 1995 (1922). (63) Wadsworth, Analyst 46, 32-37 (1921); Cent. 1921, II 907; C.A. 15, 1170 (1921). (64) Burgess, J. Soc. Dyers Colourists 51, 88 (1935). (65) Mosely, U.S. 1,395,860, Nov. 1, 1921; Cent. 1922, IV 934; [C.A. 16, 610 (1922)]. (66) Salzbergwerke Neu-Stassfurt, Austrian 94,342, Sept. 25, 1923; Cent. 1924, I 1585; not in C.A. (67) Balaze, Austrian 146,204, June 25, 1936; Cent. 1936, II 3351; not in C.A.: Jugoslav. 12,078; Cent. 1936, I 4794. (68) Rimpau, Plochmann, Schneider, Arch. Hyg. 107, 268-276 (1932); Cent. 1932, II 389; C.A. 26, 4624 (1932). (69) Gabbano, Z. Hyg. Infectionskrankh. 109, 183-193 (1928); Cent. 1928, II 2668; not in C.A. Joachimoglu, Biochem. Z. 124, 130-136 (1921); Cent. 1922, I 363; C.A. 16, 946 (1922).

(71) Tausz, Rumm, Z. angew. Chem. 39, 155-156 (1926). (72) Pritzker, Jungkunz, Chem. Ztg. 53, 603 (1929). (73) van der Werth, Chem. Ztg. 52, 23-24 (1928). (74) Lepper, Z. Untersuch. Lebensm. 59, 79-81 (1930). (75) Lundin, Chem. Ztg. 55, 762-763 (1931). (76) Metzger, Landw. Jahrb. Schweiz 45, 625-632 (1931); Cent. 1932, I 1287; C.A. 28, 4006 (1934). (77) Tausz, Rumm, Gas u. Wasserfach, 71, 417-420 (1928); Cent. 1928, I 3019; C.A. 22, 2651 (1928). (78) Friedrichs, Chem. Ztg. 53, 287 (1929). (79) Berth, Chem. Ztg. 51, 975-976 (1927). (80) Riesener, Kessen, Chem. Ztg. 52, 243-244 (1928); Cent. 1928, II 1052.

(81) Kingman, Ind. Eng. Chem. 18, 93-94 (1926). (82) Tucker, Burke, Analyst 60, 663-667 (1935). (83) Pritzker, Jungkunz, Z. Untersuch. Lebensm. 57, 520-524 (1929). (84) Pritzker, Jungkunz, Mitt. Lebensm. Hyg. 20, 65-69 (1929); Cent. 1929, II 609; C.A. 24, 1315 (1930). (85) McConnell, J. Am. Med. Assoc. 109, 762 (1937). (86) Forbes, Brt. Med. J. 1943, I 348-350; C.A. 37, 435 (1943). (87) Schwander, Arch. Gewerbepath. Gewerbehyg. 7, 109-116 (1939); Cent. 1939, II 1331; not in C.A. (88) Freitag, Rayon Text. Monthly 18, 543-545 (1937); Cent. 1937, II 3928; not in C.A. (89) Gasg, Bull. trav. soc. pharm. Bordeaux 75, 87-101 (1937); Cent. 1937, I 5006; C.A. 32, 3047 (1938). (90) Burgi, Wien. klin. Wochschr. 49, 1545-1548 (1936); Cent. **1937.** I 3515; not in C.A.

(91) Barsoum, Saad, Quart. J. Pharmacol. 7, 205-214 (1934); Cent. 1934, II 2550; C.A. 28, 6194 (1934). (92) Zangger, Sammlung Verguftungsfällen 5, Part A, 195-196 (1934); Cent. 1935, I 1415; not in C.A. (93) Lejeune, Arch. Gewerbepath. Gewerbehyg. 5, 274-285 (1934); Cent. 1934, II 279; not in C.A. (94) Muller, Arch. Gewerbepath. Gewerbehyg. 2, 326-329 (1931); Cent. 1931, II 1449; not in C.A. (95) Zöllinger, Arch. Gewerbepath. Gewerbehyg. 2, 298-325 (1931); Cent. 1931, II 1450; not in C.A. (96) Lutz, Arch. Gewerbepath. Gewerbehyg. 1, 740-748 (1931); Cent. 1931, I 2639; not in C.A. (97) Zangger, Schweiz. med. Wochschr. 1930, 193-201; C.A. 25, 4071 (1931); not in Cent. (98) Zangger, Schwerz. med. Wochschr. 61, 748-761 (1931); C.A. 26, 3050 (1932); not in Cent. (99) Lutz, Z. angew. Chem. 43, 807 (1930). (100) Barrett, Cunningham, Johnston, J. Ind. Hyg. Toxicol. 21, 479-490 (1939).

(101) Wright, Schaffer, Am. J. Hug. 16, 374-380 (1932). (102) Mameli, Mossini, Giorn. chim. ind. applicata 14, 450-455 (1932); Cent. 1933, I 2883, [CA. 27, 805 (1933)]. (103) Plagge, Biochem. Z. 118, 129-143 (1921); C.A. 15, 2894 (1921); not in C.A. (104) Bonino, Mazzucchetti, Arch. biol. 2, 71-80 (1926); Ber. ges. Physiol. 37, 883-884 (1926); Cent. 1927, I 2084; not in C.A. (105) Winteringham, J. Soc. Chem. Ind. 61, 190-192 (1942); C.A. 37, 1951 (1943). (106) Smyth, Ind. Eng. Chem., Anal. Ed. 8, 379 (1936). (107) Elkins, Hobby, Fuller, J. Ind. Hyg. Toxicol. 19, 474-485 (1937). (108) Winteringham, J. Soc. Chem. Ind. 61, 186-187 (1942); C.A. 37, 1951 (1943). (109) Dains, Brewster, J. Am. Chem. Soc. 42, 1576 (1920). (110) Gowing-Scopes,

Analyst 39, 385-388 (1914).

(111) Barrett, J. Ind. Hyg. Toxicol. 18, 341 (1936). (112) Hanson, Ind. Eng. Chem., Anal. Ed. 13, 119-123 (1941). (113) Thorpe, Whitely, "Dictionary of Applied Chemistry," 4th ed. (1937), 1, 98-99. (114) Klebanskii, Gosudarst. Inst. Prikladnoi Khim., Sbornik Statei 1919-1939, 359-383 (1939); C.A. 36, 2521 (1942). (115) Favorskii, Margules, Davuidova, Trans. State Inst. Applied Chem. (U.S.S.R.) 24, 47-54 (1935); C.A. 29, 7271 (1935). (116) Suknevich, Khomutin, Trans. State Inst. Applied Chem. (U.S.S.R.) 24, 54-66 (1935); C.A. 29, 7271 (1935). (117) Shagalov, Trans. Mendeleev Congr. Theor. Applied Chem. 6th Congr. 1932, II Pt. 1, 730-737 (1935); Cent. 1936, II 2226, [C.A. 30, 1893 (1936)]. (118) Miloslavskii, Postovskii, J. Chem. Ind. (U.S.S.R.) 7, 1414-1419 (0930); Cent. 1931, II 1164; C.A. 25, 5391 (1931). (119) Kraft, Alekseev, J. Chem. Ind. (U.S.S.R.) 8, 861-863 (1931); Cent. 1931, II 2385; C.A. 26, 79 (1932). (120) Valyashko, Kosenko, Ukrain. Khem. Zhur. 7, No. 1, Sci. Pt. 12-35 (1932); Cent. 1933, I 3554; C.A. 27, 1611 (1933).

(121) Peters, Neumann, Z. angew. Chem. 45, 261-266 (1932). (122) Langguth, Chimie & industrie 25, 22-25 (1931). (123) Tramm (to Ruhrchemie, A.G.), U.S. 2,016,658, Oct. 8, 1935; Cent. 1936, I 875; C.A. 29, 8005 (1935): French 743,778, April 6, 1933; Cent. 1933, II 605; C.A. 27, 3941 (1933). (124) Ruppert, Fischer, Vogt, Hennig (to I.G.), U.S. 1,868,077, July 19, 1932; C.A. 26, 5106 (1932): Brit. 310,964, June 26, 1929; Cent. 1930, II 2957; C.A. 24, 630 (1930): Ger. 553,149, Sept. 30, 1932; Cent. 1932, II 3303; [C.A. 27, 736 (1933)]: Swiss 141,529, Oct. 1, 1930; Cent. 1931, I 1823: French 739,183, Jan. 6, 1933; Cent. 1933, I 2312; C.A. 27, 1894 (1933). (125) Dow, U.S. 1,437,636, Dec. 5, 1922; C.A. 17, 770 (1923). (126) Roka (to Holzverkohlungs Ind., A.G.), U.S. 1,418,882, June 6, 1922; [Cent. 1923, II 1152], C.A. 16, 2695 (1922): Brit. 174,-635, March 29, 1922; Cent. 1922, IV 941; C.A. 16, 1779 (1922): Ger. 387,452, Dec. 28, 1923; [Cent. 1924, I 1867]. (127) Consortium für Elektrochem. Ind., Brit. 366,348, Feb. 25, 1932; French 714,995, Nov. 23, 1931; Cent. 1932, I 3345; C.A. 26, 1624 (1932). (128) A. Wacker Soc. Chem. Ind., Ger. 733,750, March 4, 1943; C.A. 38, 980 (1944). (129) Mugdan, Sixt (to Consortium für Elektrochem. Ind.), Ger. 659,434, May 3, 1938; Cent. 1938, II 3005; C.A. 32, 5857 (1938). (130) Compagnie des Prod. Chim. d'Alais et de la Camargue, Ger. 410,529, March 11, 1925; [Cent. 1925, I 2185], not in C.A.: Austrian 93,604, July 25, 1923; Cent. 1924, I 1866; not in C.A.

(131) Chem. Fabrik Griesheim-Elektron, Ger. 204,883, Dec. 12, 1908; Cent. 1909, I 325; C.A. 3, 1457 (1909). (132) Ornstein, Ger. 241,559, Dec. 5, 1911; Cent. 1912, I 174; C.A. 6, 2291 (1912). (133) Consortium für Elektrochem. Ind., Ger. 154,677, Oct. 7, 1904; Cent. 1904, II 1177; not in C.A. (134) Lidholm, Ger. 204,516, Nov. 25, 1908; Cent. 1909, I 114; C.A. 3, 1457 (1909). (135) Lidholm, Ger. 201,705, Sept. 9, 1908; Cent. 1908, II 1071; C.A. 3, 359 (1909). (136) Hilpert, Ger. 368,892, Feb. 10, 1923; Cent. 1923, II 907; not in C.A. (137) Compagnie des Prod. Chim. d'Alais et de la Camargue, French 744,359, April 19, 1933; Cent. 1933, II 935; C.A. 27, 3951 (1933). (138) I.G., French 687,307, Aug. 7, 1930; Cent. 1939, II 3637; C.A. 25, 715 (1931). (139) Berthelot, Jungfleisch, Ann. Suppl. 7, 254-255 (1870). (140) Tompkins, Ger. 196,324, March 19, 1908; Cent. 1908, I 1504; C.A. 2, 2289 (1908).

(141) Moyer (to Solvay Process Co.), U.S. 2,152,357, March 28, 1939; Cent. 1939, II 1775; C.A. 33, 5001 (1939). (142) Maze, U.S. 1,425,669, Aug. 15, 1922; C.A. 16, 3314 (1923). (143) Michel, Z. angew. Chem. 19, 1096 (1906). (144) Salzbergwerk Neu-Stassfurt, Ger. 174,068, Sept. 8, 1906; Cent. 1906, II 1297; C.A. 1, 950 (1907). (145) Irvine, Haworth (to Carbide and Carbon Chem. Co.), U.S. 1,496,675, June 3, 1924; Cent. 1924, II 1511; [C.A. 18, 2345 (1924)]. (146) Askenasy, Heller, Ger. 549,341, April 26, 1932; Cent. 1932, II 287; C.A. 26, 3807 (1932). (147) Maier, French 655,930, April 25, 1929; Cent. 1929, II 1347; C.A. 23, 3931 (1929). (148) Levine (to du Pont Co.), Can. 395,846, April 15, 1941; C.A. 35, 4482 (1941); Brit. 505,196, June 1, 1939; Cent. 1939, II 2712; C.A. 33, 7814 (1939). (149) Müller, Schumacher, Z. physik. Chem. B-35, 455-457 (1937). (150) Kharasch, Brown, J. Am. Chem. Soc. 61, 3433 (1939).

(151) Müller, Schumacher, Z. physik. Chem. B-35, 285-297 (1935). (152) Müller, Schumacher, Z. Elektrochem. 43, 807-808 (1937); Cent. 1938, I 3453. (153) Müller, Hönn, J. prakt. Chem. (2) 133, 289-290 (1932). (154) Rodebush (to U.S. Industrial Alc. Co.), U.S. 1,402,318, Jan. 3, 1922; Cent. 1923, II 960; [C.A. 16, 935 (1922)]. (155) van de Walle, Henne, Bull. acad. roy. Belg. (5) 11, 793 (1925); Cent. 1926, I 3136. (156) E. Erdmann, H. Erdmann, Ber. 38, 239 (1905). (157) Roesslacher and Hasslacher Chem. Co., French 732,569, Sept. 22, 1932; Cent. 1932, II 3785; C.A. 27, 304 (1933): Ger. 573,105, March 3, 1932; [C.A. 27, 2961 (1933)]. (158) Imperial Chem. Ind., Ltd., French 744,128, April 12, 1933; Cent. 1933, II 605. (159) Müller, Huther, Ber. 64, 593, 599 (1931). (160) Ghighi, Ann. chim. applicata 28, 363-368 (1938); Cent. 1938, I 86; C.A. 33, 6792 (1939).

(161) Nicodemus, J. prakt. Chem. (2) 83, 312-317 (1911). (162) Schering-Kahlbaum, A.G., Brit. 374,949, July 14, 1932; Cent. 1932, II 2107; not in C.A. (163) Chem. Fabrik Buckau, Ger. 274,782, May 27, 1914; Cent. 1914, II 95; C.A. 8, 3350 (1914). (164) Tompkins (to Clayton Aniline Co.), Ger. 222,622, June 2, 1910; Cent. 1910, II 121; C.A. 4, 2866 (1910). (165) Chem. Fabrik. Griesheim Elektron, Ger. 263,457, Aug. 8, 1913; Cent. 1913, II 829; C.A. 7, 4048 (1913). (166) Körner, Suchy (to A. Wacker Soc. Elektrochem. Ind.), Ger. 464,320, Aug. 21, 1928; Cent. 1929, I 1044; C.A. 22, 4132 (1928). (167) A. Wacker Soc. Elektrochem. Ind., Brit. 480,568, March 24, 1938; Cent. 1938, I 4236; C.A. 32, 5857 (1938). (168) Bozel-Maletra (to Soc. Ind. Prod. Chim.), French 715,421, Dec. 3, 1931; Cent. 1932, I 3345; C.A. 26, 1946 (1932). (169) Consortium für Elektrochem. Ind., Brit. 302,321, Feb. 6, 1929; Cent. 1929, II 794; C.A. 23, 4231 (1929). (170) Andrusov (to I.G.), Ger. 634,549, Aug. 29, 1936; Cent. 1936, II 4048; C.A. 31, 419 (1937): French 805,563, Nov. 24, 1936; Cent. 1937, I 2255; C.A. 31, 4345 (1937).

(171) Kali-Chemie, A.G., Italian 383,229, June 4, 1940; Cent. 1942, I 3143. (172) A. Wacker Soc. Elektrochem. Ind., Brit. 468,921, Aug. 12, 1937; Cent. 1937, II 3813; C.A. 32, 596 (1938). (173) A. Wacker Soc. Elektrochem. Ind., French 832,749, Oct. 3, 1938; Cent. 1938, II 4126; C.A. 33, 2540 (1939). (174) Mailhe, Compt. rend. 172, 1583 (1921); Bull. soc. chim. (4) 29, 535-536 (1921). (175) Consortium für Elektrochem. Ind., Ger. 216,070, Nov. 11, 1909; Cent. 1909, II 2103; C.A. 4, 812 (1910). (176) A. Wacker Soc. Elektrochem. Ind., Ger. 345,259, Dec. 8, 1921; [Cent. 1922, II 443]; not in C.A.: Brit. 156,080, Jan. 27, 1921, Cent. 1921, II 1061; C.A. 15, 1535 (1921). (077) Consortium für Elektrochem. Ind., Ger. 217,554, Jan. 17, 1910; Cent. 1910, I 700; C.A. 4, 1651 (1911). (178) Wiegand (to Chem. Fabrik von Heyden), Ger. 566,034, Dec. 14, 1932; Cent. 1933, I 1350; C.A. 27, 1012 (1933). (179) Wiegand (to Chem. Fabrik von Heyden), Ger. 567,272, Dec. 31, 1932; Cent. 1933, I 1842; C.A. 27, 1365 (1933). (180) Sebanejev, Ann. 216, 262 (1882).

(181) Müller, Lüber, Ber. 65, 985-987 (1932). (182) Müller, Ehrmann, Ber. 69, 2207-2210 (1936). (183) Guyot, Simon, Compt. rend. 170, 736 (1920). (184) Bisealski, Z. angew. Chem. 37, 307 (1924). (185) Müller, J. Am. Chem. Soc. 62, 341-342 (1940). (186) Swarts, Cent. 1903, I 13. (187) Gruner (to Kali-Chemie, A.G.), Ger. 712,478, Oct. 21, 1941; Cent. 1942, I 1053;

C.A. 37, 4407 (1943). (188) Salsbergwerk Neu-Stassfurt, Ger. 248,982, July 6, 1912; Cent.
1912, II 299; C.A. 6, 2824 (1912). (189) Loiseau, French 565,356, Jan. 25, 1924; Cent. 1926,
II 1227; not in C.A. (190) Mkryan, Babayan, Sbornik Trudov Armyanskogo Filiala Akad.
Nauk 1946, No. 2, 51-58; C.A. 37, 5694 (1943).

(191) Blas, Cervas, Anales fis. quim. 37, 298-315 (1941); C.A. 37, 74 (1943). (192) Kokatnur, J. Am. Chem. Soc. 41, 120-124 (1919). (193) Mouneyrat, Bull. soc. chim. (3) 19, 454-455 (1898). (194) Erdmann, J. prakt. Chem. (2) 85, 84 (1912). (195) Perkins (to du Pont Co.), U.S. 1,999,995, April 30, 1935; C.A. 29, 4026 (1935); Brit. 447,135, June 11, 1936; Cent. 1936, II 2448; [C.A. 36, 6763 (1936)]. (196) Ruggli, Henze, Helv. Chrm. Acta 12, 362-364 (1929). (197) Grangaard, Purves, J. Am. Chem. Soc. 61, 428-429, 755 (1939). (198) Ott (to Chem. Fabrik Weilerter-Meer), Ger. 362,743, Nov. 2, 1922; Cent. 1923, II 743; C.A. 18, 991 (1924). (199) Fischer, Taube, Ber. 59, 850-856 (1926). (200) Consortum für Elektrochem. Ind., Ger. 171,900, June 18, 1906; Cent. 1906, II 571; Ger. 208,834, April 8, 1909; Cent. 1909, I 1785; C.A. 3, 2210 (1909).

(201) MacMillan (to Niagara Alkali Co.), U.S. 1,397,134, Nov. 15, 1921; Cent. 1922, IV 941; C.A. 16,565 (1922). (202) Shagalov, Dobromil'skaya, Trans. State Inst. Applied Chem. (U.S.S.R.) 24, 67-77 (1935); C.A. 29, 7272 (1935). (203) Sastry, J. Soc. Chem. Ind. 35, 450-452 (1916); Cent. 1916, II 306; C.A. 10, 1942 (1916). (204) Ward, J. Chem. Soc. 1930, 2144. (205) Taylor, Ward, J. Chem. Soc. 1934, 2003. (206) Petrenko-Kritschenko, Ber. 61, 853 (1928). (207) Huntress, Hershberg, unpublished results. (208) Consortium für Elektrochem. Ind. Ger. 257,878, March 22, 1913; Cent. 1913, I 1373; C.A. 7, 2836 (1913). (209) Metx, J. prakt. Chem. (2) 135, 142-144 (1932). (210) Compagnie des Products Chimiques d'Alais et de la Camargue, Ger. 351,463, April 7, 1922; Cent. 1922, IV 154; not in C.A.; Brit. 132,755, May 14, 1919, C.A. 14, 285 (1920). Guyot, U.S. 1,343,716, June 15, 1920; C.A. 14, 2344 (1920).

(211) Mkryan, Sbornik Trudov Armyanskogo Filiala Akad. Nauk 1940, No. 2, 36-41; C A. 37, 5694 (1943). (212) Pogosyan, Mkryan, Russ. 50,533, Feb. 28, 1937; Cent. 1938, II 412; C.A. 31, 8549 (1937). (213) British Dyestuffs Corp., Levinstein, Imbert, Brit. 173,540, Feb. 2, 1922; French 527,554, Oct. 27, 1921; Swiss 93,576, March 16, 1922, Cent. 1922, IV 761; C.A. 16, 1435 (1922). (214) Gowing-Scopes, Analyst 39, 7 (1914). (215) Formanek, Chem. Obzor 5, 57-59 (1922): Cent. 1930. II 976: C.A. 24, 4492 (1930). (216) Staudinger, Z. angew. Chem. 35, 668-

(1922); Cent. 1930, II 976; C.A. 24, 4492 (1930). (216) Staudinger, Z. angew. Chem. 35, 658-659 (1922). (217) Lenze, Metz, Z. ges. Schress-u. Sprengstoff. 27, 255-258, 293-296, 337-340, 373-376 (1932). (218) Mouneyrat, Bull. soc. chim. (3) 19, 499-500 (1898). (219) Harlow, Ross (to Dow Chem. Co.), U.S. 1,891,415, Dec. 20, 1932; Cent. 1933, I 1682; C.A. 27, 1890 (1933).

(220) Whitmore, Thurman, J. Am. Chem. Soc. 51, 1497 (1929).

(221) Binaghi, Gazz. chim. ital. 57, 670, 675 (1927); Cent. 1928, I 908-909; C.A. 22, 573-574 (1928). (222) Swarts, Bull. soc. chim. (4) 25, 146,168-170 (1919). (223) Sastry, J. Soc. Chem. Ind. 35, 94-95 (1916). (224) Weber, Chem. Zlg. 57, 836 (1933); Cent. 1933, II 3889, C.A. 28, 727 (1934). (225) Doughty, J. Am. Chem. Soc. 41, 1129-1131 (1919). (226) Phillips, Enas, J. Assoc. Official Agr. Chem. 27, 442-446 (1944). (227) Coyer, Hahnemannian Monthly 79, 230-241 (1944); C.A. 38, 3358 (1944). (228) Strosacker, Amstutz (to Dow Chem. Co.), U.S. 2,322,258, June 22, 1943; C.A. 38, 114 (1944). (229) von Oettingen, J. Ind. Hyg. Toxicol. 19, 399-403 (1937). (230) Rauscher, Ind. Eng. Chem., Anal. Ed. 9, 296-299 (1937).

(231) Tzurikh, Trans. State Inst. Applied Chem. (U.S.S.R.) 24, 77-80 (1935); C.A. 29, 7272 (1935); not in Cent. (232) Lehman, Schmidt-Kchl, Arch. Hyg Bakt. 116, 131-268 (1936); C.A. 31, 477 (1937); not in Cent. (233) Yamaguchi, J. Chem. Soc. Japan 55, 1227-1231, 1232-1235 (1934); C.A. 29, 4326 (1935). (234) Igi, J. Chem. Ind. Japan 23, 1217-1237 (1920); C.A. 15, 2273 (1921). (235) Askenssy, Vogelsohn, Z. Elektrochem. 15, 773 (1909). (236) Aten, Chem. Weekblad 19, 352 (1922); Cent. 1922, III 984; C.A. 16, 3593 (1922).

3:5755 1,1-DICHLOROPROPANOL-2 $C_3H_6OCl_2$ Beil. I - 363 $(\beta,\beta$ -Dichloroisopropyl alcohol; CH_3 —CH— $CHCl_2$ I_1 — dichloromethyl methyl-carbinol) OH I_2 -(383)

B.P. 146-148° at 765 mm. (1) $D_{22}^{22} = 1.3334$ (1)

Moderately sol. aq., very sol. alc., ether.

[For prepn. of \tilde{C} from dichloroacetaldehyde (3:5180) with MeMgBr in dry ether (57.4% yield) see (1); from 1,1-dichloropropanone-2 (unsym.-dichloroacetone) (3:5430) with anhydrous acetaldehyde + Al(OEt)₃ in dry ether (45% yield) see (2).] — [Note that the levorotatory stereoisomer of \tilde{C} , b.p. 146-148°, $[\alpha]_D^- = -9^\circ$, has been obtd. (54% yield) from unsym.-dichloroacetone (3:5430) by reduction with yeast (3).]

[For behavior of C with NaOEt in alc. or ether see (4).]

- [Č with paraformaldehyde + $ZnCl_2$ gives (23.5% yield (5)) formaldehyde bis-(β,β -dichloroisopropyl)acetal [Beil. I-575], b.p. 81° at 0.2 mm. (4).]
 - —— β,β-Dichloroisopropyl benzoate: oil, b.p. 92-94° at 0.15-0.17 mm. (4). [From C with BzCl refluxed 4 hrs. at 150° (80% yield (4)).]
 - —— β,β-Dichloroisopropyl carbamate: unreported. [Note, however, that the corresp. deriv. of levorotatory C (obtd. with carbamyl chloride in ether) has m.p. 61-63° (3).]
- 3:5755 (1) Wohl, Roth, Ber. 40, 217-218 (1907). (2) Nord, Ger. 434,728, Oct. 5, 1926; Cent. 1926, II 2845. (3) Sen. J. Indian Chem. Soc. 1, 1-8 (1924/25); Cent. 1925, I 537; C.A. 19, 816 (1925); Biochem. Z. 151, 51-53 (1924); Cent. 1924, II 2272; C.A. 19, 3277 (1925). (4) Wohl, Ber. 41, 3606-3608 (1908).

3:5760 3,3,3-TRICHLORO-1,2-EPOXYPROPANE
$$C_3H_3OCl_3$$
 Beil. S.N. 2362 $(\omega,\omega,\omega$ -Trichloropropylene oxide) Cl_3C — CH — CH_2

B.P.
$$149^{\circ}$$
 at 764 mm. (1) $D_{25}^{25} = 1.4921$ (4) $n_{\rm D}^{25} = 1.4737$ (4) 149° at 750 mm. (2) 49° at 11 mm. (1) $D_{4}^{20} = 1.495$ (5) $n_{\rm He}^{20} = 1.4768$ (5) $44-45^{\circ}$ at 13 mm. (2) $41-42^{\circ}$ at 10 mm. (3) $D_{4}^{19} = 1.4962$ (5) $39-40^{\circ}$ at 11 mm. (4)

Colorless mobile liq. with sweetish not unpleasant odor suggesting epichlorohydrin (3:5358). [Note that \bar{C} was at first (1) erroneously supposed to be 1,1,1-trichloroacetone (3:5620).]

[For prepn. of \bar{C} from chloral (3:5210) (1) (2) (4) or chloral hydrate (3:1270) (3) with diazomethane in ether (yields: 64% (2), 48% (4), 47.5% (3)) see indic. refs.]

C does not (2) react with aq. o-nitrophenylhydrazine HCl or with aq. semicarbazide.

[\bar{C} with 5 pts. conc. aq. HCl evolves heat and by opening of epoxy ring yields (2) 1,1,1,3-tetrachloropropanol-2 (3:9036), b.p. 95-96° at 17 mm. (2). — \bar{C} with Ac₂O + trace sublimed FeCl₃ gives (2) in analogous fashion 3,3,3-trichloro 1,3-diacetoxypropane, b.p. 126-128° at 16 mm. (2).]

[C with alcohols gives (3) corresp. alkoxymethyl-hemiacetals of chloral.]

[\bar{C} with MeMgI in dry ether at -15° gives (59% yield (4)) 1,1,1-trichloro-3-iodopropanol-2, ndls. from pet. ether, m.p. 54-55° (4). — \bar{C} with MeLi in dry ether at -75° gives (85% yield (4)) 1,1,1-trichlorobutanol-2 (3:5955).]

3:5760 (1) Schlotterbeck, Ber. 42, 2561 (1909). (2) Arndt, Amende, Ber. 61, 1121-1122 (1928). (3) Meerwein, Bersin, Burneleit, Ber. 62, 1002-1003, 1006-1009 (1929). (4) Gilman, Abbott, J Org. Chem. 8, 227-228 (1943). (5) von Auwers, Ber. 62, 1319 (1929).

3:5765 METHYL
$$\beta$$
-CHLOROPROPIONATE C₄H₇O₂Cl Beil. II - 250 ClCH₂.CH₂.CO.O.CH₃ II₁— II₂-(227)

B.P. 148-150° at 760 mm. (1)
$$D_4^{20} = 1.1634$$
 (7) $n_D^{20} = 1.4265$ (7) 148° (2) $40-42^\circ$ at 10 mm. (3) $D_4^{12} = 1.1874$ (1) $n_D^{12} = 1.4319$ (1)

[For prepn. of \bar{C} from β -chloropropionic ac. (3:0460) by esterification with MeOH + HCl see (2) (3); from acrylic acid chloride (3:7153) + MeOH see (2) (4), from methyl

acrylate (1:3025) by addn. of HCl see (1), from acrylonitrile + HCl to β -chloropropionitrile followed by reactn. with MeOH (96% yield (5)) see (5).]

[Note that the b.p. of 155-157° reported by (4) has been characterized as erroneous (2) (1).]

C on htg. with diethylaniline at abt. 200° gives (1) (78% yield (3)) methyl acrylate (1:3025), b.p. 80° (1).

[For study of acid hydrolysis of C see (6).]

3:5765 (1) Moureu, Murat, Tampier, Ann. chim. (9) 15, 244 (1921). (2) Moureu, Ann. chim. (7) 2, 170-171 (1894). (3) Spath, Spitzy, Ber. 58, 2276 (1925). (4) Henry, Compt. rend. 106, 116 (1885); J. prakt. Chem. (2) 31, 127 (1885). (5) British (to I.G.) 352,802, Aug. 6, 1931; Cent. 1931, II 2658. (6) Palomaa, Ber. 74, 1866-1870 (1941); C.A. 36, 5413 (1942). (7) Schjanberg, Z. physik. Chem. A-172, 231 (1935).

B.P. abt. 150° dec. (1)
$$D_{20}^{20} = 1.1259$$
 (1) 87.5° at 27 mm. (1) 78-83° at 12 mm. (2)

[For prepn. from cyclohexanol (1:6415) + phosgene (3:5000) see (1); for application in prepn. of textile auxiliaries see (3).]

© Cyclohexyl carbamate: from C + conc. aq. NH₄OH; m.p. 110° (2).

3:5770 (1) Kretov, Bakakina, Zhur. Priklad. Khim. 2, 809-816 (1929); C.A. 24, 1998 (1930); Cent. 1930, I 2876. (2) Puyal, Montagne, Bull. soc. chim (4) 27, 862 (1920). (3) French 731,405, Sept. 2, 1932; Cent. 1933, I 313.

B.P. M.P.
$$+8^{\circ}$$
 (4) $D_{4}^{19} = 1.2363$ (4) $n_{D}^{19} = 1.4598$ (4) 150.5° at 760 mm. (2) 143.5° (3) $D_{4}^{0} = 1.2507$ (4) 143.5° at 10 mm. (4) 143.5° at 5 mm. (4)

[See also the isomeric 1,3-dichloro-2-methylpropanol-2 (3:5977).]

PREPARATION OF C

[For prepn. of \bar{C} from 1-chloro-2-methylpropene-1 (β,β -dimethylvinyl chloride = "isocrotyl chloride") (3:7120) by addn. of HOCl with Cl_2 + aq., aq. HOCl, or even alkyl or alkaryl hypochlorites as directed see (2) cf. (5) (3).]

[For prepn. of \bar{C} from α,α -dichloroacetone (3:5430) with MeMgBr in ether see (1).]

[For prepn. of C from ethyl dichloroacetate (3:5850) with MeMgBr (74% yield (4)) or MeMgI (63% yield (6)) cf. (4) or from methyl dichloroacetate (3:5655) with MeMgBr (7) see indic. refs.]

CHEMICAL BEHAVIOR OF C

With inorganic reagents. C does not (1) react with aq. HCl. — C cannot (4) be hydrolyzed to the corresp. aldehyde, viz., α-hydroxyisobutyraldehyde [Beil. I-829, I₂-(871)], either by aq., aq. Na₂CO₃, aq. CaCO₃, or aq. PbO.

 $[\ddot{\mathbf{C}}$ with 5 N abs. alc. NH₃ in s.t. at 100° as directed gives (8) 2,2,5,5-tetramethyldihydropyrazine, m.p. 83-84° (8) (9).]

With organic reactants. [For behavior of \tilde{C} with MeNH₂ yielding a prod. of compn. $C_{16}H_{32}N_4$ see (8).]

[Č with Me₂NH in C₆H₆ in s.t. at 130° not only introduces the dimethylamino group for one chlorine but also ring-closes with loss of HCl giving (52% yield (8)) 1-(dimethylamino)-2-methyl-1,2-epoxypropane (α,α -dimethyl- α' -(dimethylamino)ethylene oxide), b.p. 28-30° at 13 mm., $D_{-}^{22.5} = 0.8725$, $n_{-}^{22.5} = 1.4216$ (8).]

- —— α -Hydroxyisobutyraldehyde di- β -naphthylacetal [(CH₃)₂-C(OH)CH(O.C₁₀H₇)₂]: [This cpd. which might be expected from \bar{C} with sodium β -naphtholate is unreported; note that 1,3-dichloro-2-methylpropanol-2 (3:5977) with sodium β -naphtholate gives the corresp. di- β -naphthyl ether, m.p. 151–152°.]
- ---- unsym.-Dichloro-ter-butyl acetate: unreported.
- ---- unsym.-Dichloro-ter-butyl benzoate: unreported.
- ---- unsym.-Dichloro-ter-butyl p-nitrobenzoate: unreported.
- ---- unsym.-Dichloro-ter-butyl 3,5-dinitrobenzoate: unreported.
- unsym.-Dichloro-ter-butyl carbamate: m.p. 122° (7). [Prepd. from unsym.-dichloro-ter-butoxy MgBr by treatment with phosgene (3:5000) followed by NH₄OH (7).]

3:5772 (1) Henry, Compt. rend. 142, 131, Note 1 (1906); Bull. soc. chim. Belg. 29, 152-156 (1906); Cent. 1906, II 1178-1179. (2) Groll, Hearne (to Shell Development Co), U.S. 2,060,303, Nov. 10, 1936; Cent. 1937, I 4155; [C.A. 31, 419 (1937)]: N. V. de Bataafsche Petroleum Maatschapij, Brit. 437,573, Oct. 31, 1935; Cent. 1936, II 2227; [C.A. 30, 2199 (1936)]: French 787,529, March 19, 1935; Cent. 1936, II 2227, C.A. 30, 1067 (1936). (3) Oeconomides, Compt. rend. 92, 1237 (1881). (4) Avy, Bull. soc. chim. (4) 49, 12-18 (1931). (5) Burgin, Hearne, Rust, Ind. Eng. Chem. 33, 385-388 (1941). (6) Iositch, J. Russ. Phys.-Chem. Soc. 36, 1551 (1906). (7) Yoder, J. Am. Chem. Soc. 45, 478-479 (1923). (8) Avy, Bull. soc. chim. (4) 49, 514-522 (1931). (9) Conant, Aston, J. Am. Chem. Soc. 50, 2788 (1928).

3:5775 2,2,2-TRICHLOROETHANOL-1 $Cl_3C.CH_2OH$ $C_2H_3OCl_3$ Beil. I - 338 $(\beta,\beta,\beta$ -Trichloroethyl alcohol) I₁-(170) I₂-(337)

B.P.			M.P.	
151°	cor.	(1)	18° (5)	$D_{23.5}^{23.5} = 1.5500 (2)$
151°	at 737 mm.	(2)	17° (6)	
151°	sl. dec.	(3)		
149.5-150.5	s° at 765 mm.	(4)		
149-150°	at 760 mm.	(4)		
148-150°	at 720 mm.	(5)		
111°	at 170 mm.	(6)		
94-97°	at 125 mm.	(3)		
67-68°	at 25 mm.	(7)		
58-60°	at 16 mm.	(8)		
55-56°	at 11 mm.	(9)		
52-54°	at 10 mm. (1	l 0)		

Colorless when pure, but slightly brown if distilled at ord. press. — Sol. in 12 pts. aq., vol. with steam; miscible with alc. or ether. — Solid is very hygroscopic.

Č is an important pharmaceutical. — [Although full consideration of its pharmacology is beyond the scope of this text, for studies and reviews of this aspect see (11) (12) (13) (14) (40).] — Č in the organism is in part excreted (15) (16) as urochloralic acid [Beil. I-620].

PREPARATION OF C

Č is readily obtd. from trichloroacetaldehyde (chloral) (3:5210) by various types of reducing actions which are able to effect reduction of the aldehyde group without serious interference with the halogen atoms.

By use of various alcoholates. [For prepn. of \bar{C} from chloral (3:5210) with Al(OEt)₃ in abs. EtOH (yields: 85% (17), 84% (3), 80% (18)) (6) (10) (19) cf. (23) see indic. refs.; with Al isopropylate in isopropyl alc. (20) in pres. of acetaldehyde (yield 72-87% (21)) see indic. refs.; with C_2H_5OMgBr (9), (CH₃)₂CHOMgBr (9), or other metallic isopropylates (22) see indic. refs.]

By use of RMgX. [For form. of Č from chloral (3.5210) during reaction with MeMgBr (24), with EtMgBr (25) (4), with iso-AmMgBr (4), with cyclohexyl MgBr (26), and various other RMgBr cpds. (7) (25) (yields: 65% (25), 50-60% (4), 42-52% (26)) see indic. refs.]

By use of metal alkyls. [For formn. of \tilde{C} from chloral (3:5210) by use of ZnEt₂ (2) (27) or AlEt₃ cpd. with ether (88.5% yield (8)) see indic. refs.; note, however, that SnEt₄ is not (8) effective.]

By phytochemical agents. [For prepn. of \tilde{C} from chloral (3:5210) by reduction with fermenting yeast see (28) (5).]

By misc. methods. [For form. of \bar{C} from urochlorate acid [Beil. 1-620] by hydrolysis with dil. mineral acid see (1); for form. of \bar{C} in small amts, from EtOH + Cl_2 see (29).]

CHEMICAL BEHAVIOR OF C

WITH INORGANIC REACTANTS

Oxidation. \bar{C} reduces Fehling's soln. on warming (2). — \bar{C} with fumg. HNO₃ is oxidized to trichloroacetic acid (1) (2).

Behavior with alkalies. [\bar{C} in conc. aq. NaOH first dissolves then gives a white ppt. of Na deriv. (33). — \bar{C} with aq. KOH dissolves and soon afterward reacts vigorously yielding (2) various prods. including chloroacetic acid (3:1370), β,β,β -trichloroethoxyacetic acid [Beil. III-233], m.p. 69.5° (2), and formic acid (1:1005).]

Behavior with inorganic acid chlorides. [$\bar{\mathbb{C}}$ with PCl₃ evolves HCl and yields (27) tris- $(\beta,\beta,\beta$ -trichloroethyl) phosphite, b.p. 263°, no formation of 1,1,1,2-tetrachloroethane (3:5555) being evident. — $\bar{\mathbb{C}}$ with PCl₅ at 140° evolves HCl yielding (27) tris- $(\beta,\beta,\beta$ -trichloroethyl) phosphate, m.p. 73–74° (sublimes without decn.) accompanied by a trace of 1,1,1,2-tetrachloroethane (3:5555).]

[Č with SOCl₂ gives (30) bis- $(\beta,\beta,\beta$ -trichloroethyl) sulfite, b.p. 139.5-140° at 5 mm., m.p. 6-7°. — Č with SO₂Cl₂ in pyridine at 100° gives (30) bis- $(\beta,\beta,\beta$ -trichloroethyl) sulfate, m.p. 118.5-119.5° cor., also obtd. (30) by oxidn. of the preceding sulfite with acid KMnO₄ in acetone.]

Behavior with AlBr₃. [\tilde{C} with AlBr₃ in CS₂ (31) (32) undergoes replacement of chlorine by bromine yielding acc. to conditions β -bromo- β , β -dichloroethanol, m.p. 17.5 (32), m.p. 17.5° (32), or β , β -dibromo- β -chloroethanol, m.p. 50°, b.p. 80° at 8 mm. (32).]

WITH ORGANIC REACTANTS

(See also below under derivatives.) — [\bar{C} with diazomethane in heptane (33), n-BuOH (34), or acetone (33) (but not in ether (33)), yields β,β,β -trichloroethyl methyl ether, b.p. 35-36° at 16 mm. (33).]

[Č with 2,3-dichlorodioxane-1,4 (3:9105) gives (50% yield (18)) 2-chloro-3- $(\beta,\beta,\beta$ -trichloroethoxy)dioxane-1,4, m.p. 77-78°.]

[\ddot{C} with BEt₃ at 150° evolves C₂H₆ and gives (44% yield (8)) β,β,β -trichloroethyl diethylborate, CCl₃CH₂OB(C₂H₅)₂, b.p. 78-79° at 12 mm. (8).]

- β,β,β -Trichloroethyl acetate: oil, b.p. 167° sl. dec. at 736 mm. (2), 71° at 18.3 mm. (2), 88–91° (35), $D_D^{28} = 1.4239$ (35), $n_D^{28} = 1.4691$ (35). [From \bar{C} with AcCl in s.t. at 130° for several hrs. (2).]
- —— β,β,β-Trichloroethyl benzoate: oil (29). [Note, however, that no constants are reported in the literature.]
- \mathfrak{D} β,β,β -Trichloroethyl *m*-nitrobenzoate: m.p. 75° (29) (26). [From $\tilde{\mathbb{C}}$ + *m*-nitrobenzoyl chloride + aq. alk. (29).]
- \mathfrak{D} β,β,β -Trichloroethyl p-nitrobenzoate: m.p. 71° (28) (25). [From $\tilde{C}+p$ -nitrobenzoyl chloride + aq. alk. (28).]
- \mathfrak{D} β,β,β -Trichloroethyl 3.5-dinitrobenzoate: m.p. 142-143° (25).
- $\[\widehat{\mathbf{D}} \]$ β,β,β -Trichloroethyl carbamate: m.p. 64-65° (28) (36) (37) (38), 64° (39). [From $\[\widehat{\mathbf{C}}\]$ (1 mole) with carbamyl chloride (1 mole) in dry ether (28) (note that $\[\widehat{\mathbf{C}}\]$ with excess of carbamyl chloride gives (28) β,β,β -trichloroethyl allophanate, m.p. 182-183°), or from $\[\widehat{\mathbf{C}}\]$ by treatment with phosgene (3:5000) followed by NH₃ (37). Note that this prod. comprises the hypnotic pharmaceutical known as "Voluntal." It also forms molecular cpds. with various other pharmaceuticals; e.g., "Voluntal," m.p. 64-65° + pyramidone (2,3-dimethyl-4-dimethylamino-1-phenyl-pyrazolone-5) [Beil. XXV-452, XXV₁-(672)], m.p. 108°, give a 1:1 mol. cpd., m.p. 75-76°, known as "Compral"; for f.p./compn. data and diagrams on this (and similar systems) see (39).]
- β,β,β -Trichloroethyl N-phenylcarbamate: m.p. 87° (39). [For f.p./compn. data and diagrams of this prod. (also known as N-phenylvoluntal) with antipyrine, etc., see (39).]
- \oplus β,β,β -Trichloroethyl N-(α -naphthyl)carbamate: m.p. 120° (7), 119° (26). [From $\bar{C} + \alpha$ -naphthyl isocyanate at 120–135° for 2 hrs. (7).]

3:5775 (1) von Mering, Z. physiol. Chem. 6, 487 (1882). (2) Garsarolli-Thurnlackh, Ann. 210, 64-68 (1881). (3) Chalmers, Org. Syntheses, Coll. Vol. 2 (1st ed.), 598-601 (1943); 15, 80-84 (1935). (4) Jotsitch, J. Russ. Phys.-Chem. Soc. 36, 443-446 (1904); Bull. soc. chim. (3) 34, 329-330 (1905). (5) Lintner, Luers, Z. physiol. Chem. 88, 122-123 (1913). (6) Callen (to Winthrop Chem. Co.), U.S. 1,725,054, Aug. 20, 1929; [Cent. 1930, I 434]; C.A. 23, 4709 (1929); Ger. 437,160, Nov. 18, 1926; Cent. 1927, I 802; not in C.A.: Brit. 286,797, April 5, 1928; Cent. 1928, I 2750; C.A. 23, 395 (1929). (7) Dean, Wolf, J. Am. Chem. Soc. 58, 332-333 (1936). (8) Meerwein, Hinz, Majert, Sonke, J. prakt. Chem. (2) 147, 236, 243 (1936). (9) Callsen (to I.G.), Ger. 565,157, Nov. 26, 1932; Cent. 1933, I 1514; C.A. 27, 992 (1933): Brit. 384,156, Dec. 22, 1932; Cent. 1933, I 1351; [C.A. 27, 4240 (1933)]. (10) Nakai, Biochem. Z. 152, 272 (1924); Cent. 1925, I 637; [C.A. 19, 2807 (1925)].

(11) Case, Anesthesiology 4, 523-527 (1943); C.A. 38, 3352 (1944). (12) Lehmann, Knight, Am. J. Med. Sci. 197, 639-646 (1939); C.A. 34, 3365 (1940). (13) Lehmann, Knight, J. Pharmacol. 63, 453-465 (1938); C.A. 33, 4321 (1939). (14) Molitor, Robinson, Anesthesia and Analgesia 17, 258-263 (1938); C.A. 32, 9269 (1938). (15) Akamatsu, Wasmuth, Arch. exptl. Pathol. Pharmakol. 99, 108-116 (1923); Cent. 1923, III 1185; C.A. 18, 112 (1924). (16) Külts, Z. Biol. 20, 161. (17) Meerwein, Schmidt, Ann. 444, 221-234 (1925). (18) Böeseken, Tellegen, Plusje, Rec. trav. chim. 57, 74-75 (1938). (19) Meerwein (to F. Bayer Co.), U.S. 1,572,742, Feb. 9, 1926; Cent. 1926, I 3627; [C.A. 26, 1243 (1926)]: Brit. 235,584, June 27, 1926; [Cent. 1926, I

1097]; C.A. 20, 917 (1926). (20) Callsen (to I.G.), Ger. 489,281, Jan. 15, 1930; Cent. 1930, I 3104; [C.A. 24, 2140 (1930)]; Swiss 126,963, July 16, 1928; Cent. 1929, I 1741; C.A. 23, 852 (1929). (21) Nord, Ger. 434,728, Oct. 5, 1926; Cent. 1926, II 2845; not in C.A. (22) I.G., Brit. 370,490, May 5, 1932; Cent. 1932, II 3303-3304; C.A. 27, 2961 (1933). (23) Dworzak, Monatsh. 47, 12-13 (1926). (24) Kharasch, Kleiger, Martin, Mayo, J. Am. Chem. Soc. 63, 2306-2307 (1941). (25) Gilman, Abbott, J. Org. Chem. 8, 224-229 (1943). (26) Floutz, J. Am. Chem. Soc. 65, 2255 (1943). (27) Delacre, Bull. soc. chim. (2) 48, 784-788 (1887). (28) Willstatter, Duisberg, Ber. 56, 2284-2285 (1923). (29) Altschul, Meyer, Ber. 26, 2758 (1893). (30) Sporzynski, Arch. Chem. Farm. 2, 243-247 (1935); Cent. 1935, II 2941; C.A. 30, 5938 (1936).

(31) Muller (to Winthrop Chem. Co.), U.S. 2,057,964, Oct. 20, 1936; C.A. 31, 112 (1937); not in Cent.: Brit. 366,581, March 3, 1932; Cent. 1932, II 770; [C.A. 27, 1893 (1933)]. (32) Schranz, Göth, Kuhn, Kayser, Ger. 600,769, July 31, 1934; Cent. 1934, II 2285; [C.A. 28, 7429 (1934)]. (33) Meerwein, Bersin, Burneleit, Ber. 62, 1006-1007 (1929). (34) Meerwein, Hinz, Ann. 484, 23 (1930). (35) Baum, Vogt, Hennion, J. Am. Chem. Soc. 61, 1458 (1939). (36) Willstätter, Straub, Hauptmann, Munch. med. Wochschr. 69, 1651-1654 (1922); Cent. 1923, I 1196, not in C.A. (37) F. Bayer & Co., Ger. 358,125, Sept. 4, 1922; Cent. 1922, IV 888; C.A. 17, 2172 (1923). (38) Mentzel, Pharm. Zentralhalle 63, 579-580 (1922); 64, 10-11 (1923); Cent. 1923, II 549. (39) Pfeiffer, Seydel, Z. physiol. Chem. 178, 81-96 (1928). (40) Burtner, Lehmann, J. Pharmacol. 63, 183-192 (1938); C.A. 32, 6741 (1938).

3:5780 β -CHLOROETHYL CHLOROFORMATE $C_3H_4O_2Cl_2$ Beil. III - 11 $(\beta$ -Chloroethyl chlorocarbonate) ClCH₂.CH₂.O.CO.Cl III₁— III₂-(10)

B.P. 152.5° at 752 mm. (1) $D_4^{20} = 1.3825$ (1) $n_D^{20} = 1.4465$ (1)

Colorless lachrymatory liq. which fumes in air. — Insol. aq., eas. sol. alc., ether. [For prepn. from β -chloroethanol (ethylene chlorohydrin) (3:5552) + phosgene (3:5000) see (1).]

 $\bar{\mathbf{C}}$ on slight warming with quinoline dec. at $41-42^{\circ}$ into ethylene dichloride (3:5130) + \mathbf{CO}_{2} (2).

 \tilde{C} is readily hydrolyzed by warm aq. or dil. alk. to β -chloroethanol (3:5552) + CO₂ + HCl (1).

- \oplus β -Chloroethyl carbamate: from $\ddot{C}+2$ moles conc. aq. NH₄OH; m.p. 76° (3) (4) (5). [The value of 115° given in Beil. III-11 is wrong (5).]
- Φ β-Chloroethyl N-phenylcarbamate: from C in C₆H₆ added to C₆H₆ soln. of aniline (2 moles); after filtering off the pptd. aniline hydrochloride, the C₆H₆ is evapd. (6); white ndls., m.p. 51° (3). [This deriv. on short boilg. with dil. aq. or alc. alk. loses HCl and by ring closure yields 3-phenyloxazolidone-2 [Beil. XXVII-136], lfts. from alc., m.p. 124° (3), 122° (7).]
- Φ β-Chloroethyl N-p-tolycarbamate: white ndls. from C₆H₆, m.p. 45° (6). [On treatment with alk. this gives 3-(p-tolyl)oxazolidone-2, white ndls. from alc., m.p. 91° (6).]
- \mathfrak{D} β -Chloroethyl phenylcarbazate: from $\tilde{\mathbb{C}}$ on treatment with 1 mole phenylhydrazine in aq. pyridine; the red oil initially formed soon solidifies and is recrystd. from \mathbb{C}_0H_6 ; white ndls., m.p. 89° (8).

3:5780 (1) Nekrassow, Komissarow, J. prakt. Chem. (2) 123, 163 (1929). (2) Carré, Bull. soc. chim. (5) 3, 1069 (1936). (3) Nemirowsky, J. prakt. Chem. (2) 31, 174-175 (1885). (4) Ger. 387,963, Jan. 1, 1924; Cent. 1924, II 403. (5) Kuroda, Cent. 1927, II 243. (6) Adams, Segur, J. Am. Chem. Soc. 45, 787-789 (1923). (7) Otto, J. prakt. Chem. (2) 44, 17 (1891). (8) Dox, J. Am. Chem. Soc. 48, 1952 (1926).

3:5785 1,1,1,2-TETRACHLOROPROPANE Cl
$$(\beta,\beta,\beta$$
-Trichloroisopropyl chloride) CH₃—C—CCl₃ I_1 —107 I_2 —

B.P. F.P. 152-153° cor. at 760 mm. (1)
$$-65^{\circ}$$
 (1) $D_{22}^{22} = 1.4695$ (6) $n_{D}^{20} = 1.4855$ (6) 150-151° at 751 mm. (6) -64° (6) $D_{20}^{20} = 1.473$ (1) $n_{-}^{-} = 1.4867$ (1) 87-88° at 104 mm. (6)

Colorless liq. insol. aq. [For use as dry-cleaning solvent see (2).]

[For prepn. of \bar{C} from 1,1,1-trichloropropanol-2 (3:0846) via reactn. with PCl₃ and action of Cl₂ on this product see (1); for prepn. of \bar{C} with 1,1-dichloropropene-1 (3:5120) + Cl₂ + cat. at 0-30° in absence of light see (3) (4); from 3,3,3-trichloropropene-1 (3:5345) by addn. of HCl in pres. of 3% FeCl₃ in s.t. at 50° for 50-100 hrs. see (6).]

C with aq. or alc. NaOH or KOH for 3 hrs. at 95° gives (93% yield (5)) 1,1,2-trichloro-propene-1 (3:5395), b.p. 118° (5).

3:5785 (1) Henry, Rec. trav. chim. 24, 333-334 (1905). (2) Sharp, U.S. 2,010,038, Aug. 6, 1935; Cent. 1935, II 3859; C.A. 29, 6440 (1935). (3) Cass (to du Pont), U.S. 2,097,442, Nov. 2, 1937; Cent. 1938, I 1218; C.A. 32, 194 (1938). (4) du Pont Co. & Cass, Brit. 471,187, Aug. 30, 1937; Cent. 1938, I 1218; C.A. 32, 958 (1938). (5) du Pont Co. & Cass, Brit. 469,051, July 19, 1937; Cent. 1938, I 1218; C.A. 32, 596 (1938). (6) Kharasch, Rossin, Fields, J. Am. Chem. Soc. 63, 2558-2560 (1941).

3:5800 METHYL TRICHLOROACETATE $C_3H_3O_2Cl_3$ Beil. II - 208 $Cl_3C.COOCH_3$ II₁— II₂-(199)

B.P.	F.P.	
153.8° at 760 mm. (1)	-17.5° (1) $D_4^{20} = 1.4874$ (8)	$n_{\rm D}^{20}=1.4572 \ (8)$
153° (2)	1.4864 (7)	1.45717(7)
152.3-152.5° at 765.3 mm. (3)		
150.0-150.5° at 679 mm. (4)		
52-54° at 12 mm. (5)		
44.5-44.6° at 12 mm. (6)		
46.5-47.0° at 11 mm. (7)		

[For prepn. of \bar{C} from trichloroacetic acid (3:1150) with MeOH at 60° (50-66% yield (2)), with MeOH + Hcl at 50° (74.6% yield (2)), with MeOH + H₂SO₄ (9), with MeOH + BF₃.Et₂O at 64° (73% yield (2)), or with Me₂SO₄ in s.t. at 200° (10) see indic. refs.; from trichloroacetamide + MeOH + BF₃ (53% yield) see (2); from "tetrachloroethylidene trichlorolactate" [Beil. XIX-105] with MeOH see (5).]

[For studies on hydrolysis of \ddot{C} under various circumstances see (11) (6) (7) (12).] [For speed of reactn, with pyridine at $18-20^{\circ}$ see (13).]

3:5800 (1) Timmermans, Bull. soc. chim. Belg. 31, 392 (1922). (2) Toole, Sowa, J. Am. Chem. Soc. 59, 1971-1973 (1937). (3) Schiff, Z. physik. Chem. 1, 379 (1887). (4) Sudborough, Karve, J. Indian Inst. Soc. 5, 16 (1922); Cent. 1923, I 295; C.A. 17, 665 (1923). (5) Anschütz, Haslam, Ann. 253, 124 (1889). (6) Skrabal, Monatsh. 71, 298-308 (1938). (7) Palomaa, Salmi, Korte, Ber. 72, 790-797 (1939). (8) Schjanberg, Z. physik. Chem. A-172, 229 (1935). (9) Dumaa, Ann. 32, 111 (1839). (10) Simon, Compt. rend. 176, 585 (1923).

(11) Olivier, Berger, Rec. trav. chim. 41, 642 (1921); 44, 643, 647-648 (1925). (12) Salmi, Suonpaä, Ber. 73, 1126-1131 (1940). (13) Tronov, Akivis, Orlova, J. Russ. Phys.-Chem. Soc. 61, 345-353 (1929); Cent. 1929, II 2550; C.A. 24, 590 (1930).

3:5820 3-CHLOROPROPEN-2-OL-1 CH=CH—CH₂ C₃H₅OCl
$$I_1$$
— I_2 —

High-boiling stereoisomer

B.P. 153.6° at 756 mm. (1) $D_4^{35} = 1.1582$ (1) $n_D^{35} = 1.4600$ (1) $D_4^{26} = 1.1681$ (1) $n_D^{25} = 1.4641$ (1) $D_4^{20} = 1.1729$ (1) $n_D^{20} = 1.4664$ (1)

Low-boiling b.P. 146.3° at 746 mm. (1) $D_4^{25} = 1.1623$ (1) $n_D^{35} = 1.4573$ (1) $D_4^{25} = 1.1720$ (1) $n_D^{25} = 1.4617$ (1) $D_4^{20} = 1.1769$ (1) $n_D^{20} = 1.4638$ (1)

Colorless liquids; both stereoisomers possess a delayed vesicant actn., and care should be taken in handling them.

[For prepn. of \bar{C} from 1,3-dichloropropene-1 (γ -chloroallyl chloride) (3:5280) by hydrolysis for 2 hrs. under reflux with aq. 10% Na₂CO₃ (10% excess over 1 equiv.) see (1); note that the high-boiling stereoisomer of γ -chloroallyl chloride gives (76% yield) of the high-boiling \bar{C} , and that the lower-boilg. stereoisomer of γ -chloroallyl chloride gives (81% yield) the lower-boiling stereoisomer of \bar{C} (1).—Note that from γ -chloroallyl acetate (which was presumably a mixture of the acetates of both stereoisomers of \bar{C}) by hydrolysis with cold aq. NaOH \bar{C} (presumably a mixt. of stereoisomers) has been reported (2).]

The two stereoisomers of \tilde{C} behave differently with hot aq. NaOH (1): the higher-boilg, stereoisomer fails to give any propargyl alcohol but some acetylene and sodium formate are formed; the lower-boiling stereomer on refluxing with aq. 12.5% NaOH (10% excess) for 3 hrs. gives (by dehydrochlorination) 69% yield of propargyl alcohol (propyne-1-ol-3) [Beil. I-454], b.p. 114-115° (for study of influence of NaOH concn. and time see (1)).

 \mathfrak{D} γ -Chloroallyl N-phenylcarbamate: ndls. from pet. ether, m.p. 75° (2). [From $\tilde{\mathbb{C}}$ + phenyl isocyanate (note, however, that the $\tilde{\mathbb{C}}$ employed very probably was a mixt. of the two stereoisomers (2).]

3:5820 (1) Hatch, Moore, J. Am. Chem. Soc. 66, 285-287 (1944). (2) Kirrmann, Pacaud, Dosque, Bull. soc. chim. (5) 1, 868 (1934).

3:5825 1,1,2,2-TETRACHLOROPROPANE Cl
$$C_3H_4Cl_4$$
 Beil. I - 107 CH_3 — C — $CHCl_2$ I_1 — I_2 —

B.P. 153-154° (1) $D_{13}^{13} = 1.47$ (1) 153° (3)

Liquid; misc. with alc. or ether; insol. aq.

[For prepn. of \tilde{C} from α,α -dichloroacetone (3:5430) + PCl₅ see (3); from 1,2-dichloropropene-1 (3:5150) by addn. of Cl₂ see (1); for formn. of \tilde{C} in small amt. as by-product of actn. of Cl₂ on propylene see (2).]

 \ddot{C} with warm alc. KOH, or with alc. NH₃ at 140° splits off HCl yielding (3) (1) 1,1,2(?)-trichloropropene-1, (3:5395), b.p. 115° (3), 116-117° (1).

3:5825 (1) Szenic, Taggesell, Ber. 28, 2667-2668 (1895). (2) Goudet, Schenker, Helv. Chim. Acta 10, 136 (1927). (3) Borsche, Fittig, Ann. 133, 114-117 (1865).

B.P. M.P. 155° at 760 mm. (1) (6)
$$-38.7^{\circ}$$
 (4) $D_4^{20} = 1.1598$ (2) $n_D^{20} = 1.4566$ (2) 74.7° at 50 mm. (2) 53-58° at 12 mm. (3)

The b.p. of 163° (3) is erroneous (1).

[For prepn. from N-benzoylpyrrolidine [Beil. XX-5] + PCl₅ see (3); from N,N'-dibenzoyltetramethylenediamine + PCl₅ see (5); from butanediol-1,4 (tetramethylene glycol) (1:6516) + SOCl₂ see (10); from 1-chlorobutane by chlorination in light (together with other products) see (2) (7) (8) (9); from tetrahydrofuran [Beil. XVII-10, XVII₁-(5)] with HCl gas in pres. of 50% ZnCl₂ (59% yield) see (15) [note that in absence of ZnCl₂ only 4-chlorobutanol-1 (3:9170) is formed (15) (16).]]

- [\bar{C} on passing over alkali (NaOH, K_2CO_3 , soda-lime, etc.) at elevated temperatures (e.g., 700-750°) yields butadiene-1,3.] [For studies of this reaction see (7) (8) (9).]
- C can be hydrolyzed to tetramethylene glycol (1:6516) only very slowly (6).
- C htd. with p-toluidine (3 moles) at 100° for 10 hrs. gives (70% yield (11)) N-p-tolyl-pyrrolidine, b.p. 120° at 8 mm., cryst. from dil. alc., m.p. 42° (11). [For corresp. behavior with aniline yielding N-phenylpyrrolidine see (12).]
 - ---- 1,4-Diphthalimidobutane: obtd. indirectly (13) and as by-product (14) of prepn. of N-(δ-chloro-n-butyl)phthalimide; pr. from AcOH, m.p. 219° (43).
- 3:5835 (1) Hass, J. Chem. Education 13, 493 (1936). (2) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 893-896 (1937); C.A. 31, 5755 (1937); Cent. 1938, II 2575. (3) von Braun, Beschke, Ber. 39, 4361 (1906). (4) Timmermans, Bull. soc. chrm. Belg. 31, 390 (1922). (5) von Braun, Lemke, Ber. 55, 3530 (1922). (6) Tishchenko, J. Gen. Chem. (U.S.S.R.) 9, 1380-1388 (1939); C.A. 34, 1611 (1940). (7) Muskat, Northrup, J. Am. Chem. Soc. 52, 4050-4052 (1930). (8) Carothers (to du Pont), U.S. 2,038,593, April 28, 1936; Cent. 1936, II 3358; C.A. 36, 3912 (1936). (9) Muskat (to du Pont), U.S. 2,070,609, Feb. 16, 1937, Cent. 1937, II 2597; C.A. 31, 2236 (1937). (10) Schmidt, Manchen (to General Aniline and Film Corp), U.S. 2,222,302, Nov. 19, 1941; C.A. 35, 1806 (1941).
- (11) Craig, Hixon, J. Am. Chem. Soc. 53, 189 (1931). (12) Craig, Hixon, J. Am. Chem. Soc. 52, 807 (1930). (13) Langenbeck, Waltersdorf, Blachnitzky, Ber. 72, 671-672 (1939). (14) Keil, Ber. 63, 1614-1615 (1930). (15) Fried, Kleene, J. Am. Chem. Soc. 63, 2691 (1941). (16) Starr, Hixon, J. Am. Chem. Soc. 56, 1596 (1934).

B.P. F.P. [158° (1)] -14.7° (2)
$$D_{-}^{20} = 1.394$$
 (7) $n_{\rm D}^{20} = 1.4858$ (5) 157° (6) 156.85° (2) $D_{-}^{15} = 1.417$ (8) 154-156° (4) 154.6-155.6° at 788 mm. (5)

[For prepn. of \tilde{C} from glycerol (1:6540) with 3 moles SOCl₂ + 3 moles pyridine at 110–120° (78% yield) see (9); from either 1,3-dichloropropanol-2 (glycerol α -dichloropydrin) (3:5985) or 2,3-dichloropropanol-1 (glycerol β -dichlorohydrin) (3:6060) with PCl₅ see

(10) (11); from 1,3-dichloropropanol-2 (see above) with POCl₃ at 180° (but only as byprod.) see (12), or with SOCl₂ + diethylaniline see (13); from allyl chloride (3:7035) with Cl₂ (6) or with SO₂Cl₂ (80-90% yield (14)) see indic. refs.; from allyl iodide (15) or isopropyl iodide (8) (16) with Cl₂ see indic. refs.; from propane + Cl₂ see (17) (16); from 1,2-dichloropropane (propylene dichloride) (3:5200) with Cl₂ + Fe in ultra-violet light at -18° (18) (19) or with SO₂Cl₂ in pres. of org. peroxides (26) cf. (27) see indic refs.; from propylene with Cl₂ in gas phase in dark in absence of Fe see (20).

C on htg. with 20 pts. aq. in s.t. at 160° (11) or with aq. NaHCO₃ + Cu under press. at 130° for 5-6 hrs. (21) or with steam over cat. at 550-850° (25) yields glycerol (1:6540).

Č on warming with solid KOH loses HCl yielding (22) mainly 2,3-dichloropropene-1 (3:5190) together with some 1,3-dichloropropene-1 (3:5280).

[C with alc. KSH yields (23) trithioglycerol [Beil. I-519] cf. (24).]

[C with SbCl₅ at 190° yields (6) 1,1,2,3-tetrachloropropane (3:6035).]

3:5849 (1) Carius, Ann. 124, 223 (1862). (2) Timmermans, Bull. soc. chim. Belg. 30, 67 (1921). (3) Gibson, J. Soc. Chem. Ind. 50, 950 (1931). (4) Herzfelder, Ber. 26, 1259 (1893). (5) Kohlrausch, Ypsilanti, Z. physik. Chem. B-32, 416 (1936). (6) Herzfelder, Ber. 26, 2435 (1893). (7) Blanchard, Bull. soc. chim. (4) 43, 1198 (1928). (8) Linneman, Ann. 136, 48 (1865). (9) Carré, Mauclere, Bull. soc. chim. (4) 49, 1152 (1931). (10) Fittig, Pfeffer, Ann. 135, 359 (1865).

(11) Berthelot, Luca, Jahresber. 1857, 477. (12) Hill, Fischer, J. Am. Chem. Soc. 44, 2588 (1922). (13) Darzens, Compt. rend. 152, 1314 (1911). (14) Kharasch, Brown, J. Am. Chem. Soc. 61, 3432-3434 (1939). (15) Oppenheim, Ann. 133, 383-384 (1865). (16) Berthelot, Ann. 155, 108 (1870). (17) Schorlemmer, Ann. 152, 159-163 (1869). (18) Cass, Levine (to du Pont. Co.) Brit. 471,188, Sept. 30, 1937; Cent. 1938, I 1218; C.A. 32, 957 (1938). (19) Friedel, Silva, Zeit. für. Chemie 1871, 683. (20) Laughlin, Brown (to Standard Oil Development Co.), U.S. 2,300,159, Oct. 27, 1942; C.A. 37, 1725 (1943).

(21) Matter, Ger. 369,502, Feb. 20, 1923; Cent. 1923, II 742. (22) Reboul, Ann. chim. (3) 66, 38-40 (1860). (23) Ref. 1, pp. 236-240. (25) Lillienfeld, Brit. 385,980, Feb. 2, 1933; Cent. 1933, 1928. (25) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994. (26) Kharasch, Brown, J. Am. Chem. Soc. 61, 2145 (1939). (27) Zellner (to Tide Water Associated Oil Co.) U.S. 2,370,342, Feb. 27, 1945; C.A. 39, 3535 (1945).

3:5845 TRICHLOROACRYLOYL CHLORIDE Cl C₃OCl₄ Beil. II —
$$II_{1}$$
-(187) II_{2} — II_{2} — II_{2} — II_{2} — II_{2} — II_{2} — II_{3} B.P. 158° at 760 mm. (1) (2) II_{2} II_{3} II_{2} II_{3} II_{4} II_{2}

[For prepn. of \bar{C} from trichloroacrylic acid (3:1840) with SOCl₂ (2½ moles) refluxed for 12 hrs. (80-90% yield) see (2) cf. (6).]

Č with AlCl₂ in CS₂ gives (1) a very stable 1:1 addn. prod.; on htg. it does not lose CO but ultimately decomposes giving (1) trichloroacetic acid (3:1150).

 \tilde{C} with C_6H_6 + AlCl₃ gives (100% yield (1)) (3) phenyl α,β,β -trichlorovinyl ketone [Beil. VII₁-(190)], oil, b.p. 138° at 2 mm. (2), $D_4^{25} = 1.3902$ (2); $n_2^{25} = 1.5798$ (2); for analogous behavior of \tilde{C} with toluene + many other arom. hydrocarbons + AlCl₃ see (2).

[Č with 3% $\rm H_2O_2$ + 25% aq. NaOH at -3° to 0° gives (69% yield (3)) cis-(trichloro-acryloyl) peroxide, cryst. from alc., m.p. 49°.]

- Trichloroacrylic acid amide: m.p. 97° (4), 96-97° (5), 96° (2). [From \bar{C} with conc. aq. NH₄OH (5) or from ethyl trichloroacrylate with alc. NH₃ (4).] [For crystallographic study see (4).]
- ---- Trichloroacrylic anilide: ndls. from pet. ether, m.p. 98° (6). [From C (1 mole) with aniline (2 moles) in CHCl₃ at 0° (77% yield (6)).]
- --- Trichloroacrylic p-toluidide: unreported.

3:5845 (1) Böeseken, Hasselbach, Rec. trav. chim. 32, 10-11 (1913). (2) Böeseken, Dujardin, Rec. trav. chim. 32, 101-111 (1913). (3) Böeseken, Gelissen, Rec. trav. chim. 43, 266-268 (1924). (4) Gilta, Bull. soc. chim. Belg. 39, 587-588 (1930). (5) Fritsch, Ann. 297, 317-318 (1897). (6) Bergmann, Haskelberg, J. Am. Chem. Soc. 63, 1438 (1941).

3:5850	ETHYL DICHLOROACETATE	$C_4H_6O_2Cl_2$	Beil. II - 203		
	Cl ₂ CH.Co	$Cl_2CH.COOC_2H_5$			
			Π_{2} -(196)		

B.P. 158.3-158.7° (1) 158-158.2° cor. (2) 157.7° at 754.6 mm. (3) 157° (4) 156° at 738.2 mm. (5) 154-155° at 749.5 mm. (6)

[For prepn. of \tilde{C} from dichloroacetic acid (3:6208) with EtOH + HCl see (7) (8); from chloral (3:5210) or chloral hydrate diacetate with EtOH/KCN (88% and 80% yield, respectively) see (4); from chloral cyanohydrin with abs. EtOH + conc. KOH (8) or abs. EtOH + anhyd. NaOAc (9) see indic. refs.; from tetrachloroethylene (3:5460) with NaOEt in s.t. at 100-120° see (10); from α,β -dichlorovinyl ethyl ether (3:5540) with Cl₂ followed by aq. see (11); from β,β -dichloro- α -acetoxyacrylonitrile with EtOH in s.t. at 150° see (12); for formn. of \tilde{C} in reactn. of EtOH with Cl₂ see (13).]

Č on boilg. with alc. KOH yields (14) glycolic acid (1:0430) and oxalic acid (1:0445); Č on htg. with NaOEt in abs. alc. yields (15) a small amt. ethyl diethoxyacetate together with larger amts. of diethyl oxalo-chloroacetate diethylacetal on its decn. products.

[$\ddot{\mathbf{C}}$ on boilg. with EtOH + KCN yields (16) K dichloroacetate, AcOH, and oxalic acid; $\ddot{\mathbf{C}}$ on boilg. with EtOH + KF yields (17) KCl, SiF₄ + ethyl glyoxylate.]

[C in ether treated with Na or htd. with Ag yields (18) diethyl maleate (1:3791).]

Č on shaking with aq. + benzylamine yields (19) N-benzyl-dichloroacetamide, m.p. 94.8-95.6° cor. (19), 95-96° (20).

C on hydrolysis with acid yields EtOH (1:6130) + dichloroacetic acid (3:6208). [For study of kinetics of this hydrolysis see (21) (22) (23).]

3:5850 (1) Cheng, Z. physik. Chem. B-24, 306 (1934). (2) Perkin, J. Chem. Soc. 65, 423 (1894). (3) Schiff, Ann. 220, 108 (1883). (4) Chattaway, Irving, J. Chem. Soc. 1929, 1042, 1047. (5) Brühl, Ann. 203, 22 (1880). (6) Zincke, Kegel, Ber. 22, 1475 (1889). (7) Müller, Ann. 133, 160 (1865). (8) Wallach, Ber. 10, 1525-1527 (1877). (9) Wallach, Ber. 10, 2121-2124 (1877). (10) Fischer, Geuther, Jahresber. 1864, 316.

(11) Crompton, Triffitt, J. Chem Soc. 119, 1874-1875 (1921). (12) Kötz, J. prakt. Chem. (2) 103, 232 (1921/22). (13) Altschul, Meyer, Ber. 26, 2757 (1893). (14) Claus, Ber. 14, 1066 (1881). (15) Cope, J. Am. Chem. Soc. 58, 570-572 (1936). (16) Claus, Ber. 11, 496-498; 1043-1044 (1878). (17) Swarts, Cent. 1903, I 14. (18) Tanatar, Ber. 12, 1564 (1879). (19) Buehler, Mackenzie, J. Am. Chem. Soc. 59, 421-422 (1937). (20) Mannich, Kuphal, Arch. Pharm. 256, 544 (1912).

(21) Newling, Hinshelwood, J. Chem. Soc. 1936, 1357-1361. (22) Timm, Hinshelwood, J. Chem. Soc. 1938, 862-869. (23) Salmi, Suonpaä, Ber. 73, 1126-1131 (1940).

3:5860
$$d$$
, l - α -CHLORO- n -VALERYL CHLORIDE C_5H_8 OCl₂ Beil. II - 302 CH₃.CH₂.CH₂.CH₋C=O II₁- II₂- Cl Cl

B.P. 155-157° at 763 mm. (1) $D_{-}^{-} = 1.246 (1)$

[For prepn. of \tilde{C} from α -chloro-n-valeric acid (3:8783) with PCl₃ at 70-80° see (1).]

Beil. II - 414

 \bar{C} on hydrolysis with eq. yields (1) α -chloro-n-valeric acid (3:8783), b.p. 222°.

3:5860 (1) Servais, Rec. trav. chim. 20, 46-47 (1901).

3:5870 METHYL α-CHLOROCROTONATE

B.P. 161.8° at 774 mm.

M.P. 50°

See 3:0846. Division A: Solids.

3:5870 METHYL
$$\alpha$$
-CHLOROCROTONATE $C_bH_7O_2Cl$ Beil. II - 414 CH_3 —C—H II_1 -(189) II_2 -(395) Cl—C—COOCH₃

B.P. 161-162° (1) $D_4^{23.7} = 1.1570$ (1) $D_2^{23.1} = 1.1575$ (1) $n_D^{23.1} = 1.45689$ (1) 161° (3)

161° (3)
160.8° (4)
$$D_4^{22.6} = 1.1587$$
 (2) $n_D^{22.6} = 1.45634$ (2)
158-159° (5) $D_2^{10} = 1.160$ (1)
59.0-59.5° at 16 mm. (5) $D_-^{10} = 1.166$ (5) $n_-^{19} = 1.455$ (5)

Note that the stereoisomeric methyl α -chloroisocrotonate is unreported.

[For prepn. of C from α-chlorocrotonic acid (3:2760) in MeOH with HCl gas (65% vield (5)) (1) (4); from α, α, β -trichloro-n-butyraldehyde (butylchloral) (3:1905) (as hydrate) in MeOH below 15° with KCN (2 moles) (85% yield (3)); or from methyl α-chloro-αvinylacetate (5) by isomerization with NaOAc/AcOH on refluxing 30-40 hrs. (5) see indic. refs.]

 $\ddot{\mathbf{C}}$ is unaffected by AgOH (dif. from methyl α -chloro- α -vinylacetate (5)).

3:5870 (1) von Auwers, Ber. 45, 2806 (1912). (2) Eisenlohr, Ber. 42, 3208 (1911). (3) Chattaway, Irving, J. Chem. Soc. 1929, 1045. (4) Kahlbaum, Ber. 12, 343-344 (1879). (5) Rambaud, Bull. soc. chim. (5) 1, 1353-1354 (1934).

3:5875 FUMARYL (DI)CHLORIDE
$$H-C-C=O$$
 $H_2O_2Cl_2$ Beil. II - 743 $II_{1-}(302)$ $II_{2-}(639)$ $O=C-C-H$

B.P.
$$161-164^{\circ}$$
 (1) $D_4^{20} = 1.408$ (3) $n_D^{18.1} = 1.50038$ (3) 160° (2) $D_4^{16.8} = 1.4117$ (3) $D_4^{16.8} = 1.4117$ (4) $D_4^{16.8} = 1.4117$ (5) $D_4^{16.8} = 1.4117$ (7) $D_4^{16.8} = 1.4117$ (8) $D_4^{16.8} = 1.4117$

[For prepn. of C from fumaric acid (1:0895) with PCl_b (1) (2) (3), with SOCl₂ (8) (10) (cf. (9) (11)), with phthalyl dichloride (3:6900) (12) (9) (10), or with benzotrichloride (3:6540) at 170° (27) see indic. refs.; from maleic anhydride (1:0625) by htg. 2 hrs. at 130-135° with phthaloyl dichloride (3:6900) + ZnCl₂ (82-95% yield (7)) or with PCl₅ (13) (6): for formn. of Č from succinyl dichloride (3:6200) with Cl₂ see (14), from calcium malate with PCl₅ see (15).]

Č on htg. with fumaric acid (1:0895) at 175° (9) (16) or with silver fumarate (13) is largely converted to maleic anhydride (1:0625), b.p. 197-199°, m.p. 52°.

 \bar{C} with Cl_2 in CCl_4 in sunlight adds halogen almost quant. (19) yielding (17) (18) (20) meso- α,α' -dichlorosuccinyl dichloride (3:9087). — \bar{C} adds Br_2 at 150° (2) or in CCl_4 in sunlight (20) yielding alm. quant. (19) meso- α,α' -dibromosuccinyl dichloride, b.p. 113° at 18 mm. (20) (this prod. hydrolyzes with aq. to meso- α,α' -dibromosuccinic acid, m.p. 257-258° in s.t. (20).

[Č with 1,4-diphenylbutadiene-1,3 yields (10) 3,6-diphenyltetrahydrophthaloyl dichloride, colorless ndls. from lgr., m.p. 143-144° cor. (10); this prod. on long bollg. (7½ hrs.) with aq. alc. NaOH gives (10) on acidif. 3,6-diphenyltetrahydrophthalic acid, ndls. from AcOH, m.p. 230-231° cor. dec. (10).]—[For color reactns. of C with various polyenes see (21).]

[\bar{C} on htg. at 100° with AlCl₃ is partially conv. to maleyl dichloride accompanied by evolution of HCl + CO (22). — \bar{C} with AlCl₃ + C₆H₆ gives (yield: 78-83% (23), 74% (24)) trans-α,β-dibenzoylethylene (1,4-diphenybuten-2-dione-1,4), cryst. from C₆H₆ by addn. of alc., pale yel. ndls., m.p. 109-110° (23).] [For corresp. reactn. of \bar{C} + AlCl₃ with toluene (24) (25), chlorobenzene (24), mesitylene (24), anisole (24), m-xylene (25), and biphenyl (25) see indic. refs.]

 \bar{C} with excess MeOH yields (8) dimethyl fumarate (1.2415), m.p. 101.7°. (Note, however, that \bar{C} with 1 equiv. MeOH in C_6H_6 stood 5 hrs. at room temp. (5) or in ether (26) yields fumaric methyl ester chloride, b.p. 83° at 17 mm. (26), 76° at 22 mm. (5), m.p. 16° (5); this on shaking with aq. gives alm. quant. (5) methyl hydrogen fumarate, cryst. from C_6H_6 , m.p. 144.5° cor. (5).

 \bar{C} with phenol (6) or with sodium phenolate in C_6H_6 (28) yields diphenyl fumarate, ndls. from alc., m.p. $161-162^\circ$ (6); note, however, that the half ester, phenyl hydrogen fumarate, has m.p. 130° (28).

Č with aq. readily hydrolyzes yielding fumaric acid (1:0895), m.p. abt. 293-295° subl.; for the diamide, dianilide, and other derivs. corresp. to Č see fumaric acid (1:0895).

3:5875 (1) Perkin, J. Chem. Soc. 53, 575 (1888). (2) Kekulé, Ann. Suppl. 2, 86-87 (1862/63). (3) von Auwers, Schmidt, Ber. 46, 480 (1913). (4) Wassermann, Ann. 488, 225 (1931). (5) Lutz, J. Am. Chem. Soc. 52, 3430 (1930). (6) Anschutz, Wirtz, Ber. 18, 1947-1949 (1885). (7) Kyrides, Org. Syntheses, 20, 51-54 (1940). (8) Meyer, Monatsh. 22, 421-422 (1901). (9) W. A. van Dorp, G. C. A. van Dorp, Rec. trav. chim. 25, 96-99 (1906). (10) Kuhn, Wagner-Jauregg, Ber. 63, 2664, 2678-2679 (1930).

(11) McMaster, Ahmann, J. Am. Chem. Soc. 50, 147 (1928). (12) Kyrides, J. Am. Chem. Soc. 59, 208 (1937). (13) Perkin, Ber. 14, 2545-2549 (1881). (14) Kauder, J. prakt. Chem. (2) 31, 24-25 (1885). (15) Perkin, Duppa, Ann. 112, 24-26 (1859). (16) G. C. A. van Dorp, P. J. Montagne, Rec. trav. chim. 37, 295 (1918). (17) Michael, Tissot, J. prakt. Chem. (2) 43, 394-395 (1892). (18) Holmberg, J. prakt. Chem. (2) 84, 148 (1911). (19) Lutz, J. Am. Chem. Soc. 49, 1109-1110 (1927). (20) Michael, J. prakt. Chem. (2) 52, 295 (1895).

(21) Kuhn, Wagner-Jauregg, Helv. Chim. Acta 13, 11 (1930). (22) Ott, Ann. 392, 272-273 (1912). (23) Lutz, Org. Syntheses 20, 29-32 (1940). (24) Conant, Lutz, J. Am. Chem. Soc. 45, 1303-1307 (1923). (25) Oddy, J. Am. Chem. Soc. 45, 2156-2160 (1923). (26) Anschütz, Ann. 461, 188-189 (1928). (27) Faber (to Turnbull), U.S. 1,793,917, Feb. 24, 1931; Cent. 1931, II 155. (28) Bischoff, von Hedenström, Ber. 35, 4086-4088 (1902).

Beil. I - 87

C2HCl5

See also Note 1.

Colorless liquid with odor suggesting chloroform. — C is widely used in industry as solvent, degreasing agent, dry cleaner, component of insecticides, etc. - Note that comml. Č is likely to contain other prods., notably tetrachloroethylene (3:5460) q.v.

Č is very spar. sol. aq.; e.g., 1 g. Č requires for soln. at 25° 2900 g. aq. (19): for study of soly. of C in aq. at 20° see (20); for study of soly. of aq. in C at 0°, 25°, and 30° as detd. by Karl Fischer reagt. see (21).

Binary systems contg. \bar{C} . For f.p./compn. data on systems $\bar{C} + 1.2$ -dichloroethane (ethylene dichloride) (3:5130), eutectic, f.p. -62° , contg. about 56 wt. % \overline{C} (22); \overline{C} + 1,1,1-trichloroethane (methylchloroform) (3:5085), eutectic, f.p. -69.0° contg. 72.3% \ddot{C} (14); $\ddot{C} + 1,1,2,2$ -tetrachloroethane (acetylene tetrachloride) (3:5750), eutectic, f.p. -73° . contg. 59.9 wt. % \bar{C} (22); \bar{C} + tetrachloroethylene (3:5460), eutectic, f.p. -54.8° , contg. 41.6% \bar{C} (14); \bar{C} + CCl_4 (3:5100), eutectic, f.p. -68° (82), \bar{C} + CBr_4 (82) see indic. refs.

C forms binary azeotropes with various org. cpds.; e.g., C with chloroacetic acid (3:1370) forms a const.-boilg. mixt., b.p. 158.65° at 760 mm., contg. 90.1 wt. % $\bar{\mathrm{C}}$ (23); $\bar{\mathrm{C}}$ with trichloroacetic acid (3:1150) forms a const.-boilg. mixt., b.p. 161.8° at 760 mm., contg. 96.5 wt. % C (24). — For other examples see Beil. I₂-(57).

Č either as liquid or vapor is extremely toxic; for further details see (83) (25) (26) (27) (28) (29); for extensive study of anthelmintic action see (19).

[For study of soly. in C of gaseous HCl (30) (11), H₂S (30), or NH₃ (30) see indic. refs.: for study of thermal conductivity of C see (31); for study of influence of vapors of C on

the explosion limits of mixtures of air with hydrogen, carbon monoxide, methane, acetylene, etc., see (32) (33) (34) (35).]

Preparation of C. [For prepn. of C from chloral (3:5210) with PCl₅ (7) (37) or with AlCl₃ (38) see indic. refs.; note that in latter case (38) presence of AlCl₃ also facilitates loss of HCl from C with consequent formn. of tetrachloroethylene (3:5460); from triehloroethylene (3:5170) by addn. of Cl₂ in aq. (39) or under influence of ultra-violet light (40) (41) (note that O₂ retards addition of halogen (41)), or with S₂Cl₂ in s.t. at 140-150° (42), see indic. refs.]

[For form. of \bar{C} (together with various other by-products) from ethyl chloride (3:7015) (43) or from 1,2-dichloroethane (ethylene dichloride) (3:5130) (44) with Cl₂ see indic. refs.; from chloroform (3:5050) in electric arc (45) or in dark electric discharge (46) see indic. refs.; from CCl₄ in dark elec. discharge see (46); from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) or from trichloroethylene (3:5170) with Cl₂ at 80°, 95°, or 115° in ultra-violet light (41), over pumice at 700° (47), or with FeCl₃ on htg. in s.t. (48) see indic. refs.; from trichloroethylene (3:5170) with large excess Cl₂O in CCl₄ at -20° see (10); from β,β' -dichlorodiethyl sulfide ("mustard gas") with dry Cl₂ at 100° see (49).]

[For stabilization of \bar{C} by addn. of not over 0.1% alkyl amines such as Et₃N (50) or with a wide variety of other org. N cpds. (81) see indic. refs.]

[For studies of detn. of \tilde{C} by reactn. with Na + ethanolamine in dioxane (51) followed by volumetric (51) or gravimetric (71) detn. of resultant chloride ion see indic. refs. (note that use of Stepanov's method (Na + EtOH) for detn. of Cl in \tilde{C} gives low results unless after addn. of Na mixt. is refluxed at least 20 hrs. (12)); for detn. of \tilde{C} by thermal decn. and subsequent detn. of chlorine see (52).]

Chemical behavior of \bar{C} . $[\bar{C}$ with dry Cl₂ at 70° in diffuse light does not react and even after 30 hrs. no HCl is formed (52); however, \bar{C} with dry Cl₂ + AlCl₃ at 70° (53), or \bar{C} + Cl₂ over activated charcoal at 300-400° (54), yields hexachloroethane (3:4835).]

[\bar{C} with F_2 at 90° over a 10-hr. period yields (8) a mixt. of prods. contg. fluoropenta-chloroethane, m.p. 99.8–110° (in s.t.) (b.p. 137–139°), hexachloroethane (3:4835), tetra-chloroethylene (3:5460), sym.-difluorotetrachloroethane, b.p. 91–92°, together with other materials. — For behavior of \bar{C} with SbF₃ see (55).]

 \bar{C} with $K_2Cr_2O_7/H_2SO_4$ is only partially oxidized to CO_2 (56). — [\bar{C} on photochem. oxidn. with O_2 in ultra-violet light (57) (58) gives a mixt. consisting of 80% trichloroacetyl chloride (3:5420) + 20% phosgene (3:5000). — \bar{C} with fumg. H_2SO_4 (60% SO_3) at 50–60° yields (59) dichloroacetyl chloride (3:5290).]

Č under various circumstances loses HCl yielding tetrachloroethylene (3:5460) [e.g., Ĉ over bone char at 280° (60) or over NiCl₂ at 330° (61), or with AlCl₃ at 70° (53) or under reflux (95% yield (72)) (62), or with liq. NH₃ at −18 to −34° under reduced press. (63) (64), or with prim. or sec. aliph. amines (84), or with MeOH over Al₂O₃ at 290° (methyl chloride (3:7005) is also formed) (65), or with acetylene over cat. at 200–300° (vinyl chloride (3:7010) is also formed) (68), or with alc. KOH (44) (66), or in alc. with 2 N aqueous NaOH in cold (98% yield (12)) gives tetrachloroethylene (3:5460). — For detn. of Č by titration of chloride ion thus split off see (67); for study of kinetics of reactn. of Č with EtOH/NaOH see (12).]

Č under certain conditions yields trichloroethylene (3:5170) [e.g., Č with H₂ over Ni at 270° (61), or Č on electrolysis at Pb cathode (69), or Č with MeMgI (70) gives trichloroethylene (3:5170).]

[Č with CHCl₃ (3:5050) + AlCl₃ gives (72) (73) (74) (75) unsym.-heptachloropropane (3:0200); note that this reactn. first involves loss of HCl under influence of AlCl₃ (see also above) and subsequent condensation of the resultant tetrachloroethylene (3:5460)

with CHCl₃. — \tilde{C} (1 mole) + 1,2-dichloroethylene (presumably mixt. of cis (3:5042) and trans (3:5028) stereoisomers) + AlCl₃ (1% of sum of wts. of reactants) stood 12 days at 40° gives (76) (in addition to a residue a fraction volatile with steam which consists of 1,1,2,2,3,4,4-heptachlorobutane (3:9056)), two stereoisomeric 1,1,2,3,4-pentachlorobutanes, viz., the solid isomer (3:0750) and the liquid isomer (3:9068); for genesis of these compds. see (76).]

[For survey of actn. of \bar{C} on various common metals see (77). — \bar{C} with Na or K or their alloys may (like many other polychloro compds.) explode under certain conditions; for an extensive study of this behavior including sensitivity to mechanical shock see (78).]

- Č with excess phenylhydrazine on stdg. at ord. temp. evolves N₂, ppts. phenylhydrazine hydrochloride, and yields benzene (67); the full mechanism of this behavior seems never to have been established, but these same three prods. are similarly obtd. from hexachlorocthane (3:4835) and to a lesser degree from 1,1,2,2-tetrachlorocthane (3:5750).
 - D Color test with NH₄OH/Cu₂Cl₂. \bar{C} (1-2 drops) in small glass-stoppered bottle filled with conc. aq. NH₄OH treated with powdered Cu₂Cl₂, stopper quickly inserted (to force out air and excess liq.) and shaken, gives within 5 mins. a blue color which rapidly darkens; note that this test is not specific for \bar{C} and is also shown by other cpds. contg. the —CCl₃ group such as trichloroacetic acid (3:1150), ethyl trichloroacetate (3:5950) CHCl₃ (3:5050), CCl₄ (3:5100), although hexachloroethane (3:4835) develops color at surface only after several hours; for further details see {79}.
- 3:5880 (1) Timmermans, Martin, J. chim. phys. 23, 775-776 (1926). (2) Timmermans, Bull. soc. chim. Belg. 27, 334-343 (1914), Cent. 1914, I 618. (3) Lecat, Rec. trav. chim. 46, 244 (1927). (4) Staedel, Ber. 15, 2563 (1882). (5) Earp, Glasstone, J. Chem. Soc. 1935, 1712. (6) Kanonni-koff, J. prakt. Chem. (2) 32, 520 (1885). (7) Thorpe, J. Chem. Soc. 37, 192-194 (1880). (8) Miller, J. Am. Chem. Soc. 62, 342 (1940). (9) Bonino, Gazz. chim. ital. 55, 342 (1925). (10) Goldschmidt, Schüssler, Ber. 58, 569-570 (1925).
- (11) Hamai, Bull. Chem. Soc. Japan 10, 207-211 (1935). (12) Taylor, Ward, J. Chem. Soc. 1934, 2003-2010. (13) Herz, Rathmann, Chem. Zty. 36, 1417 (1912). (14) Van de Vloed, Bull. soc. chim. Belg. 48, 259-260 (1939). (15) Deffet, Bull. soc. chim. Belg. 44, 63 (1935). (16) Herz, Rathmann, Chem. Zty. 37, 621 (1913). (17) Emmons, Am. Mineral. 14, 482-483 (1929). (18) Nelson, Ind. Eng. Chem. 22, 972 (1930). (19) Wright, Schaffer, Am. J. Hyg. 16, 325-428 (1932). (20) van Arkel, Vles, Rec. trav. chim. 55, 410 (1936).
- (21) Staverman, Rec. trav. chim. 60, 836-841 (1941); Cent. 1942, I 1352; C.A. 37, 2638 (1943). (22) Timmermans, Veselovsky, Bull. soc. chim. Belg. 40, 506 (1931). (22) Lecat, Ann. soc. sci. Bruxelles 47, I 25 (1927). (24) Lecat, Rec. trav. chim. 47, 17 (1923). (25) Jacobs, "The Analytical Chemistry of Industrial Poisons, Hazards and Solvents," Interscience Publishers, Inc., New York (1941). (26) Smyth, N. Y. State J. Med. 42, 1072-1079 (1942); C.A. 36, 4626 (1942). (27) Barsoun, Saad, Quart. J. Pharm. Pharmacol. 7, 205-214 (1934); Cent. 1934, II 2550; C.A. 28, 6194 (1934). (28) Lazarev, Arch. exptl. Path. Pharmakol. 141, 19-24 (1929); Cent. 1929, II 451; C.A. 25, 3074 (1931). (29) Lehmann, et al., Arch. Hyg. 74, 1-60 (1911); Cent. 1911, II 885-886; C.A. 6, 3125 (1912). (30) Bell, J. Chem. Soc. 1931, 1376-1377.
- (31) Bates, Hazzard, Palmer, Ind. Eng. Chem. 33, 375-376 (1941). (32) Langen van der Valk, Rec. trav. chim. 48, 201-219 (1929). (33) Jorissen, Ind. Eng. Chem. 19, 430-431 (1927). (34) Coward, Jones, Ind. Eng. Chem. 18, 970-974 (1926). (35) Jorissen, Meuwissen, Rec. trav. chim. 44, 132-140 (1925). (36) Jorissen, Velisek, Rec. trav. chim. 43, 80-86 (1924). (37) Paterno, Ann. 151, 116-121 (1869). (38) Mouneyrat, Bull. soc. chim. (3) 19, 260-261 (1898). (39) Groll, Hearne (to N. V. de Bataafsche Petroleum Maatschappij), Brit. 436,357, Nov. 7, 1935; French 789,290, Nov. 25, 1935; Cent. 1936, II 865; C.A. 39, 1812 (1936). (40) Salzberg Neustassfurt und Theilnehmer, Ger. 248,982, July 6, 1912; Cent. 1912, II 299; [C.A. 6, 2824 (1912)].
- (41) Müller, Schumacher, Z. physik. Chem. B-35, 458-462 (1937); Z. Elektrochem. 43, 807-808 (1937).
 (4) Pope, Smith, J. Chem. Soc. 119, 396 (1920).
 (43) Regnault, Ann. 33, 321-323 (1840).
 (44) Pierre, J. prakt. Chem. (1) 43, 301-307 (1848).
 (45) Tarczynski, Z. Elektrochem.
 22, 254 (1916).
 (46) Berson, Fournier, Compt. rend. 156, 1119 (1910).
 (47) Nicodemus, J. prakt. Chem. (2) 83, 315-322 (1911).
 (48) Erdmann, J. prakt. Chem. (2) 85, 84 (1912).
 (49) Mann, Pope, J. Chem. Soc. 121, 597 (1922).
 (50) Imperial Chem. Ind., Ltd., French 744,128; Cent. 1933, II 605.

(51) Winteringham, J. Soc. Chem. Ind. 61, 186-187 (1942); C.A. 37, 1951 (1943). (52) Winteringham, J. Soc. Chem. Ind. 61, 190-192 (1942); C.A. 37, 1951 (1943). (53) Mouneyrat, Bull. soc. chim. (3) 17, 797-799 (1897); (3) 19, 182-183 (1898). (54) Mkryan, Babayan, Sbornik Trudov. Armyanskogo Filiala Akad. Nauk 1940, No. 2, 51-58; C.A. 37, 5694 (1943). (55) Henne, Ladd, J. Am. Chem. Soc. 58, 402-403 (1936). (56) Guyot, Simon, Compt. rend. 170, 736 (1920). (57) Schumacher, Thirauf, Z. physik. Chem. A-189, 183-199 (1941); Cent. 1942, I 1485; C.A. 38, 4418 (1942). (58) Muller, Ehrmann, Ber. 69, 2207-2210 (1936). (59) Chem. Fabrik. Weilerter-Meer, Ger. 362,748, Oct. 31, 1922; Cent. 1923, II 405. (60) Körner, Suchy (to Dr. A. Wacker Soc. Chem. Ind.), Ger. 464,320, Aug. 21, 1928; Cent. 1929, I 1044.

(61) Mailhe, Sabrou, Bull. soc. chim. (4) 47, 349-350 (1930). (62) Mugdan, Wimmer (to Consortium fur Elektrochem. Ind.), U.S. 2,249,512, July 15, 1941; C.A. 35, 6601 (1941): Brit. 500,176, March 2, 1939; Cent. 1939, I 3798; C.A. 33, 5417 (1939): Ger. 694,884, July 11, 1910, C.A. 35, 5134 (1941): French 841,962, June 2, 1939; Cent. 1939, II 2280; C.A. 34, 4395 (1940). (63) Mkryan, Sbornik Trudov Armyanskogo Filiala Akad. Nauk 1940, No. 2, 36-41; C.A. 37, 5694 (1943). (64) Pogossjan, Mkryan, Russ. 50,533, Feb. 28, 1937; Cent. 1938, II 412. (65) I.G., French 805,563, Nov. 24, 1936; Cent. 1937, I 2258. (66) Sastry, J. Soc. Chem. Ind. 35, 450-452 (1916). (67) Gowing-Scopes, Analyst 39, 385-388 (1914). (68) Dr. A. Wacker Soc. Chem. Ind. Brit. 480,568, March 24, 1938; Cent. 1938, I 4236; C.A. 32, 5857 (1938). (69) Sandonnini, Borghello, Atti accad. Lincei (6) 20, 334-340 (1934); Cent. 1935, I 3654. (70) Rebek, Mandrino, Oesterr. Chem. Ztg. 41, 363-384 (1938); Cent. 1939, I 900; C.A. 33, 1266 (1939).

(71) Rauscher, Ind. Eng. Chem., Anal. Ed. 9, 296-299 (1937). (72) Prins, Rec. trav. chim. 54, 250 (1935). (73) Böeseken, Prins, Verhandl. Akad. Wetenschappen 1911, 776-778, Cent. 1911, 1466; C.A. 5, 2845 (1911). (74) Prins, J. prakt. Chem. (2) 89, 415 (1914). (75) Farlow, Org. Syntheses, Coll. Vol. 2 (1st ed.), 312-313 (1943); 17, 58-59 (1937). (76) Prins, Rec. trav. chim. 56, 119-120, 124-125 (1937). (77) Gowing-Scopes, Analyst 39, 7 (1914). (78) Lenze, Mets, Z. ges. Schiess-u. Sprengstoffu. 27, 255-258, 293-296, 337-340, 373-376 (1932); Cent. 1933, I 1716; C.A. 27, 844 (1933). (79) Doughty, J. Am. Chem. Soc. 41, 1129-1131 (1919). (80) Eckart, Brennstof-Chem. 4, 24-25 (1923); C.A. 17, 2356 (1923).

(81) Missbach (to Stauffer Chem. Co.), U.S. 2,043,257-2,043,260, incl., June 9, 1936; Cent. 1936, II 3845; C.A. 30, 5240 (1936). (82) Verstraete, Bull. soc. chim. Belg. 43, 523-527 (1934).

(83) Lehman, Schmidt-Kehl, Arch. Hyg. Bakt. 116, 131-268 (1936); C.A. 31, 477 (1937); not in Cent. (84) Rueggeberg, Falkof, J. Am. Chem. Soc. 67, 2052 (1945).

3:5885 1,2,3-TRICHLORO-2-METHYLPROPANE C4H7Cl3 Beil. S.N. 10

B.P. $162.0-163.1^{\circ}$ cor. (1) $D_4^{25} = 1.3020$ (1) $n_D^{20} = 1.4765$ (1)

[For prepn. of \bar{C} from ter-butyl chloride (3:7045) + Cl₂ see (1), for formn. of \bar{C} (5%) from 3-chloro-2-methylpropene-1 (methallyl chloride) (3:7145) by addn. of Cl₂ with Cl₂/aq. at 30° (main prod. is 1,3-dichloropropanol-2 (3:5985) in 70% yield) (2), or better with SO₂Cl₂ (83% yield (4)) see indic. refs.; from 1,3-dichloro-2-methylpropane (3:7960) with Cl₂, or with SO₂Cl₂ + Bz₂O₂ (73% yield) see (4).]

Č on pyrolysis at 450-550° gives (3) three isomeric dichloroisobutenes, viz., cis and trans 1,3-dichloro-2-methylpropene (3:5590) and 3-chloro-2-(chloromethyl)propene-1 (3:5633).

[Č on dehydrohalogenation with equimolal proportion of quinoline at b.p. 1½ hrs. gives (73-83% yield (4)) 1,3-dichloro-2-methylpropene-1 (3:5590).]

 \ddot{C} on hydrolysis with excess 5% aq. NaOH gives (84% yield (3)) a mixt. of *cis* and *trans* stereoisomers of γ -chloro- β -methyl-allyl alcohol (3:8340).

3:5885 (1) Rogers, Nelson, J. Am. Chem. Soc. 58, 1027-1029 (1936). (2) Burgin, Hearne, Rust, Ind. Eng. Chem. 33, 387 (1941). (3) Rogers, Nelson, J. Am. Chem. Soc. 58, 1029-1031 (1936). (4) Mooradian, Cloke, J. Am. Chem. Soc. 68, 787 (1946).

3:5890 ISOPROPYL DICHLOROACETATE $C_5H_8O_2Cl_2$ Beil. S.N. 160 (CH₃)₂CH.O.CO.CHCl₂

B.P. 163.8–164.8° (1)
$$D_4^{25} = 1.1989$$
 (2) $n_D^{25} = 1.4306$ (2) 164.0° at 747 mm. (2) $D_4^{20} = 1.2053$ (3) $n_D^{20} = 1.4328$ (3)

[For prepn. (48.6% yield (2)) from isopropyl alc. (1:6135) + dichloroacetic ac. (3:6208) see (2); for prepn. (39.5% yield (2)) from propylene and dichloroacetic ac. (3:6208) see (2).

[For study of hydrolysis of C see (3).]

3:5890 (1) Cheng, Z. physik. Chem. B-24, 310 (1934). (2) Dorris, Sowa, Nieuwland, J. Am. Chem. Soc. 56, 2689-2790 (1934). (3) Schianberg, Z. physik. Chem. A-172, 229 (1935).

Colorless liq. with characteristic penetrating ethereal odor. — Insol. in aq.; eas. sol. alc., ether.

[For prepn. of \bar{C} from 2,3-dichloropropene-1 (3:5190) with Cl_2 see (1); from 1,2,2-tri-chloropropane (3:5475) with $SbCl_5$ at 100° see (2).]

C with alc. KOH splits out HCl yielding (1) 1,2,3-trichloropropene-1 (3:5650), b.p. 142°.

3:5895 (1) Pfeffer, Fittig, Ann. 135, 360-361 (1865). (2) Herzfelder, Ber. 26, 2436 (1893).

3:5900 1,3-DICHLOROBUTANONE-2 H
$$C_4H_6OCl_2$$
 Beil. I - 670 (α -Chloroethyl chloromethyl ketone) Cl.CH₂.CO—C—CH₃ I₁-(348) I₂—

B.P. 165° (2) at 753 mm. (1)
$$D_4^{20} = 1.3116$$
 (3) $n_D^{20} = 1.4686$ (3) 65° at 17 mm. (2) $D_4^{15} = 1.3189$ (3) $n_D^{15} = 1.4702$ (3) 55–55.5° at 10 mm. (3)

Colorless liq. when freshly distd. but gradually turns red. — Strong lachrymator and nasal irritant (1). — Insol. aq.; sol. alc., ether, and most org. solvents.

[For prepn. from ethyl methyl ketone (1:5405) by actn. of Cl₂ (1), from 1,3-dichlorobutanol-2 (3:9145) by oxidn. (3); from 3-chloro-2-(chloromethyl)butene-1 (3:9206) with O_3 (4) see indic. refs.]

 \ddot{C} with satd. aq. NaHSO₃ soln. yields cryst. NaHSO₃ cpd. (1). — \ddot{C} with Zn dust + AcOH yields (1) (3) ethyl methyl ketone (1:5405).

1.3-Dichlorobutanone-2 semicarbazone: m.p. 114° (2), 107-108° (4).

3:590 (1) Démètre-Vladesco, Bull. soc. chim. (3) 6, 829-830 (1891). (2) Blaisé, Bull. soc. chim. (4) 15, 733 (1914); Compt. rend. 156, 794 (1913). (3) Petrov, J. Gen. Chem. (U.S.S.R.) 11, 713-721 (1941); C.A. 36, 404 (1941). (4) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4223; [C.A. 33, 4190 (1939)].

3:5910
$$\alpha,\alpha,\beta$$
-TRICHLORO- n -BUTYRALDEHYDE C_4H_8 OCl₃ Beil. I - 664 ("Butyrchloral"; "Butylchloral"; Cl I₁-(346) I₂-(725) CH₃.CH.C.CHO Cl Cl Cl Cl B.P. 164.5-165.5° at 760 mm. (1) $D_4^{20} = 1.3956$ (4) $n_D^{20} = 1.47554$ (4) 165° (2)

 $D_{15}^{18.8} = 1.4237 (5)$

[See also "Butyrchloral hydrate" (3:1905).]

at 750 mm. (3) (4)

(6)

Oily liq.

164-165°

163-164°

[For prepn. of \bar{C} from acetaldehyde (1:0100) (3) (7) or paraldehyde (1:0170) (7) (8) with Cl_2 see indic. refs.; from α -chlorocrotonaldehyde (3:8117) by addn. of Cl_2 (6) (10) (36) in CCl_4 soln. (9); from crotonaldehyde (1:0150) by satn. with HCl gas followed by treatment with Cl_2 see (11) cf. (37).]

[For prepn. of \tilde{C} from its polymers (see below) by distn. at atmospheric press. (2), or from its hydrate (3:1905) by distn. with half its wt. of Ac₂O (2), or shaking with conc. H₂SO₄ (1) cf. (2), see indic. refs.]

 $[\bar{C}$ on reduction with fused Al(OEt)₃ in boilg. abs. alc. under H₂ or N₂ for 14 hrs. (12) or with fused Al(OEt)₃ + AlCl₃ in boilg. abs. alc. under H₂ or N₂ for 14 hrs. (13), or with C₂H₅OMgBr in dry ether followed by aq. (19), or by treatment with diethylzinc (14), di-n-propylzinc (15), or di-isobutylzinc (15) (followed by aq.) gives (92% yield (12)) 2,2,3-trichlorobutanol-1 (3:1336), m.p. 62°.—Note that \bar{C} (as hydrate) (3:1905) is reduced by fermenting yeast (16) to dextrorotatory 2,2,3-trichlorobutanol-1, m.p. 62°.]

[\bar{C} with Zn + HCl or Zn + aq. (17) is dehalogenated to a mixt. of α -chlorocrotonaldehyde (3:8117) + crotonaldehyde (1:0150); \bar{C} with Fe filings + AcOH at room temp. for 8 days (18) dehalogenates to a mixt. of n-butyraldehyde (1:0130) + n-butyl alc. (1:6180) + crotonyl alc. [Beil. I-442, I₁-(227), I₂-(480)].]

 \bar{C} on oxidn. with 2 pts. fumg. HNO₃ stood overnight at ord. temp. yields (3) α,α,β -trichloro-n-butyric acid (3:1280) (cf. corresp. behavior of butyrchloral hydrate (3:1905)). — \bar{C} on oxidn. with boilg. aq. K₄Fe(CN)₅ also loses 2 atoms of chlorine giving (41% yield (29)) α -chlorocrotonic acid (3:2760).

 \bar{C} (1 mole) with H_2O (1 mole) readily combines with evolution of heat yielding (3) (9) crystn. butyrchloral hydrate (3:1905). — Similarly, \bar{C} combines with equiv. amt. of alcohols giving the corresp. alcoholates: e.g., \bar{C} with EtOH yields (20) butyrchloral-ethylalcoholate [Beil. I-665, I_1 -(346)]; \bar{C} with butanol-2 yields (1) butyrchloral-sec-butylalcoholate, etc. — Note that butyrchloral-ethylalcoholate in excess EtOH on satn. with dry HCl gas gives (50% yield (21)) α,α,β -trichloro-n-butyraldehyde diethylacetal, b.p. 232-233°, 135° at 30 mm. (21). — [For study of dissociation of addn. cpds. of \bar{C} with various prim., sec., and ter. alcohols see (22).]

 \tilde{C} or its hydrate (3:1905) q.v. in pres. of conc. H_2SO_4 or pyridine at ord. temp. can be trimerized to a mixt. of two parabutyrchlorals (2); these are colorless, crystalline, sharp melting solids, sol. in org. solvents but insol. in aq.; the less sol. α -parabutyrchloral, rhombic cryst. from boilg. AcOH or boilg. EtOH, has m.p. 180°; the more soluble β -parabutyrchloral (stereoisomer?), cryst. from boilg. AcOH or boilg. EtOH, has m.p. 157°; these polymers can be distilled at 15 mm., but attempts to distill them at ord. press. result in complete dissociation to \tilde{C} (2).

[Č with anhydrous acetaldehyde (1:0100) (2 moles) with dry HCl gas at 0° for 15–20 hrs. condenses to give (67% yield (23)) 2,4-dimethyl-6- $(\alpha,\alpha,\beta$ -trichloro-n-propyl)trioxane-1,3,5, b.p. 118° at 13 mm. (23).]

[Č in CHCl₈ with H₂S gives (24) bis- $(\alpha$ -hydroxy- β , β , γ -trichloro-n-butyl)sulfide ("butyr-chloralsulfhydrate"), m.p. 85° (24).]

[C with PCl₅ (1.4 wt. pts.) at 110-120° apparently has its oxygen replaced by equivalent chlorine but also loses 1 HCl yielding (25) a cpd. of compn. C₄H₂Cl₄, presumably 1,1,2,3-tetrachlorobutene-2, although no other report of this cpd. can be found.]

[Č with aq. HCN gives only butyrchloral hydrate (3:1905) since this prod. is too spar. sol. aq. to enter further reaction, but upon addn. of alc. and subsequent digestion this system yields (26) (27) α,α,β -trichloro-n-butyraldehyde cyanohydrin [Beil. III-322, III₂-(226)], pl. from aq., m.p. 101-102° (27) (28), also obtd. from butyrchloral hydrate with aq. KCN (2 moles) at 40° (28). — See also further comments under butyrchloral hydrate (3:1905).]

[\bar{C} with ethyl diazoacetate gives (71% yield (30)) ethyl β -keto- γ,γ -trichloro-n-caproate [Beil. III-684], b.p. 149° at 20 mm. (30).]

Č in CHCl₃ with NH₃ gas gives on evapn. of solvent (31) butyrchloralammonia, cryst., m.p. 62° [see also under butyrchloral hydrate (3:1905)].

Č also readily adds amides yielding cpds. of type CH₃.CHCl.CH₂CH (OH).NH.CO.R; e.g., Č with acetamide (1 mole) gives on htg. (31) (32) (33) (34) butyrchloralacetamide, obtd. by these workers in two isomeric forms one of m.p. 170° (spar. sol. hot alc.) (32) (33) (34), the other m.p. 158° (readily sol. in hot 50% alc.) (31) (32) (33); note, however, that butyrchloral hydrate (3:1905) with acetamide (1 mole) htd. at 100° until solidification occurs gives only (21) a prod. m.p. 208−210°; Č with benzamide (1 mole) gives on htg. butyrchloralbenzamide, obtd. in two isomeric forms, one of m.p. 146° (32) (33) cf. (34), the other of m.p. 132° (31) (32) (33); note, however, that butyrchloral hydrate (3:1905) with benzamide yields only (21) a prod. m.p. 176°.

Č (3.5 g.) with urea (1.2 g.) htd. at 100°, cooled, powdered and recrystd. from alc., gives (yield not stated (35)) butyrchloralurea, m.p. 156°.

3:5910 (1) Willcox, Brunel, J. Am. Chem. Soc. 38, 1837 (1916). (2) Chattaway, Kellett, J. Chem. Soc. 1928, 2709-2714. (3) Krämer, Pinner, Ber. 3, 383-390 (1870). (4) Brühl, Ann. 203, 20 (1880). (5) Dobrosserdow, Cent. 1911, I 955. (6) Pinner, Ber. 8, 1564-1566 (1875). (7) Pinner, Ann. 179, 24-30 (1875). (8) Freundler, Bull. soc. chim. (4) 1, 68-69 (1907). (9) Moureu, Murat, Tampier, Bull. soc. chim. (4) 29, 33 (1921). (10) Lieben, Zeisel, Monatsh. 4, 533-536 (1883).

(11) High (to Udylite Corp.), U.S. 2,280,290, April 21, 1942; C.A. 36, 5482 (1942). (12) Meerwein, Schmidt, Ann. 444, 233-234 (1925). (13) Meerwein (to F. Bayer & Co.), U.S. 1,572,742, Feb. 9, 1926; Cent. 1926, I 3627: Brit. 251,890, June 3, 1926; Cent. 1926, II 1097. (14) Garsarolli-Thurnlackh, Ann. 213, 369-372 (1882). (15) Garzarolli-Thurnlackh, Papper, Ann. 223, 166-169 (1884). (16) Rosenfeld, Brochem. Z. 156, 54-57 (1925); Cent. 1925, I 2301; C.A. 19, 2683 (1925). (17) Sarnow, Ann. 164, 108 (1872). (18) Lieben, Zeisel, Monatsh. 1, 840-843 (1880). (19) I.G., Brit. 384,156, Dec. 22, 1932; Cent. 1933, I 1351. (20) Pinner, Ann. 179, 38-42 (1875).

(21) Freundler, Bull. soc. chim. (4) 1, 201, 203-204 (1907); Compt. rend. 143, 684 (1906). (22) Willcox, Brunel, J. Am. Chem. Soc. 38, 2533-2535 (1916). (23) Helferich, Besler, Ber. 57, 1279-1280 (1924). (24) Voswinkel, Ger. 233,857, April 24, 1911; Cent. 1911, I 1467. (25) Judson, Ber. 3, 790 (1870). (26) Pinner, Bischoff, Ann. 179, 97-99 (1875). (27) Pinner, Klein, Ber. 11, 1488 (1878). (28) Chattaway, Irving, J. Chem. Soc. 1929, 1043-1046. (29) Wallach, Ber. 10, 1530 (1877). (30) Schlotterbeck, Ber. 42, 2572 (1909).

(31) Schiff, Tassinari, Ber. 10, 1784-1786 (1877). (32) Schiff, Ber. 25, 1690-1691 (1892). (33) Tarugi, Gazz. chim. ital. 24, I 230-236 (1894). (34) Pinner, Ann. 179, 39-40 (1875). (35) Feist, Kublinski, Arch. Pharm. 274, 430, 434 (1936). (36) Chem. Fabrik vorm. Weiler ter-Meer, Ger. 351,137, April 3, 1922; Cent. 1922, IV 155. (37) Brown, Plump (to Pennsylvania Salt Mfg. Co.), U.S. 2,351,000, June 13, 1944; C.A. 38, 5226 (1944).

B.P.
$$165^{\circ}$$
 (1) $D_4^{34} = 1.5274$ (1) $n_D^{18} = 1.5272$ (1) $165-167^{\circ}$ (2)

Colorless oil.

[For prepn. (70% yield (2)) from sym.-pentachloropropane (3:6280) by actn. of alc. KOH (1 mole) see (2).]

C with conc. H₂SO₄ at 30-40° gives quant. yield of chloromalondialdehyde [Beil. I-765].

3:5920 (1) Prins, J. prakt. Chem. (2) 89, 421-422 (1914). (2) Heilbron, Heslop, Irving, J. Chem. Soc. 1936, 783.

3:5935 1,2,3-TRICHLOROBUTANE
$$Cl\ Cl\ Cl\ C_4H_7Cl_3$$
 Beil. I - 119 CH_3-C-CH_2 I_{1-1} I_{2-1} I_{2-1} (82)

B.P.
$$165-167^{\circ}$$
 at 759 mm. (1) $D_4^{20}=1.3164$ (1) $n_D^{20}=1.4790$ (1) $165-168^{\circ}$ at 725 mm. (2) $79-80^{\circ}$ at 32 mm. (3) $D_4^{18}=1.3172$ (1) $D_0^{0}=1.3241$ (3)

Insol. aq., sol. alc., ether, CHCl₃.

[For formn. of \bar{C} (36.5%) from 2,3-dichlorobutane (3:7615) + sl. excess Cl₂ in dark at -17° (together with 18% 2,2,3-trichlorobutane (3:5680)) see (1); for formn. of \bar{C} (19%) from 1,2-dichlorobutane (3:7680) + sl. excess Cl₂ in dark at -17° (together with 28% 2,2,3-trichlorobutane (3:5680) see (1); for formn. of \bar{C} from 1-chlorobutene-2 (3:7205) + Cl₂ in CHCl₃ see (3); for formn. of \bar{C} from butene-1 with Cl₂/aq. (together with 1,2-dichlorobutane (3:7680)) see (2).]

Č with solid KOH at 150° loses HCl yielding (1) mixt. of cis-1,2-dichlorobutene-2 (3:5615), b.p. 125-127°), and trans-1,2-dichlorobutene-2 (3:5360), b.p. 116-118° at 765 mm. (1).

3:5935 (1) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 6, 1553-1558 (1936); C.A. 31, 2165 (1937); Cent. 1937, I 3786. (2) de Montmollin, Matile, Helv. Chim. Acta 7, 108 (1924). (3) Charon, Ann. chim. (7) 17, 230-231 (1899).

B.P. 167° M.P. 96-97°

See 3:2662. Division A: Solids.

```
3:5950 ETHYL TRICHLOROACETATE
                                                            C4H5O2Cl3
                                                                              Beil. II - 209
                                                                                    II1-( 94)
                                             Cl<sub>2</sub>C.COOC<sub>2</sub>H<sub>5</sub>
                                                                                    II_{2}-(200)
                                                 D_4^{20} = 1.3826 \quad (8)
                                                                        n_{\rm D}^{20} = 1.45068  (8)
  B.P. 167.5-168.0° cor.
                                        (1)
       167.5°
                                        (2)
                                                         1.3823 (10)
                                                                               1.45046 (10)
       166.7-167.1° at 754.8 mm.
                                       (3)
       167°
                                       (4)
       166°
                                       (13)
                       at 738.2 mm.
       166°
                                       (8)
       164-166°
                                       (5)
       164°
                                       (6)
       163.0-163.5° at
                            682 mm.
                                       (7)
       74°
                             28 mm.
                                       (9)
                       at
       58.0-59.0°
                             13 mm. (10)
                       at
       62°
                             12 mm. (11)
                       at
       60-61°
                             12 mm. (12)
                       at
```

[For prepn. of \tilde{C} from trichloroacetic acid (3:1150) with abs. EtOH + dry HCl (yield: 90% (13), 53% (16)) or with H₂SO₄ (50-60% yield (13)) (14) (15), or with Twitchell's reagt. (62.6% yield (5)) see indic. refs.; from trichloroacetyl chloride (3:5420) with ethyl orthoformate (1:3241) see (17); from "tetrachloroethylidene trichlorolactate" [Beil. XIX-105] with EtOH see (12); for formn. of \tilde{C} from chloral (3:5210) with Al(OEt)₃ in C₆H₆ (11), or with acetaldehyde + Al(OEt)₃ or Mg(OMe)₂ in dry ether (18), see indic. refs.]

[$\tilde{\mathbf{C}}$ on warming with KCN in abs. alc. dec. (6) into chloroform (3:5050) + CO₂; $\tilde{\mathbf{C}}$ with NaOEt gives on warming (19) triethyl orthoformate (1:3241) + Na ethyl carbonate + NaCl.]

[\overline{C} with excess H₂ over Ni at 320° gives {14} ethyl dichloroacetate (3:5850) + ethyl chloroacetate (3:5700) + EtOAc (1:3015) + acetaldehyde (1:0100).]

Č with Cu₂Cl₂ in conc. aq. NH₄OH gives dark blue color within 2 min. (21); also shown by chloral hydrate (3:1270) and trichloroacetic acid (3:1150) (the latter, however, acting instantly); for further limitations see (21). [Č htd. at 100° with Cu powder for 6-8 hrs. (22) gives diethyl tetrachlorosuccinate, b.p. 156° at 13 mm. (22).]

Č with conc. aq. NH₄OH gives in the cold (14) trichloroacetamide, spar. sol. aq., cryst. from hot aq. or dil. alc., m.p. 141°. — Č on shaking with aq. benzylamine gives in the cold (23) trichloroacet-N-benzylamide, cryst. from lgr., m.p. 93.6-94.4° cor. (23). [Note, however, that the corresp. dichloroacet-N-benzylamide (from ethyl dichloroacetate (3:5850) has almost the same m.p., viz., 94.8-95.6° cor. (23), while chloro-acet-N-benzylamide (from ethyl chloroacetate (3:5700)) has m.p. 93.0-93.6° cor. (23).]

Č hydrolyzes very readily (5) yielding ethyl alcohol (1:6130) and trichloroacetic acid (3:1150). [For kinetic studies of hydrolysis of Č under various conditions (including very high pressure (9)) see (10) (2) (24); for kinetic study of alcoholysis of Č with MeOH+HCl see (25).]

Sesso (1) Perkin, J. Chem. Soc. 65, 423 (1894).
 Timm, Hinshelwood, J. Chem. Soc. 1938, 862-869.
 Schiff, Ann. 229, 108 (1883); Z. physik. Chem. 1, 379 (1887).
 Cheng, Z. physik. Chem. B-24, 306 (1934).
 Zaganiaris, Varvogles, Ber. 69, 2280 (1936).
 Claus, Ann. 191, 58-63 (1878).
 Sudborough, Karne, J. Indian Inst. Sci. 5, 7 (1922); Cent. 1923, I 295; C.A. 17, 665 (1923).
 Brühl, Ann. 263, 22-23 (1880).
 Newitt, Linstead, Sapiro, Boorman, J. Chem. Soc. 1937, 876-883.
 Palomaa, Salmi, Korte, Ber. 72, 790-797 (1939).
 Dworsak, Monatsh. 47, 11-15 (1926).
 Anschütz, Haslam, Ann. 253, 125 (1889).
 Ly Spiegel, P. Spiegel, Ber. 46, 1734 (1907).
 Clermont, Compt. rend. 133, 737-738

(1901). (15) Dumas, Ann. 32, 112 (1839). (16) Toole, Sowa, J. Am. Chem. Soc. 59, 1972 (1937).
(17) Levaillant, Compt. rend. 195, 882 (1932). (18) Nakai, Biochem. Z. 152, 269-273 (1924).
(19) Klein, Jahresber. 1876, 521. (20) Sabatier, Mailhe, Compt. rend. 169, 760 (1919).

(21) Doughty, J. Am. Chem. Soc. 41, 1129-1131 (1919). (22) Doughty, Freeman, J. Am. Chem. Soc. 44, 638-639 (1922). (23) Buehler, Mackenzie, J. Am. Chem. Soc. 59, 421-422 (1937).
(24) Berger, Rec. trav. chim. 43, 168, 173 (1924). (25) Kolhatkar, J. Chem. Soc. 107, 930 (1915).

3:5955
$$d,l-1,1,1$$
-TRICHLOROBUTANOL-2 $C_4H_7OCl_3$ Beil. I — (Ethyl-trichloromethyl-carbinol) H Cl I_1 — I_2 -(403) CH_3 . CH_2 — C — Cl OH Cl I_2 -(403) I_2 -(403) I_3 — I_4 -(403) I_4 -(403) I_5 -(

Oil. — Eas. sol. MeOH, EtOH, ether, acetone, C₆H₆, CHCl₃, CCl₄, CS₂. [Note that b.p. of 99° at 680 mm. (4) may be a typographical error (1).]

[For prepn. of \bar{C} from chloral (3:5210) via conversion with diazomethane to 3,3,3-trichloro-1,2-epoxypropane (3:1336) and reactn. of latter with 1 N LiMe in dry ether at -75° (yield 85%) see (1); from chloral (3:5210) with EtMgBr (4) (5) or EtMgI (2) in ether (yields: 44% (4), 16% (2), 15% (5)) see indic. refs. (note, however, that by virtue of reducing acta. of EtMgX large amounts of 2,2,2-trichloroethanol-1 (3:5775) are also formed (5) (2) (1)); from chloral (3:5210) with PbEt₄ (20% yield (6)) (note, however, that this could not be confirmed (1)), from trichloroacetyl chloride (3:5420) with EtMgBr at 10° see (3).]

 \bar{C} with conc. HCl + ZnCl₂ (Lucas' reagent) stood for 1 hr. at room temp. gives (1) 1.1.1,2-tetrachlorobutane (3:5622).

 \tilde{C} with 5% soln. of Na₂CO₃ in 50% aq. alc. refluxed for 10 hrs. (1) or \tilde{C} with aq. KOH, NaOH, Na₂CO₃, Ba(OH)₂, Mg(OH)₂, CaCO₃, etc., (2) undergoes both hydrolysis and hydrolytic cleavage giving respectively α -hydroxy-n-butyric acid [Beil. III-302, III₁-(114), III₂-(216)] (yields: 46% (1), 21% (2)), m.p. 43°, and propionaldehyde (1:0110) (29% yield (2)).

- Ethyl-trichloromethyl-carbinyl acetate: b.p. 164-165° at 680 mm. (4). [From C with Ac₂O at 130-135° for 2 hrs. (4). Note that in light of subsequent work (1) the identity of this prod. has been questioned.]
- Ethyl-trimethyl-carbinyl benzoate: b.p. 217-218° at 680 mm. (4). [From $\bar{\mathbf{C}}$ with BzCl + cold dil. aq. alk. (4). Note that in light of subsequent work (1) the identity of this prod. has been questioned.]
- Ethyl-trimethyl-carbinyl p-nitrobenzoate: cryst. from pet. ether, m.p. 70-71.5° (1).
 [Note that this m.p. is identical with that of the p-nitrobenzoate of 2,2,2-trichloroethanol-1 (3:5775); although each appears to be authentic, whether their mixture shows depression of m.p. is not reported.]

3:5955 (1) Gilman, Abbott, J. Org. Chem. 8, 224-229 (1943). (2) Hébert, Bull. soc. chim. (4) 27, 49, 55 (1920). (3) Jacob, Bull. soc. chim. (5) 7, 581-586 (1940); C.A. 36, 3507 (1942). (4) Howard, J. Am. Chem. Soc. 48, 774-775 (1926). (5) Iotsich, J. Russ. Phys.-Chem. Soc. 38, 445 (1904); Bull. soc. chim. (3) 34, 329 (1905). (6) Meerwein, Hins, Majert, Sönke, J. prakt. Chem. (2) 147, 234, Note 1 (1936).

3:5957 1,1,3-TRICHLOROPROPANONE-2
$$C_1H_3OCl_3$$
 Beil. I - 655 $(\alpha,\alpha,\gamma$ -Trichloroscetone) CH_2 — C — $CHCl_2$ I_1 — I_2 —

B.P. 172° (1)

[For prepn. of \bar{C} from 1,1-dichloro-3-bromopropanone-2 (1) with alc. HgCl₂ see (1); for formn. from acetone (1:5400) with Cl₂ in pres. of NiCl₂ at 70° (together with other prods.) see (2).]

C with aq. or alc. NH₄OH fails (1) to give chloroform; C with KOH + aniline fails (1) to give phenylisocyanide. [Dif. from isomeric 1,1,1-trichloropropanone-2 (3:5620).]

[Č with diazotized aniline in pres. of NaOAc couples (3) to yield a cpd. having composition $C_9H_7ON_2Cl_3$ (and presumably structure $C_6H_5.NH.N=C(Cl).CO.CHCl_2$), cryst from pet. ether, m.p. 115-116° (3).]

3:5957 (1) Cloëz, Ann. chim. (6) **9,** 176 (1886). **(2)** Akashi, Bull. Inst. Phys.-Chem. Research (Tokyo) **12,** 329-340 (1933); Cent. **1933,** I 3066; C.A. **27,** 3447 (1933). **(3)** Favrel, Bull. soc. chim. (5) **1,** 986-987, 989 (1934).

3:5960
$$m$$
-DICHLOROBENZENE Cl $C_0H_4Cl_2$ Beil. V - 202 V_1 -(111) V_2 -(154)

B.P. F.P. (1)
$$-24^{\circ}$$
 (6) $D_4^{20 \, 9} = 1.2879 \, \{11\}$ $n_D^{20 \, 9} = 1.5470 \, (11)$ 172.0-172.6° (2) -24.1° (12) 172-173° (7) -24.2° (12) $D_4^{20} = 1.2881$ (8) 172° cor. at 766 mm. (3) -24.4° (8) 1.289 (11) 172.1° at742.4 mm. (4) -24.8° (7) 1.287 (1) 169-170° at 755 mm. (5) -25° (5) $n_D^{17 \, 3} = 1.5472 \, \{8\}$ 170° cor. at 744 mm. (6) -26.25° (9) $n_D^{15} = 1.5480 \, \{7\}$ (66° at 20 mm. (7) (10) $D_4^{15} = 1.2937 \, \{8\}$

Č when pure is colorless oil, volatile with steam.

[For f.p./compn. data and diagram of system $\bar{C}+o$ -dichlorobenzene (3:6055) (eutectic, m.p. -45.9°, contg. 51.3% \bar{C}) see (12); on system $\bar{C}+p$ -dichlorobenzene (3:0980) (eutectic, m.p. -29.9°, contg. 88.0% \bar{C}) see (12); for f.p./compn. data on ternary system of all three dichlorobenzenes see (7); for f.p./compn. data on systems: $\bar{C}+f$ fluorobenzene, $\bar{C}+c$ chlorobenzene (3:7903), $\bar{C}+c$ bromobenzene, and $\bar{C}+c$ -chlorotoluene (3:8245) see (9).]

[For data on densities of solns. of \bar{C} in C_6H_6 (1:7400) and in *n*-hevane (1:8530) see (13).] [\bar{C} is very spar. sol. aq. (for study of this over range 20-60° see (14)).]

[For prepn. of C from m-chloroaniline [Beil. XII-602, XII₁-(300)] via diazotization and use of Cu₂Cl₂ reactn. (yields: 80% (15), 70% (16)) (7) (17) or by pptn. of the diazonium chloroplatinate and htg. of latter with Na₂CO₃ (4) see indic. refs.; from 2,4-dichloroaniline [Beil. XII-621, XII₁-(309)] via diazotization in alc. (18) (17) (3) (4) or isoamyl alc. (19) followed by replacement of orig. amino group by H by actn. of the alc. (60% yield (15)) or with hypophosphorous acid (50% yield (19)) (use of alk. SnCl₂ or oxidn. of the corresp. 2,4-dichlorophenylhydrazine with CuSO₄ gave only very low yields (15)) see indic. refs.; from m-phenylenediamine [Beil. XIII-33, XIII₁-(10)] via tetrazotization in AcOH with

nitrosylsulfuric acid followed by use of Cu₂Cl₂ reactn. (70.4% yield (20)) (21) see indic. refs.]

[For prepn. of \tilde{C} from *m*-chloronitrobenzene [Beil. V-243, V₁-(129)] with SOCl₂ in s.t. at 190-200° for 12 hrs. (71% yield (22)), from *m*-nitrobenzenesulfonic acid [Beil. XI-68, XI₁-(21)] with SOCl₂ in s.t. at 180-200° (23), from *m*-bromonitrobenzene [Beil. V-248, V₁-(131)] with PCl₅ in s.t. at 180° (24), from 2,6-dichlorobenzoic acid (3:4200) by htg. in acetamide at 225-235° for 6 hrs. (93% yield (25)), or from 2,6-dichlorobenzaldehyde (3:1690) with 50% KOH under N₂ at 100° for 5 hrs. (84% yield (6)) see indic. refs.]

[For formn. of \bar{C} from 2,6-dichloroacetophenone (5), 2,4-dichlorobenzophenone (3:0825) (26), 2,6-dichlorobenzophenone (3:1285) (26), or 3,5-dichlorobenzophenone (3:1505) (26) by fusion with KOH/NaOH see indic. refs.; for formn. of \bar{C} from 1,3-dichlorocyclohexadiene-1,3 [Beil. V-114] with PCl₅ or with Br₂ in CHCl₃ see (27).]

[For formn. of \bar{C} from C_6H_6 (1:7400) or chlorobenzene (3:7903) with Cl_2 + cat. at 400-700° (50-60% yield (12)) (28) or with Cl_2 in pres. of AlCl₃ (29) cf. (30) see indic. refs.] [\bar{C} with Cl_2 + Al/Hg (31) or with Cl_2 + AlCl₃ (30) cf. (29) gives mainly 1,2,4-trichlorobenzene (3:6420). — \bar{C} suspended in 1% aq. NaOH adds 3 Cl_2 in sunlight giving (32) m-dichlorobenzene hexachloride, cryst. from alc., m.p. 81.8° (32). — For study of photochemical chlorination of \bar{C} see (33).]

[\bar{C} with Mg (1 mole) + I_2 (0.25 equiv.) gave (34) after 3 days 62.5% *m*-chlorophenyl MgCl.]

 $[\bar{C} \text{ with CHCl}_3 + \text{AlCl}_3 \text{ at } 65^\circ \text{ for } 14 \text{ hrs. as directed gives } (18\% \text{ yield } (35)) \text{ tris-}(2,4-\text{dichlorophenyl}) \text{methane, white cryst. from hot acetone, m.p. } 227-228.5^\circ (35). — <math>\bar{C}$ with CCl₄ + AlCl₃ as directed gives (60% yield (35)) 2,4,2',4'-tetrachlorobenzophenone dichloride, white pl. from hot acetone, m.p. $139.0-140.5^\circ$ (35), 140° (36); hydrolysis of this prod. with AcOH/H₂SO₄ yields (37) 2,4,2',4'-tetrachlorobenzophenone, m.p. 78° (37), accompanied by some 2,4-dichlorobenzoic acid (3:4560), m.p. 161° (37).]

[\bar{C} with acetyl chloride (3:7065) + AlCl₃ gives (15% yield (38)) 2,4-dichloroacetophenone, b.p. 140-150° at 15 mm. (38), m.p. 33-34° (38). — \bar{C} with chloroacetyl chloride (3:5235) + AlCl₃ in CS₂ yields (39) 2,4-dichlorophenacyl chloride (2,4, ω -trichloroacetophenone), pr. from lgr., m.p. 57° (39). — \bar{C} with β -chloro-n-butyric acid (3:0035) + AlCl₃ or conc. H₂SO₄ yields (40) by condens. and subsequent ring closure 4,6-dichloro-3-methylindanone-1, m.p. 67-70° (40). — \bar{C} with σ -bromobenzoyl chloride + AlCl₃ in CS₂ gives (43% yield (41)) 2-bromo-2',4'-dichlorobenzophenone, b.p. 227-228.5°, m.p. 33-34°.]

[C with phthalic anhydride + AlCl₃ at 100-110° for 7 hrs. gives (17% yield on the anhydride (42)) (43) o-(2,4-dichlorobenzoyl)benzoic acid, white cubes from C₆H₆ or CHCl₃, m.p. 106-107° (42), 100-101° (43), accompanied (44) (especially if acetylene tetrachloride is used as solvent) by 3,3-bis-(2',4'-dichlorophenyl)phthalide, m.p. 176° (44); the above o-(2,4-dichlorobenzoyl)benzoic acid with fumg. H₂SO₄ at 155-160° ring-closes (90% yield (42)) to 1,3-dichloroanthraquinone [Beil. VII-787, VII₁-(411)], yel. ndls. from AcOH, m.p. 209-210° (42).]

[C on hydrolysis with steam + cat. at 550-850° yields (45) m-chlorophenol (3:0255) and/or resorcinol (1:1530). — For studies of reactn. of C with NaOMe/MeOH see (46) (47) (48).]

[\bar{C} with conc. aq. NH₄OH in pres. of CuO under press. at 150-200° (49) cf. (50) (51) yields m-phenylenediamine. — \bar{C} with K diphenylamine gives on htg. (16) (52) N,N,N',N'-tetraphenyl-m-phenylenediamine [Beil. XIII-42], m.p. 137.5-138° (16) (52) (note that this same prod. is similarly obtd. from o-dichlorobenzene (3:6055) and in part also from p-dichlorobenzene (3:0980).]

[\bar{C} on mononitration, e.g., by soln. in 4.5 moles HNO₃ (D=1.5) in cold followed by 10 min. htg. at 70° (53) or with 5 pts. fumg. HNO₃ (D=1.52) at 0° (90% yield (54)) cf.

(3). (27) (17) gives 1,3-dichloro-4-nitrobenzene [Beil. V-245, V_{1} -(131)], cryst. from alc., m.p. 34° (55), 33–34° (27), 33° (53) (3), accompanied by a little (2.6% at -30° , 4% at 0° (17)) 1,3-dichloro-2-nitrobenzene [Beil. V-246, V_{1} -(131)], m.p. 70.5° (55), 70° (56) (reactn. prod. with piperidine is 3-chloro-2-nitro-1-piperidinobenzene, m.p. 63° (57)).]—[The only other possible mononitro-m-dichlorobenzene, viz., 1,3-dichloro-5-nitrobenzene [Beil. V-246, V_{1} -(131)], m.p. 65° (55), has been prepd. indirectly.]

C on dinitration, e.g., with 3.4 wt. pts. HNO₃ (D = 1.54) + 6.8 wt. pts. conc. H₂SO₄ at 99° for 1 hr. (56) (cf. (22) (58) (27) (59) (60) (61)) gives (85% yield (56)) 1,3-dichloro-4,6-dinitrobenzene [Beil. V-265, V₁-(138)], cryst. from alc., m.p. 103° (22) (60), 102-103° (58), 102° (27), 101° (56), accompanied by 15% yield (56) of 1,3-dichloro-2,4-dinitrobenzene [Beil. V-265], m.p. 68° (56). — For f.p./compn. data and diagram for these two cpds. (eutectic, m.p. 48.1°, contg. 38% of the former) see (56). — Note that 1,3-dichloro-4,6-dinitrobenzene with piperidine in alc. boiled for 10 min. replaces 1 chlorine yielding (62) 1-chloro-4,6-dinitro-3-piperidinobenzene, yel. cryst. from alc., m.p. 119° (62); with piperidine in pyridine (requires cooling) it replaces both chlorine atoms yielding (62) 4,6-dinitro-1,3-dipiperidinobenzene, yel. lfts. from AcOH, m.p. 130-131° (62). — [Both of the other two possible dinitro-m-dichlorobenzenes are known, viz., 1,3-dichloro-2,5-dinitrobenzene [Beil. V₁-(138)], m.p. 114°, and 1,3-dichloro-4,5-dinitrobenzene [Beil. V-264], m.p. 98°, but have been prepd. indirectly.]

[The direct trinitration of C has not been reported; of the four possible trinitro-m-dichlorobenzenes only one, viz., 1,3-dichloro-2,4,6-trinitrobenzene [Beil. V-275], m.p. 128°, is known.]

[\bar{C} on monosulfonation with fumg. H_2SO_4 at 230° (3) or with fumg. H_2SO_4 (7% SO_3) at 100° (7) or with fumg. H_2SO_4 (12% SO_3) (54) gives (82% yield (54)) 1,3-dichlorobenzene-sulfonic acid-4 [Beil. XI-55, XI₁-(15)], m.p. 86° (54) (corresp. sulfonyl chloride, m.p. 54.6° (7), corresp. sulfonamide, m.p. 182° (7) (see also below)), both \bar{C} and its *ortho* isomer (3:6055) sulfonate with about equal case, both much more readily than p-dichlorobenzene (3:0980) (use in sepns. from latter).]

[C on disulfonation with fumg. H₂SO₄ (45% SO₃) at 140-150° for 5 hrs. (63) gives 1,3-dichlorobenzenedisulfonic acid-4,6 (corresp. bis-(sulfonyl chloride), m.p. 122-123° (63) (64), corresp. bis-(sulfonamide), m.p. 276° (63); unlike the corresp. 1,3-dichloro-4,6-dinitrobenzene the halogen in this disulfonic acid is unreactive (63).]

[For study of kinetics of sulfonation of C see (66).]

① 1,3-Dichlorobenzenesulfonamide-4 (2,4-dichlorobenzenesulfonamide-1): cryst. from dil. alc., m.p. 179-180° u.c. (65). [From C on treatment as directed (65) with Cl.SO₃H followed by conv. of the intermediate 1,3-dichlorobenzenesulfonyl chloride-4, m.p. 52-53° u.c. (65), to the sulfonamide by means of (NH₄)₂CO₃.] — [Note that although the m.p. of this sulfonamide is practically identical with that from p-dichlorobenzenesulfonyl chlorides, viz., 52-53° for C, 38° for the p-isomer, may also serve to distinguish them (65).]

3:5960 (1) Groves, Sugden, J. Chem. Soc. 1937, 1783. (2) Dadieu, Pongratz, Kohlrausch, Monatsh. 61, 431 (1932). (3) Beilstein, Kurbatow, Ann. 182, 97-98 (1876). (4) Koerner, Gazz. chim. ital. 4, 341 (1874). (5) Lock, Bock, Ber. 70, 922 (1937). (6) Lock, Ber. 66, 1530 (1933). (7) Holleman, van der Linden, Rec. trav. chim. 30, 305-341 (1911). (8) Narbutt, Ber. 52, 1031 (1919). (9) Timmermans, Bull. soc. chim. Belg. 43, 632-634 (1934). (10) Timmermans, Bull. soc. chim. Belg. 30, 67 (1921).

(11) von Auwers, Ann. 422, 164, 168 (1921).
(12) Wibaut, van der Lande, Wallagh, Rec. trav. chim. 56, 65-70 (1937).
(13) Smyth, Morgan, Boyce, J. Am. Chem. Soc. 50, 1542 (1928).
(14) Klemenc, Löw, Rec. trav. chim. 49, 637 (1930).
(15) Borsche, Bahr, Ann. 402, 88-90 (1914).

(16) Haeussermann, Ber. 33, 940-941 (1900). (17) Holleman, Reiding, Rec. trav. chim. 23,

359-360, 369-379 (1904). (18) Chattaway, Evans, J. Chem. Soc. 69, 850-851 (1896). (19) Raiford, Oberst, Am. J. Pharm. 107, 242-244 (1935). (20) Hodgson, Walker, J. Chem. Soc. 1935, 530.

(21) Sandmeyer, Ber. 17, 2652 (1884). (22) Davies, Hickox, J. Chem. Soc. 121, 2648-2649 (1922). (23) Kinzlberger and Co., Ger. 280,379, Nov. 26, 1914; Cent. 1915, I 104. (24) Schmidt, Wagner, Ann. 387, 164-165 (1911). (25) Norris, Klemka, J. Am. Chem. Soc. 62, 1434 (1940). (26) Lock, Rodiger, Ber. 72, 868-870 (1939). (27) Crossley, Haas, J. Chem. Soc. 83, 502-503 (1903). (28) Wibaut, van der Lande, Wallagh (to Dow Chem. Co.), U.S. 2,123,857, July 12, 1938; Cent. 1939, I 250; C.A. 32, 7058 (1938). (29) Mouneyrat, Pouret, Compt. rend. 127, 1027 (1898). (30) Olivier, Rec. trav. chim. 39, 411-413 (1920).

(31) Cohen, Hartley, J. Chem. Soc. 87, 1364 (1905). (32) von der Linden, Ber. 45, 415-416 (1912). (33) Fisk, Noyes, J. Am. Chem. Soc. 58, 1707-1714 (1936). (34) E. L. St. John, N. B. St. John, Rec. trav. chim. 55, 587 (1936). (35) Wilson, Cheng, J. Org. Chem. 5, 223-226 (1940). (36) Jaeger, Z. anorg. allgem. Chem. 101, 143-144 (1917). (37) Boeseken, Rec. trav. chim. 27, 8-9 (1908). (38) Roberts, Turner, J. Chem. Soc. 1927, 1846. (39) Kunckell, Ber. 40, 1702-1703 (1907). (40) I.G., Swiss 126,404, June 16, 1928; 127,692-127,703, Sept. 1, 1928; 128,366,

Oct. 16, 1928; Cent. 1929, I 1271-1272.

(41) Meisenheimer, Hanssen, Wächterowitz, J. prakt. Chem. (2) 119, 350-355 (1928). (42) Goldberg, J. Chem. Soc. 1931, 2829-2830. (43) Gubelmann, Weiland, Stallmann (to Newport Co.), U.S. 1,711,144, April 30, 1929; Cent. 1929, II 796; Brit. 288,884; Cent. 1928, II 1821. (44) Barnett, Goodway, Wilson, Ber. 66, 1876, 1881 (1933). (45) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994. (46) Holleman, de Mooy, Rec. trav. chim. 35, 27-28 (1915). (47) Holleman, Rec. trav. chim. 37, 203 (1917). (48) Clark, Crozier, Trans. Roy. Soc. Can. (3) 19, III 153-154 (1925); Cent. 1926, II 20; C.A. 20, 388 (1926). (49) Williams (to Dow Chem. Co.), U.S. 1,775,360, Sept. 9, 1930; Cent. 1931, II 1195. (50) Federal Phosphorus Co., Brit. 370,774, May 5, 1932; Cent. 1932, II 1237.

(51) Booth (to Swann Research, Inc.), U.S. 1,954,469, April 10, 1934; Cent. 1934, II 1846. (52) Haeussermann, Ber. 34, 38-40 (1901). (53) Roberts, Turner, J. Chem. Soc. 127, 2011 (1925). (54) van de Lande, Rec. trav. chim. 51, 98-99 (1932). (55) Kremer, Bendich, J. Am. Chem. Soc. 61, 2659-2660 (1939). (56) Dann, J. Chem. Soc. 1929, 2460-2462. (57) Loudon, J. Chem. Soc. 1940, 1526. (58) Jois, Manjunath, Half-Yearly J. Mysore Univ. 4, 239-240 (1930); Cent. 1930, I 1124; C.A. 25, 2981 (1931). (59) Holleman, den Hollander, Rec. trav. chim. 39, 437 (1920). (60) Hodgson, J. Soc. Dyers Colourists 42, 367 (1926).

(61) Zincke, Ann. 370, 302, Note (1909).
(62) LeFevre, Turner, J. Chem. Soc. 1927, 1118.
(63) Davies, Poole, J. Chem. Soc. 1927, 1122-1123.
(64) Pollak, Wienerberger, Monatsh. 35, 1472 (1914).
(65) Huntress, Carten, J. Am. Chem. Soc. 62, 511-514 (1940).
(66) Dresel, Hinshelwood, J. Chem. Soc. 1944, 649-652.

B.P. 173° M.P. 44°

See 3:0563. Division A: Solids.

3:5970
$$\gamma$$
-CHLORO- n -BUTYRYL CHLORIDE C₄H₆OCl₂ Beil. II - 278 CH₂.CH₂.CH₂.CH₂.C=O II₁-(124) II₂-(254) B.P. 173-174° (1) $D_4^{20} = 1.2581$ (5) $n_D^{20} = 1.4631$ (2) 83-85° at 40 mm. (2) 68° at 15 mm. (3) 60-61° at 12 mm. (4) 55-56° at 12 mm. (5) 59-60° at 11 mm. (6)

[For prepn. of \bar{C} from γ -chloro-n-butyric acid (3:0020) with SOCl₂ (82% yield (4)) (3) in pet. eth. (6), or with PCl₅ (1) (3), see indic. refs.: from n-butyryl chloride (3:7370) with Cl₂ (7) or with SO₂Cl₂ + dibenzoyl peroxide in CCl₄ (30% \bar{C} + 15% α - and 55% β -isomers (2)) see indic. refs.]

[$\bar{\mathbf{C}}$ with EtZnI at -15 to -20° yields (3) γ -chloro-n-propyl ethyl ketone (6-chlorohexanone-3) [Beil. I₁-(355), I₂-(747)], b.p. 182-183° at 761 mm. (8) (semicarbazone, m.p. 98-99° (8), 118° (3); p-nitrophenylhydrazone, m.p. 106-107° (3)), but above 0° the reactn. yields γ -chloro-n-propyl-ethyl-carbinyl γ -chloroacetate, b.p. 172-174° at 19 mm. (3).]

 $\ddot{\mathbf{C}}$ on hydrolysis with aq. yields γ -chloro-n-butyric acid (3:0020).

For the amide, anilide, p-toluidide, and other derivs. corresp. to $\bar{\mathbf{C}}$ see γ -chloro-n-butyric acid (3:0020).

3:5970 (1) Henry, Bull. soc. chim. (2) 45, 341 (1886). (2) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940). (3) Wohlgemuth, Ann. chim. (9) 2, 307, 405-408 (1914). (4) Blicke, Wright, Zienty, J. Am. Chem. Soc. 63, 2489 (1941). (5) Leimu, Ber. 70, 1050 (1937). (6) Lipp, Caspers, Ber. 58, 1012-1013 (1925). (7) Michael, Ber. 34, 4051-4053 (1901). (8) Boosere, Bull. soc. chim. Belg. 32, 29 (1923).

3:5975 ISOPROPYL TRICHLOROACETATE $C_5H_7O_2Cl_3$ Beil. S.N. 160 $(CH_3)_2CH.O.CO.CCl_3$

B.P.

173.9-174.9° (1)
$$D_4^{25} = 1.2911$$
 (2) $n_D^{25} = 1.4409$ (2) 173.5° at 747 mm. (2) $D_4^{20} = 1.3034$ (3) $n_D^{20} = 1.44355$ (3) cf. (5) 65.5-67.0° at 15 mm. (3) 65° at 10 mm. (4) $D_4^{15} = 1.2987$ (4) $n_D^{15} = 1.4440$ (4)

[For prepn. from isopropyl alc. (1:6135) + trichloroacetic ac. (3:1150) (57.8% yield (2) (3)) see (2) (3); for prepn. from propylene + trichloroacetic ac. (3:1150) + BF₃ (48.8% yield (2)) see (2).]

[For study of chlorination of \bar{C} see (4); for reaction with $C_6H_6+BF_3$ yielding ethylbenzene (1:7410) see (6).]

[For study of hydrolysis of C see (3).]

3:5975 (1) Cheng, Z. physik. Chem. B-24, 310 (1934). (2) Dorris, Sowa, Nieuwland, J. Am. Chem. Soc. 56, 2689-2690 (1934). (3) Paloma, Salmi, Korte, Ber. 72, 797 (1939). (4) Gayler, Waddle, J. Am. Chem. Soc. 63, 3358-3359 (1942). (5) Schjanberg, Z. physik. Chem. A-172, 229 (1935). (6) McKenna, Sowa, J. Am. Chem. Soc. 59, 1204-1205 (1937).

--- p-DICHLOROBENZENE Cl $C_0H_4Cl_2$ Beil. V - 203 V_1 -(111) V_2 -(154)

B.P. 174° at 764 mm.

M.P. 53°

See 3:0980. Division A: Solids.

3:5977 1,3-DICHLORO-2-METHYLPROPANOL-2
$$C_4H_8OCl_2$$
 Beil. I-382 $(sym.\text{-Dichloro-}ter\text{-butyl alcohol})$ CH_3 I_1 — I_2 — CH_2 CH_2

[See also the isomeric 1,1-dichloro-2-methylpropanol-2 (3:5772).]

Č with aq. forms a const.-boilg. mixt., b.p. 98.3°, contg. 35.2% Č (8). — Soly. of Č in aq. at 20° is 9.4 g. Č in 100 g. aq., soly. of aq. in Č at 20° is 10.8 g. aq. in 100 g. Č (8).

PREPARATION OF C

[For prepn. of $\bar{\mathbb{C}}$ from 1-chloro-2-methylpropene-2 (methallyl chloride = isobutenyl chloride) (3:7145) by addn. of HOCl with HOCl (yields: 33% (4), 32% (3)) (7), with Cl₂/aq. (70% yield (8)), or with organic hypochlorites (7) see indic. refs.; note that if the initial methallyl chloride conts. β , β -dimethylvinyl chloride (isocrotyl chloride) (3:7120) the crude HOCl addn. prod. will contain 1,1-dichloro-2-methylpropanol-2 (3:5772), but this can be separated from $\bar{\mathbb{C}}$ by fractional distillation.]

[For prepn. of \bar{C} from α, α' -dichloroacetone (3:0563) with MeMgBr (yields: 80-85% (6), 40% (5)) (1) see indic. refs.; from chloroacetone (3:5425) with diazomethane via β -methyl epichlorohydrin (3-chloro-2-methyl-1,2-epoxypropane) (3:7657) and subsequent ring opening with conc. HCl see (2).

CHEMICAL BEHAVIOR OF C

WITH INORGANIC REACTANTS

Dehydration. [\bar{C} is difficult to dehydrate but on twice htg. with equal wt. P_2O_5 at 110-195° for 2 hrs. gives (46% yield (6)) 1,3-dichloro-2-methylpropene-1 (3:5590). — \bar{C} with strong H_2SO_4 loses H_2O giving (9) 80% 3-chloro-2-(chloromethyl)propene-1 (3:5633) + 20% 1,3-dichloro-2-methylpropene-1 (3:5590).]

Dehydrohalogenation. \tilde{C} with aq. $Ca(OH)_2$ loses 1 HCl giving (93% yield (10) (11)) 3-chloro-2-methyl-1,2-epoxypropane (β -methylepichlorohydrin) (3:7657) which distils as its azeotrope, b.p. 89.8°, contg. 25.6% aq. (10). — Note that, if alk. is added in excess, reactn. is complete in a few seconds at room temp. and the process can even be used as a method for detn. of \tilde{C} in aq. soln. [For use of \tilde{C} in comml. prepn. of β -methylepichlorohydrin (3:7657), β -methylglycerol monochlorohydrin, β -methylglycidol, and β -methylglycerol see (10).]

Behavior with sodium sulfite. [C (1 mole) with aq. Na₂SO₃ (2 moles) at 70-90° for 2 hrs. yields (3) the salt of 2-methylpropanol-2-disulfonic acid-1,3; this prod. with PCl₅ not only is converted to the bis (acid chloride) but simultaneously loses H₂O yielding (3) 2-methylpropen-1,3-bis-(sulfonyl chloride), long ndls. from CCl₄, C₅H₅, or pet. ether, m.p.

79.2-79.8° (3) (corresp. bis-(sulfonamide), m.p. 152.5-154° (3); corresp. bis-(anilide), m.p. 171.5-172.5° (3)).]

BEHAVIOR WITH ORGANIC REACTANTS

[Č with KCN (2 moles) yields (4) 1,3-dicyano-2-methylpropanol-2; note, however, that attempts to purify this prod. by vacuum distn. lead only to decomposition and polymerization (4).]

- **D 1,3-Di-**(β -naphthoxy)-2-methylpropanol-2 (2-methylglycerol α,α' -di(β -naphthyl ether): colorless cryst. from alc., m.p. 151–152° (5). [From \bar{C} with sodium β -naphtholate in boilg. alc. (5).]
- ---- sym.-Dichloro-ter-butyl acetate: unreported.
- ---- sym.-Dichloro-ter-butyl benzoate: unreported.
- ---- sym.-Dichloro-ter-butyl p-nitrobenzoate: unreported.
- ----- sym.-Dichloro-ter-butyl 3,5-dinitrobenzoate: unreported.
- ---- 1,3-bis-Phthalimido-2-methylpropanol-2: unreported.

3:5977 (1) Henry, Compt. rend. 142, 132 (1901); Bull. soc. chim. Belg. 20, 152-156 (1906). (2) Arndt, Amende, Ender, Monatsh. 59, 213-214 (1932). (3) Suter, Malkemus, J. Am. Chem. Soc. 63, 980-981 (1941). (4) Hurd, Abernethy, J. Am. Chem. Soc. 63, 976-977 (1941). (5) Gibson, Harley-Mason, Litherland, Mann, J. Chem. Soc. 1942, 171. (6) D'yaknov, J. Gen. Chem. (U.S.S.R.) 10, 402-413 (1940); C.A. 34, 7861 (1940). (7) Groll, Hearne (to Shell Development Co.), U.S. 2,067,392, Jan. 12, 1937; C.A. 31, 1432; not in Cent.: (to N. V. de Bataafsche Petroleum Mastschapij), Brit. 435,096, Oct. 10, 1935; Cent. 1936, II 865; C.A. 30, 1067 (1936): French 789,289, Oct. 25, 1935; Cent. 1936, II 865; C.A. 30, 1812 (1936). (8) Burgin, Hearne, Rust, Ind. Eng. Chem. 33, 386-388 (1941). (9) Groll, Burgin (to Shell Development Co.), U.S. 2,042,-223, May 26, 1936; Cent. 1937, I 1274; C.A. 30, 4875 (1936). (10) Hearne, de Jong, Ind. Eng. Chem. 33, 940-943 (1941).

(11) Groll, Hearne (to Shell Development Co.), U.S. 2,061,377, Nov. 17, 1936; Cent. 1937, I 4862; C.A. 31, 704 (1937).

3:5980 o-CHLOROPHENOL

B.P. 175–176° c 175.4–176. 175°		8.7° (9) $D_4^{25} = 1.2456$ 8.0° (10) 1.2573 (3) (20)	
174–175° 174.5° 174.3° 90° 62.4–62.6° 64° 52–54°	at 753 mm. (5) at 749 mm. (6) at 50 mm. (114) at 14 mm. (2) at 13 mm. (7) at 7 mm. (8)	$D_4^{20} = 1.2512$	(3) $n_{\rm D}^{16.5} = 1.5612 (12)$

[See also p-chlorophenol (3:0475).]

Č has disagreeable and persistent odor (13) suggesting iodoform (14) (for study of strength of odor in aq. soln. see (14)). — Č is spar. sol. in aq. at ord. temp. (for details see (15)). Č is sol. alc. or ether. — Č is volatile with steam even from soln. in equiv. aq. NaOH (dif. and sepn. from 2.4-dichlorophenol (3:0560) (27)).

The cryoscopic const. of \bar{C} is 77.2 (16), but the m.p. of \bar{C} is not always a good criterion of its purity; e.g., the pres. of as much as 20% phenol (1:1420) lowers f.p. of \bar{C} only 1.7% (17) (see also below). — [For removal of phenol from \bar{C} by means of treatment of mixt. with 10% aq. K_2CO_3 , extraction of the phenol with ether, etc., see (18).]

Selected data on binary systems contg. \bar{C} : $\bar{C} + aq.$; for soly./temp. data see (15): $\bar{C} + C_6H_6$; for f.p./compn. data see (15); for n_D^{16} 5 compn. data see (12): $\bar{C} + acetone$; these two substances form a mol. epd., C.C₃H₆O, m.p. -39.8° (19), this mol. epd. forms with acetone a eutectic, m.p. -97.1°, contg. 7.2 mol. % \bar{C} , and with \bar{C} another eutectic, m.p. -47.6°, contg. 62.4 mol. % \bar{C} (19); for the D_4^t of mixts. of \bar{C} + acetone for t = 0-50° see (3): \bar{C} + phenol; for anal. of this mixt. by bromometric methods see (17).

- $\ddot{\mathbf{C}}$ + aniline; these two substances form a mol. cpd., $\ddot{\mathbf{C}}.\mathbf{C}_6\mathbf{H}_5\mathbf{NH}_2$, m.p. 29.4° (19); this mol. cpd. forms with aniline a eutectic, m.p. -12° , contg. 9.7 mol % $\ddot{\mathbf{C}}$, and with $\ddot{\mathbf{C}}$ another eutectic, m.p. -1.75° , contg. $\dot{\mathbf{S}}3.8$ mol % $\ddot{\mathbf{C}}$ (19); for D_4^t of mixts. of $\ddot{\mathbf{C}}$ + aniline for $t=10-150^\circ$ see (3) (21); $\ddot{\mathbf{C}}$ + p-toluidine: these two substances form a mol. cpd., $\ddot{\mathbf{C}}.\mathbf{C}_3\mathbf{H}_4$ -NH₂, m.p. 38.9° (20); this mol. cpd. forms with p-toluidine a eutectic, m.p. 25.2°, contg. 24 mol % $\ddot{\mathbf{C}}$, and with $\ddot{\mathbf{C}}$ another eutectic, m.p. 3.6°, contg. 83.6 mol % $\ddot{\mathbf{C}}$ (20); for $n_D^{\rm co}/\mathbf{C}$ compn. data and diagram of the system see (20): \ddot{C} + phenylhydrazine; for $D_2^{\rm co}/\mathbf{C}$ compn. data see (21).
- $\bar{\mathbb{C}}$ + dimethylaniline: these two substances form a mol. cpd., $\bar{\mathbb{C}}.\mathbb{C}_6H_5N$ (CH₃)₂, m.p. 16.7° (19); this mol. cpd. forms with dimethylaniline a eutectic, m.p. -4.0° , contg. 11 mol. % $\bar{\mathbb{C}}$, and with $\bar{\mathbb{C}}$ another eutectic, m.p. abt. -3° , contg. abt. 84 mol. % $\bar{\mathbb{C}}$ (19); for D_4^t of mixts. of $\bar{\mathbb{C}}$ + dimethylaniline for $t=0-80^\circ$ see (3): $\bar{\mathbb{C}}$ + pyridine; these two substances form a mol. cpd., $\bar{\mathbb{C}}.\mathbb{C}_5H_5N$, m.p. -21.6° (19); this mol. cpd. forms with pyridine a eutectic, m.p. -36.9° , contg. 23.1 mol. % $\bar{\mathbb{C}}$, and with $\bar{\mathbb{C}}$ another eutectic, m.p. -36.9° , contg. 66.1 mol. % $\bar{\mathbb{C}}$ (19); for D_4^t of mixts. of $\bar{\mathbb{C}}$ with pyridine for $t=0-110^\circ$ see (3); for data on n_D^{25} and n_D^{25} for this system see (11): $\bar{\mathbb{C}}$ + quinoline: these two subst. form a mol. cpd., $\bar{\mathbb{C}}.\mathbb{C}_5H_7N$, m.p. 47.4° (19); this mol. cpd. forms with quinoline a eutectic, m.p. -27.6° , contg. 9.6 mol. % $\bar{\mathbb{C}}$, and with $\bar{\mathbb{C}}$ another eutectic, m.p. -10.9° , contg. 79.1 mol. % $\bar{\mathbb{C}}$ (19); for D_4^t of mixts. of $\bar{\mathbb{C}}$ with quinoline for $t=0-110^\circ$ see (3): $\bar{\mathbb{C}}$ + N-methyldiphenylamine: this system does not form a mol. cpd. but shows a eutectic, m.p. -29.1° , contg. 43.6 mol. % $\bar{\mathbb{C}}$ (19); for D_4^t of mixts. of $\bar{\mathbb{C}}$ with N-methyldiphenylamine for $t=0-80^\circ$ see (3).
- $\ddot{\mathbf{C}}$ + p-chlorophenol (3:0475): this system has eutectic, m.p. about -20.5° , contg. abt. 61.5 mol. % $\ddot{\mathbf{C}}$ (9), for sepn. or detn. of $\ddot{\mathbf{C}}$ see (27): $\ddot{\mathbf{C}}$ + p-dichlorobenzene (3:0980); this system has eutectic, m.p. -0.4° , contg. 80 wt. % $\ddot{\mathbf{C}}$ (10).

[For prepn. of C from o-chloroaniline [Beil. XII-597, XII₁-(297)] via diazotization in dil. H₂SO₄ and subsequent warming of soln. (22) or adding dropwise to strong H₂SO₄ at 140° (65% yield (9)) see indic. refs.: from o-aminophenol [Beil. XIII-354, XIII₁-(108)] via diazotization, conv. to corresp. PtCl₄ double salt, and subsequent dry distn. (23), or from o-aminophenol hydrochloride via diazotization and distn. with Cu₂Cl₂ soln. (32% yield (24)) see indic. refs.]

[For prepn. of \bar{C} from phenol (1:1420) with Cl_2 without solvent at 40-155° (9) (13) (25) (26) (note that an approximately equal amt. of p-chlorophenol is also formed and that the proportion is not much affected by temp. (9) (27)) see indic. refs; from phenol with Cl_2 in pres. of aq. NaOH (28), aq. Na₂CO₃ (29), or in CCl₄ soln. (30) (31) see indic. refs.; from phenol with N,N'-dichlorourea (32), with ethyl hypochlorite (3:7022) (33), or with SO₂Cl₂ (34) see indic. refs.]

[For prepn. from 2-chlorophenolsulfonic acid-4 [Beil. XI-244] by htg. with aq. at 180-200° under press. (35) or from 2-chlorophenoldisulfonic acid-4,6 [Beil. XI₁-(58)] by distn. with steam at 120° (81% yield (36)), from phenol-p-sulfonic acid [Beil. XI-241, XI₁-(55)] in nitrobenzene at 55° with Cl₂ (72% yield (37)) see indic. refs.]

[For prepn. of Č from o-dichlorobenzene (3:6055) by partial hydrol. with aq. MeOH or EtOH alk., alk. earths, or alk. carbonates in pres. of Cu or Cu salts at elevated temps. under press. see (38)-(46) incl.]

[\bar{C} in excess dil. aq. KOH with H₂ in pres. of Ni absorbs 1 mole H₂ (47) but more slowly than m-chlorophenol (3:0255) or p-chlorophenol (3:0475). — \bar{C} is not reduced with HI in AcOH at 25° (48).]

[Č on oxidn. with 35% peracetic acid at 25° gives slowly (17 days) in small yield (49) a-chloromuconic acid (2-chlorobutadiene-1,3-dicarboxylic acid-1,4), m.p. 190° (49), + 5-chlorohexadiene-2,4-al-6-oic acid-1, m.p. 145° (49).]

[$\tilde{\mathbf{C}}$ with $\mathbf{Cl_2}$ (2 moles) in AcOH gives (80% yield (50)) 2,4-dichlorophenol (3:0560); $\tilde{\mathbf{C}}$ with $\mathbf{Cl_2}$ (3 moles) undoubtedly gives 2,4,6-trichlorophenol (3:1673). — For study of chlorination of $\tilde{\mathbf{C}}$ with HOCl see (51).]

Č with Br₂ (1 mole) in CCl₄ gives (87% yield (52)) 4-bromo-2-chlorophenol, ndls. from lgr., m.p. 48-49° (52), 49-50° (53), 50-51° (54). — Č with Br₂ (2 moles) in aq. KBr soln. gives (55) 2-chloro-4,6-dibromophenol [Beil. VI-203], ndls. from alc., m.p. 76° cor. (55), 75-76° (56). — Č with large excess Br₂ in pres. of Fe powder gives (57) 2-chloro-3,4,5,6-tetrabromophenol, ndls. from alc. or AcOH, m.p. 224° (57).

[\bar{C} in aq. alk. with I_2/KI soln. as directed (55) gives 2-chloro-4,6-di-iodophenol, ndls. from alc., m.p. 96° (55). — For study of iodination of \bar{C} see (58).]

[C on nitrosation as directed (59) (60) gives (96% yield (60)) 2-chloro-4-nitrosophenol (2-chlorobenzoquinone-1,4-oxime-4) [Beil. VII-631, VII₁-(346)], pale yel. ndls. from C_6H_6 , m.p. 145° (60), 142° (59); for discussion of tautomerism of this cpd. see also (61) (62) (63).]

[$\bar{\mathbf{C}}$ on mononitration, e.g., with cold mixt. of equal pts. HNO₃ (D=1.36) + aq. (13), with HNO₃ in MeOH (64), or with HNO₃ (D=1.5) in AcOH (65), gives a mixt. of 2-chloro-4-nitrophenol [Beil. VI-240], ndls. from aq., m.p. 110-111°, and (32% (65)) 2-chloro-6-nitrophenol [Beil. VI-239], ndls. from aq., m.p. 70-71°; of these only the latter is volatile with steam (use in detn. of $\bar{\mathbf{C}}$ in mixts. with 4-chlorophenol (3:0475) (27)). — Both of the other mononitro-o-chlorophenols are known but have been obtd. only by indirect means; e.g., 2-chloro-3-nitrophenol, m.p. 120.5° (66), 120° (67), and 2-chloro-5-nitrophenol, m.p. 119.5° (66).]

 $\tilde{\mathbf{C}}$ on dinitration, e.g., by soln. in HNO₃ (D=1.36) and subsequent warming yields (68) 2-chloro-4,6-dinitrophenol [Beil. VI-259, VI₁-(128)], cryst. from alc., m.p. 113° (68); this prod. (unlike picric acid) is volatile with steam from H₂SO₄ soln. (use in anal. of mixts. of $\tilde{\mathbf{C}}$ with phenol (17)).

[Č in alk. soln. couples with diazotized aniline giving (70% yield (69) (70) (71)) 3-chloro-4-hydroxyazobenzene (2-chlorobenzoquinone phenylhydrazone-4) [Beil. XVI-120], yel. pr. from aq. alc., m.p. 88.5° (69), 88° (70), 86° (71). — For study of corresp. coupling of C with diazotized p-nitroaniline see (72).]

[For mercuration of \bar{C} and use of products as seed disinfectants, etc., see (73); for condens. prods. of \bar{C} with C_6H_5 .Hg.OH see (74).]

[\bar{C} over pumice in a silica tube at dull red heat (75) or K salt of \bar{C} + K phenolate at 250° for 8 hrs. (81) yields diphenylene dioxide [Beil. XIX-44, XIX₁-(618)], ndls. from MeOH, m.p. 119°, readily identified by dinitration with fumg. HNO₃ in AcOH (75) to dinitrodiphenylene dioxide, ndls. from pyridine, m.p. 257° (75).]

Condensation reactions involving nuclear hydrogens. [\bar{C} with formalin (1:0145) in pres. of conc. HCl treated with HCl gas as directed (76) gives 3-chloro-4-hydroxybenzyl chloride, m.p. 92-93° (76). — \bar{C} with formalin + H₂SO₄ (60%) at 60-65° for 16 hrs. gives (76) 3,3'-dichloro-4,4'-dihydroxydiphenylmethane, m.p. 103-104° (76). — \bar{C} with formalin (1:0145) + aq. 10% NaOH as directed (77) yieds acc. to conditions 3-chloro-4-hydroxybenzyl alc., pl. from C_6H_6 , m.p. 123.5-124°, and/or 3-chloro-4-hydroxy-5-(hydroxymethyl)-

benzyl alc., ndls. from CHCl₃, m.p. 117.5-119°. — For condens. of Č with formalin in prepn. of synthetic tanning agents see (78).]

[$\bar{\mathbb{C}}$ with CHCl₃ or CHBr₃ (79) in pres. of aq. NaOH undergoes Reimer-Tiemann reaction yielding both 3-chloro-2-hydroxybenzaldehyde (3:1010) and 3-chloro-4-hydroxybenzaldehyde (3:4065). — $\bar{\mathbb{C}}$ with CCl₄ in alc. alk. in s.t. at 125–136° yields (80) 3-chloro-4-hydroxybenzoic acid (3:4675). — $\bar{\mathbb{C}}$ with α,α -dichlorodiphenylmethane (3:6960) + AlCl₃ in cold CS₂ gives (31) 3-chloro-4-hydroxyphenyl-diphenyl-carbinol, from 60% AcOH as deep orange pl. of quinonoid desmotrope, m.p. 118°, but from alc. colorless crysts. of benzenoid desmotrope (contg. ½ mole solvent), m.p. 70–72° (31); note that in hot C₆H₆, however, this reaction takes a different course yielding (31) α,α -bis-(o-chlorophenoxy)diphenylmethane, cryst. from hot alc., m.p. 191–192° (31). — $\bar{\mathbb{C}}$ with chloral hydrate (3:1270) in pres. of alk. salts condenses (82) to 3-chloro-4-hydroxyphenyl-trichloromethyl-carbinol which on hydrolysis with NaOH yields 3-chloro-4-hydroxybenzaldehyde (3:4065).]

[\bar{C} with SOCl₂ + AlCl₃ in CS₂ gives (85% yield (83)) bis-(3-chloro-4-hydroxyphenyl) sulfoxide [Beil. VI₁-(422)], ndls. from dll. alc. contg. HCl, m.p. 195°. — \bar{C} with mixt. of conc. H₂SO₄ + fumg. H₂SO₄ (25% SO₃) at 100° for 6 hrs. disulfonates to 2-chloro-4,6-disulfophenol which undergoes bimolecular condensation to the corresp. internal ester (for details see (84)).]

[\bar{C} with phthalic anhydride (1:0725) with AlCl₃ in acetylene tetrachloride (3:5750) (85) (86) (87), or with AlCl₃ + NaCl at 150° (88), gives (yields: 96% (85) (86), 87% (88)) 2-(3'-chloro-4'-hydroxybenzoyl)benzoic acid, cryst. from MeOH, m.p. 224-225° (85), cryst. from AcOH, m.p. 219.5-220° (86), 219° (88); this prod. on ring closure with 15 pts. conc. H₂SO₄ at 150° for 1 hr. (88), or with 10 pts. conc. H₂SO₄ + 1 pt. ZnCl₂ at 130° for 5½ hrs. (85), or with 16 pts. 100% H₂SO₄ + 1 pt. H₃BO₃ at 195° for 1½ hrs. (86), gives (yields: 80% (85), 76% (88), 53.5% (86)) 3-chloro-2-hydroxyanthraquinone, yel. ndls. from AcOH, nitrobenzene + AcOH, or xylene, m.p. 267-268° (85), 266.5-267° (86), 266° (88). —Note that by slight variations other products are also formed; e.g., \bar{C} + phthalic anhydride + fumg. H₂SO₄ + H₃BO₃ at 170-200° for 10 hrs. gives (89) both chloro-hydroxy-anthraquinone and dhydroxyanthraquinone (. (90) and at 255° gives (91) 1,2,4-trihydroxyanthraquinone (purpurin). — Note that \bar{C} (2 moles) with phthalic anhydride (1 mole) at 125° for 6 hrs. gives (75% yield (92)) dichlorophenolphthalein, m.p. 98°.]

Reactions of nuclear halogen of \tilde{C} . [\tilde{C} on hydrolysis with aq. alk., alk. carbonates, or alkaline earths in pres. of cat. such as Cu or Cu salts at elevated temps. and under press. yields (93) (94) (95) (96) (97) (98) pyrocatechol (1:1520) cf. (43). — \tilde{C} on fusion with KOH yields (13) pyrocatechol but some resorcinol (1:1530) is also formed (98) (99). — \tilde{C} with aq. Na₂S + NaOH at 210–215° for 24 hrs. yields (100) 2-mercaptophenol [Beil. VI-793], b.p. 216–217° cor., m.p. +5°.]

Reactions of the phenolic group of \bar{C} (see also under \oplus , below). \bar{C} behaves as a weak acid; e.g., \bar{C} dis. in conc. aq. Na₂CO₃ soln. on shaking at room temp. (dif. and sepn. from phenol (18)) and is repptd. by treatment with CO₂ (18). — Dissoc. const. of \bar{C} in aq. = 32×10^{-10} (101); for studies of dissoc. const. in 50% MeOH at 20° (7) (101) (102), in 25% EtOH at 25° (103), in 30% EtOH at 25° (4) (102) see indic. refs.

 \overline{C} has bactericidal (104) (105) (106) (107) (108) (109) and fungicidal (110) properties.

[C with alkali metals gives corresp. alk. o-chlorophenolates; for use of these as antioxidants in motor fuels see {111}. — Dry Na o-chlorophenolate with CO₂ at 140-150° under press. yields (25) 3-chloro-2-hydroxybenzoic acid (3-chlorosalicylic acid) (3:4745).]

[C in MeOH/KOH with MeI in s.t. at 130° (112), or C with aq. KOH + Me2SO₄ at ord. temp. (113), yields o-chlorophenyl methyl ether (o-chloroanisole) (3:6255). — C in abs. alc. + NaOEt with EtI yields (115) o-chlorophenyl ethyl ether (o-chlorophenetole) (3:8735). — C with allyl bromide in acetone + aq. + NaOH gives (90% yield (146))

allyl o-chlorophenyl ether; b.p. $108-110^{\circ}$ at 15 mm., $D_{25}^{25}=1.132$, $n_{25}^{25}=1.5388$; this prod. on reflux. 10 min. gives by Claisen rearr. (89% yield (146)) 2-chloro-6-allylphenol, b.p. $61-63^{\circ}$ at 1 mm., $n_{25}^{25}=1.5447$.]

[$\bar{\mathbf{C}}$ with POCl₃ refluxed for 8-11 hrs., POCl₃ distd. off, and crude product saponified yields (117) bis-(o-chlorophenyl)phosphoric acid, m.p. 105-106° cor. — For condens. of $\bar{\mathbf{C}}$ with triphenylphosphine oxide and use of prod. as seed disinfectant see (118); for use of $\bar{\mathbf{C}}$ in prepn. of triaryl phosphates (119) or of mixed triaryl thiophosphates (120) and use as plasticizers see indic. refs. — $\bar{\mathbf{C}}$ with PCl₅ gives on htg. (22) o-dichlorobenzene (3:6055).]

 $[\bar{C}]$ with malic acid (1:0450) + conc. H_2SO_4 fails (121) to give the expected von Pechmann synthesis of 8-chlorocoumarin; however, \bar{C} with α -substituted acetoacetic esters + P_2O_5 condenses to corresp. chromones; e.g., \bar{C} with ethyl α -methylacetoacetate (1:1712) + P_2O_5 gives (27% yield (122)) 8-chloro-2,3-dimethylchromone [Beil. XVII₁-(177)], pale yel. ndls. from dil. alc., m.p. 108°; for further examples see (123). — \bar{C} (as sodium salt) + diethyl fumarate (1:3761) refluxed in xylene yields (124) diethyl α -(α -chlorophenoxy)-fumarate which on subsequent hydrolysis to the acid, ring closure with conc. H_2SO_4 , and decarboxylation gives 8-chlorochromone, colorless ndls., m.p. 114-115° (124).]

Č with AlCl₃ evolves HCl and yields (125) Cl.C₆H₄.O.AlCl₂, insol. CS₂, but sol. in alc. and hydrolyzed by aq., m.p. 207-210° (125). — Č in 50% alc. with satd. soln. of PkOH in 50% alc. yields (126) a mol. cpd., Č.PkOH, pale yel. ndls., m.p. 81-82° (126).

- P FeCl₃ color reaction: C in aq. soln. with very dil. FeCl₃ gives violet coloration; C in alc. with very dilute aq. FeCl₃ gives greenish-blue.
- ---- o-Chlorophenyl benzoate [Beil. IX-117]: oil, b.p. 314-316° (?) (127), 212-213° at 745 mm. (127), 155-157° at 3 mm. (127). [From C + benzoyl chloride + aq. NaOH (127) (for study of rate see (129)).] [Note also that C + BzCl + AlCl₃ in acetylene tetrachloride yields (128) the Fries rearr. prods. to be expected from o-chlorophenyl benzoate, viz., 3-chloro-4-hydroxybenzophenone, cryst. from alc. or C₀H₀, m.p. 180-181° (128), and 3-chloro-2-hydroxybenzophenone, pale yel. cryst. from alc., m.p. 92.5-93° (128).]
- O o-Chlorophenyl m-nitrobenzoate: pr. from lgr., m.p. 98° (18). [From C with m-nitrobenzoyl chloride on shaking with 10% aq. NaOH at 35-50° (18).]
- **o-Chlorophenyl** p-nitrobenzoate: ndls. from 85% alc., m.p. 114.5-114.8°. [From $\ddot{\mathbf{C}} + p$ -nitrobenzoyl chloride in pyridine (unpublished work).]
- ---- o-Chlorophenyl 3,5-dinitrobenzoate: ndls. from 85% alc., m.p. 143.1-143.4°. [From C + 3,5-dinitrobenzoyl chloride in pyridine (unpublished work).]
- --- o-Chlorophenyl benzenesulfonate: unrecorded.
- --- o-Chlorophenyl p-toluenesulfonate: m.p. 74° (4).
- —— o-Chlorophenyl benzyl ether: oil, b.p. 138-140° at 3 mm. (130). [From C (as Na salt) + benzyl chloride but in very poor yield (7.5% (130)); note that the products elsewhere (131) (132) seem to be questionable.]
- —— o-Chlorophenyl p-nitrobenzyl ether: m.p. 100° (133). [From Č (as Na salt) with p-nitrobenzyl bromide refluxed in aq. alc. (133).]
- **O** o-Chlorophenyl 2,4-dinitrophenyl ether: greenish-yel. ndls. from alc., m.p. 99° (134). [From \bar{C} in equiv. amt. aq. NaOH refluxed with alc. 2,4-dinitrochlorobenzene (134). Note that the m.p. of 75-76° reported earlier (135) for this compd. is identical with that given later (134) for the corresp. deriv. of m-chlorophenol (3:0255).]
- © o-Chlorophenoxyacetic acid (3:4375): m.p. 145-146° (136) (137), 143-145° (138); Neut. Eq. 186.5. [From Č in aq. NaOH (2 equivs.) with chloroacetic acid (1 equiv.) refluxed for 1 hr., then acidified (138) cf. (136) (137).]

- \odot o-Chlorophenyl N-(phenyl)carbamate: cryst. from C₆H₆, m.p. 120-121° (139). [From \ddot{C} + phenyl isocyanate in dry ether (139).]
- ⊕ o-Chlorophenyl N-(p-iodophenyl)carbamate: m.p. 156-157° (147). [From C̄ + p-iodobenzazide in hot lgr. (147).]
- \odot o-Chlorophenyl N-(p-bromophenyl)carbamate: pr. from EtOAc, m.p. 141-143° cor. (140). [From \ddot{C} + p-bromobenzazide in lgr. (140).]
- © o-Chlorophenyl N-(m-nitrophenyl)carbamate: m.p. 114° u.c., 116° cor. (148). [From C + m-nitrophenyl isocyanate (148) in lgr. (148).]
- © o-Chlorophenyl N-(p-nitrophenyl)carbamate: ndls. from lgr., m.p. 143° cor. {141}. [From C + p-nitrobenzazide in lgr. {141}.] [Note that corresp. deriv. of m-chlorophenol (3:0255) has m.p. 144° cor. (141).]
- \bigcirc o-Chlorophenyl N-(3,5-dinitrophenyl)carbamate: pl. from C₆H₆, m.p. 182-183° (142). [From $\ddot{\rm C}$ + 3,5-dinitrophenylazide htd. in dry toluene (142).]
- © o-Chlorophenyl N-(3,5-dinitro-4-methylphenyl)carbamate: yel. pl. from lgr. or EtOAc, m.p. 175-176°, u.c., 180-181° cor. (143). [From C + 3,5-dinitro-4-methylbenzazide in lgr. (143).]
- \odot o-Chlorophenyl N-(α -naphthyl)carbamate: cryst. from lgr., m.p. 120° (144). [From $\ddot{C} + \alpha$ -naphthyl isocyanate in lgr. (144).]
- **D** o-Chlorophenyl N-(β -naphthyl)carbamate: pl. from lgr., m.p. 133-134° u.c., 136-137° cor. (145). [From $C + \beta$ -naphthyl isocyanate (or azide) in lgr. (145).]
- --- o-Chlorophenyl N,N-diphenylcarbamate: unreported.
- 3:5980 (1) Kramers, Ann. 173, 331 (1874). (2) Kohlrausch, Pongratz, Monatsh. 65, 201 (1935). (3) Bramley, J. Chem. Soc. 109, 436, 445-457 (1916). (4) Bennett, Brooks, Glasstone, J. Chem. Soc. 1935, 1823, 1826. (5) Linke, Z. physik. Chem. B-46, 261 (1940). (6) Zumwalt, Badger, J. Am. Chem. Soc. 62, 306 (1940). (7) Kuhn, Wassermann, Helv. Chim. Acta 11, 8, 11, 14, 26 (1928). (8) Williams, Fogelberg, J. Am. Chem. Soc. 52, 1358 (1930). (9) Holleman, Rinkes, Rec. trav. chim. 30, 79-81, 84-86, 86-92 (1911). (10) Glass, Madgin, Hunter, J. Chem. Soc. 1934, 263.
- (11) Puschin, Matavulj, Z. physik. Chem. A-164, 81 (1933). (12) Puschin, Matavulj, Z. physik. Chem. A-162, 417 (1932). (13) Faust, Müller, Ann. 173, 303-306 (1874); Ber. 5, 777-779 (1872). (14) Holleman, Rec. trav. chim. 37, 105-106 (1918). (15) Sidgwick, Turner, J. Chem. Soc. 121, 2256-2259 (1922). (16) Jona, Gazz. chim. idal. 39, II 300-301, 309 (1909). (17) Rashevskaya, Zil'berman, Chernyavskaya, Skvirskaya, J. Applied Chem. (U.S.S.R.) 10, 499-505 (1937); Cent. 1938, I 58; C.A. 31, 6212 (1937). (18) Wohleben, Ber. 42, 4369-4373 (1909). (19) Bramley, J. Chem. Soc. 103, 480-483, 486-492 (1916). (20) Burnham, Madgin, J. Chem. Soc. 1936, 789, 791.
- (21) Thole, Mussell, Dunstan, J. Chem. Soc. 103, 1114-1115 (1913).
 (22) Beilstein, Kurbatow Ann. 176, 39-40 (1875).
 (23) Schmitt, Cook, Ber. 1, 67-68 (1868).
 (24) Sandmeyer, Ber. 17, 2651-2652 (1884); Ber. 23, 1880-1881 (1890).
 (25) Varnholt, J. prakt. Chem. (2) 36, 22-23 (1887).
 (26) Merck, Ger. 76,597, Frieddinder 3, 845.
 (27) Takagi, Tanaka, J. Pharm. Soc. Japan 1925, No. 517, 253-260; Cent. 1926, I 182; C.A. 20, 2669 (1926).
 (28) Chulkov, Parini, Staroselets, Org. Chem. Ind. (U.S.S.R.) 3, 97-101 (1937); Cent. 1938, I 1419; C.A. 31, 4967 (1937).
 (29) Tishchenko, J. Russ. Phys.-Chem. Soc. 60, 152-162 (1928); Cent. 1928, II 767; C.A. 23, 3397 (1928).
 (30) Lossen, Ger. 155,631, Oct. 26, 1904; Cent. 1904, II 1486.
- (31) Gomberg, van Stone, J. Am. Chem. Soc. 38, 1601-1603 (1916). (32) Likhosherstov, J. Russ. Phys.-Chem. Soc. 61, 1019-1023; 1025-1028 (1929); Cent. 1936, I 1294; C.A. 24, 836 (1930). (33) Goldschmidt, Endres, Dirsch, Ber. 58, 576 (1925). (34) Steinkopf, Mieg, Herold, Ber. 53, 1145 (1920). (35) Hazard-Flamand, Ger. 141,751, May 13, 1903; Cent. 1935, I 1324. (36) Takagi, Kutani, J. Pharm. Soc. Japan 1925, No. 517, 260-266; Cent. 1926, I 62; C.A. 26, 2669 (1926). (37) Huston, Neeley, J. Am. Chem. Soc. 57, 2176-2178 (1935). (38) Lofton, Burroughs (to Pennsylvania Coal Prod. Co.), U.S. 2,126,648, Aug. 9, 1938; Cent. 1938, II 3006; C.A. 32, 7925 (1938). (39) Bertsch (to Monsanto Chem. Co.), U.S. 1,966,281, July 10, 1934; Cent. 1935, I 959; C.A. 28, 5471 (1934). (40) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994.
- (41) Vorozhtzov, Karlash, Compt. rend. acad. sci. U.R.S.S. 1933, 221-223; Cent. 1935, I 55;
 C.A. 28, 1991 (1934). (42) Vorozhtzov, Karlash, Russ. 30,690, June 30, 1933; Cent. 1934, I
 767. (43) Kipriyanov, Suich, Ukrain. Kehm. Zhur. 7, (Wiss-Tech. Abt.), 94-100 (1932); Cent.

1933, II 1339; C.A. 27, 3824 (1933). (44) Chemische Werke Ichendorf, Ger. 281,175, Dec. 15, 1914; Cent. 1915, I 180. (45) Boehringer und Sohne, Ger. 284,533, May 29, 1915; Cent. 1915, II 168; Ger. 286,266, July 30, 1915; Cent. 1915, II 566. (46) Holleman, de Mooy, Rec. trav. chim. 35, 18, 27 (1915). (47) Kelber, Ber. 54, 2259 (1921). (48) Shoesmith, Hetherington, Slater, J. Chem. Soc. 125, 1308 (1924). (49) Boeseken, Metz, Rec. trav. chim. 54, 350-351 (1935). (50) Groves, Turner, Sharp, J. Chem. Soc. 1929, 516.

(51) Soper, Smith, J. Chem. Soc. 1926, 1582-1591. (52) Raiford, Miller, J. Am. Chem. Soc. 55, 2127 (1933). (53) Lock, Monatsh. 67, 324 (1935/36). (54) Fox, Turner, J. Chem. Soc. 1963, 1858. (55) Kohn, Rabinowitsch, Monatsh. 48, 354, 358 (1927). (56) Lock, Monatsh. 62, 192 (1933). (57) Kohn, Domotor, Monatsh. 47, 235 (1926). (58) Aldoshin, Chalykh'yan, J. Gen. Chem. (U.S.S.R.) 9, 748-752 (1939); Cent. 1939, II 3397, C.A. 34, 397 (1940). (59) Hodgson, J. Chem. Soc. 1932, 866-869. (60) Hodgson, Nicholson, J. Chem. Soc. 1940, 811.

(61) Hodgson, J. Chem. Soc. 1932, 1395-1398. (62) Anderson, Yanke, J. Am. Chem. Soc. 56, 732-735 (1934). (63) Hodgson, J. Chem Soc. 1937, 520-527. (64) Plazek, Roczniki Chem. 10, 761-776 (1930); Cent. 1931, I 1428. (65) Chien, Adams, J. Am. Chem. Soc. 56, 1790 (1934). (66) van Erp, J. prakt. Chem. (2) 127, 22-38 (0930); (2) 129, 327-336 (1931). (67) Henley, Turner, J. Chem. Soc. 1930, 940. (68) van Alphen, Rec. trav. chim. 51, 451 (1932). (69) Hunter, Barnes, J. Chem. Soc. 1928, 2064. (70) Farmer, Hantzsch, Ber. 32, 3098 (1899).

(71) McPherson, Dubois, J. Am. Chem. Soc. 30, 818-821 (1908). (72) Richardson, J. Chem. Soc. 1937, 1363-1364. (73) Engelmann (to du Pont Co), US. 1,748,331, Feb. 25, 1930; Cent. 1939, II 802; U.S. 1,890,774, Dec. 13, 1932; Cent. 1933, I 1501; French 609,478, Aug. 16, 1926; Cent. 1927, I 347. (74) I.G., Brit. 329,987, June 26, 1930; Cent. 1930, II 1760. (75) Bell, J. Chem. Soc. 1936, 1244. (76) Buehler, Brown, Holbert, Fulmer, Parker, J. Org. Chem. 6, 902-907 (1941). (77) Hanus, J. prakt. Chem. (2) 158, 260, 262 (1941). (78) Monsanto Chem. Co. & Gladden, Brit. 464,766, May 30, 1937; Cent. 1937, II 911. (79) Hodgson, Jenkinson, J. Chem. Soc. 1929, 469-471, 1641. (80) Hasse, Ber. 10, 2192-2193 (1877).

(81) Cullinane, Davies, Rec. trav. chim. 55, 882-883 (1936). (82) Haakh, Smola, Austrian, 141,159, March 25, 1935; Cent. 1935, II 439. (83) Gazdar, Smiles, J. Chem. Soc. 97, 2252-2253 (1910). (84) Schoepfle, Van Natta, Clarkson, J. Am. Chem. Soc. 50, 1173-1174 (1928). Goldberg, J. Chem. Soc. 1931, 1776, 1787. (86) Hayashi, J. Chem. Soc. 1930, 1522-1523. Scottish Dyes, Ltd. & Tonkin & Thomas, Brit. 345,204, April 16, 1931; Cent. 1931, II 1493. (88) Waldmann, Wider, J. prakt. Chem. (2) 150, 110-111 (1938). (89) Orelup, U.S. 1,790,510, Jan. 27, 1931; Cent. 1932, I 2238. (90) Scottish Dyes, Ltd. & Thomas & Hooley, Brit. 234,533, June 25, 1925; Cent. 1926, I 245.

(91) M. Tanaka, N. Tanaka, Bull. Chem. Soc. Japan 3, 287 (1928). (92) Consonno, Apostolo, Gazz. chim. ital. 51, 63 (1921). (93) Burroughs (to Pennsylvania Coal Prod. Co.), U.S. 2,041,-592 + 2,041,593, Oct. 11, 1934; Cent. 1937, I 1016. (94) Marx, Wesche, Bittner, Saenger, Ger. 593,193, Feb. 22, 1934; Cent. 1934, I 3395. (95) Boehringer und Sohne, Gei. 269,544, Jan. 22, 1914; Cent. 1914, I 591. (96) Bayer and Co., Ger. 249,939, Aug 1, 1912; Cent. 1912, II 655. (97) Merck, Ger. 84,828, Dec. 2, 1895, Friedlander 4, 114 (1894-1897). (98) Tijmstra, Chem. Weekblad 5, 96-101 (1908); Cent. 1908, I 1051. (99) Blanksma, Chem. Weekblad 5, 93-95 (1908); Cent. 1998, I 1051. (100) Imp. Chem. Ind., Ltd. & Palmer, But. 381,237, Oct. 27, 1932; Cent. 1933, I 675.

(101) Murray, Gordon, J. Am. Chem. Soc. 57, 110-111 (1935). (102) Jenkins, J. Chem. Soc. 1939, 1139. (103) Branch, Yabroff, Bettman, J. Am. Chem. Soc. 56, 938, 941 (1934). (104) Ordal, Proc. Soc. Exptl. Biol. Med. 47, 387-389 (1941). (105) Klarmann, Shternov, Gates, J. Lab. Clin. Med. 20, 40-47 (1934); Cent. 1935, I 2199; CA. 29, 1848 (1935). (106) Kuroda, Arch. exptl. Path. Pharmakol. 112, 60-64 (1926); Cent. 1926, I 3610; C.A. 20, 2705 (1926). (107)Kuroda, Biochem. Z. 169, 281-291 (1926); Cent. 1926, I 3068; C.A. 20, 3315 (1926). (108)Cooper, Forstner, Biochem. J. 18, 941-947 (1924); Cent. 1925, I 104, C.A 19, 311 (1925). Cooper, Woodhouse, Biochem. J. 17, 600-612 (1923); Cent. 1923, III 1625; C.A 18, 403 (1923). (110) Woodward, Kingery, Williams, J. Lab. Clin. Med. 19, 1216-1223 (1934); Cent. 1935, I 256; C.A. 28, 6849 (1934).

(111) Benedict (to Universal Oil Products Co.), U.S. 2,051,814, Aug. 25, 1926; Cent. 1937, I 495. (112) Fischli, Ber. 11, 1463 (1878). (113) Kohn, Sussmann, Monatsh. 48, 196 (1927). (114) Anziletti, Curran, J. Am. Chem. Soc. 65, 609 (1943). (115) Goldsworthy, J. Chem. Soc. 1926, 1254-1256. (116) Swarts, J. chim. phys. 20, 76 (1923). (117) Zetsche, Nachmann, Helv. Chim. Acta 9, 426-427 (1926). (118) I.G., Brit. 326,137, April 3, 1930; Cent. 1930, II 801. (119) Moyle (to Dow Chem. Co.), U.S. 2,220,113, Nov. 5, 1940; C.A. 35, 1898 (1941). (120) Moyle (to Dow Chem. Co.), U.S. 2,250,049, July 22, 1941; C.A. 35, 7062 (1941).

(121) Clayton, J. Chem. Soc. 93, 2018 (1908). (122) Simonis, Schuhmann, Ber. 50, 1144-1145 (1917). (123) Chakravarti, J. Indian Chem. Soc. 9, 27-28 (1932). (124) Ruhemann,

Beil. I - 364

3:5985

70-73°

69°

Ber. 54, 916-918 (1921). {125} Perrier, Bull. soc. chim. (2) 15, 1183 (1896). {126} von Goedike,
Ber. 26, 3046 (1893). {127} Autenrieth, Arch. Pharm. 233, 41-42 (1895). {128} Hayashi, J. prakt. Chem. (2) 123, 295-297 (1929). {129} Bernouilli, St. Goar, Helv. Chim. Acta 9, 754-755, 763 (1926). {130} Huston, Guile, Chen, Headley, Warren, Baur, Mate, J. Am. Chem. Soc. 55, 4642 (1933).

(131) Ewing, Ladd, J. Am. Chem. Soc. 58, 2455 (1936). (132) Baw, J. Indian Chem. Soc. 3, 104 (1926). (133) Lyman, Reid, J. Am. Chem. Soc. 42, 615-617 (1920). (134) Bost, Nicholson, J. Am. Chem. Soc. 57, 2368-2369 (1935). (135) Fox, Turner, J. Chem. Soc. 1939, 1121. (136) Minton, Stephen, J. Chem. Soc. 121, 1600 (1922). (137) Behaghel, J. prakt. Chem. (2) 114, 297 (1926). (138) Koelsch, J. Am. Chem. Soc. 53, 304-305 (1931). (139) Michael, Cobb, Ann. 363, 91-92 (1908). (140) Sah, Cheng, Rec. trav. chim. 58, 592-593 (1939).

(141) Sah, Cheng, Rec. trav. chim. 58, 596-599 (1939). (142) Sah, Ma, J. Chinese Chem. Soc. 2, 229-233 (1934). (143) Sah, Rec. trav. chim. 58, 587-588 (1939). (144) French, Wirtel, J. Am. Chem. Soc. 48, 1737-1739 (1926). (145) Sah, Rec. trav. chim. 58, 454-458 (1939). (146) Tarbell, Wilson, J. Am. Chem. Soc. 64, 1070 (1942). (147) Sah, Young, Rec. trav. chim. 59, 357-363 (1940); C.A. 35, 4363 (1941). (148) Sah, Woo, Rec. trav. chim. 58, 1014-1015 (1939).

1,3-DICHLOROPROPANOL-2

at 14 mm. (10)

at 12 mm. (45)

CH₂Cl

C₃H₆OCl₂

(
$$\beta$$
, β' -Dichloroisopropyl alcohol; glycerol α , α' -dichlorohydrin; '' α -dichlorohydrin'') CH_2Cl $I_{1-}(185)$ $I_{2-}(383)$ I_{2-}

Note: Because of the great magnitude of the literature of C only the most important citations can be included here; for much additional data prior to 1930, the appropriate volume of Beilstein should also be consulted.

 \bar{C} dis. at 19° in 9 pts. aq.; at 72° in 6 pts. aq.; misc. with ether. [For recovery of \bar{C} from aq. solns. by extraction with immiscible solvents (12) (13) (14) or by steam distillation (12) (15) see indic_refs.]

[For prepn. of \bar{C} from glycerol (1:6540) by actn. of HCl gas at 100-110° (yield: 87% (11), 82% (6), 55-57% (10)) (12) see indic. refs.; for prepn. of \bar{C} from 3-chloro-1,2-epoxy-propane (epichlorohydrin) (3:5358) with fumg. HCl (yield 80% (11)) (16) (17) (1) (18), with MgCl₂ in dil. alc. at 125° (19), or with S₂Cl₂ (67% yield (40)) see indic. refs.; for formn. of \bar{C} (together with other prods.) from glycerol (1:6540) with SOCl₂ + pyridine see (20); from corresp. acetate (3:6318) by alcoholysis with MeOH + HCl see (21) (45); from α,α' -dichloroacetone (3:0563) reductn. with yeast see (22).]

Č with aq. alk. rapidly loses HCl giving 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358) (yield: 90% (6), 80-90% (23), 76-81% (24-B), 67-72% (24-A), 85% (25), 79% (26)).

 \ddot{C} on oxidn. with Na₂Cr₂O₇ + H₂SO₄ gives (68–75% yield (27)) α,α' -dichloroacetone (3:0563). [Overoxidn. of this prod. or \ddot{C} on oxidn. with conc. HNO₃ (28) gives chloroacetic acid (3:1370).]

[\tilde{C} on reductn. with Na/Hg in moist ether gives various products including allyl alc. (1:6145), isopropyl alc. (1:6135), propylene together with epichlorohydrin (for refs. see Beil. I-364); \tilde{C} htd. with HI + P in s.t. at 180° gives (29) isopropyl iodide.]

[For behavior of Č with NaSH yielding 1,3-dithioglycerol (Hg deriv. m.p. 185°, Pb deriv. m.p. 175-180° dec.) see (41).]

 \overline{C} on htg. with P_2O_5 (31) or $POCl_3$ (11) (30) yields 1,3-dichloropropene-1 (3:5280).

 \tilde{C} on htg. with excess EtOH + NaOH yields (by a series of definite intermediate stages (25)) (6) 1,3-diethoxypropanol-2 (glycerol α,γ -diethyl ether) b.p. 108-111° at 60 mm., $D_4^{25} = 0.953$, $n_D^{25} = 1.420$ (19) (6); similarly \tilde{C} on htg. with excess phenol + aq. NaOH as specified (19) gives 80% yield 1,3-diphenoxypropanol-2 (glycerol α,γ -diphenyl ether), cryst. from alc., m.p. 80-81° (19).

- $----\beta, \beta'$ -Dichloroisopropyl acetate: b.p. 205° (see 3:6318).
- ---- β_{β} '-Dichloroisopropyl benzoate: b.p. 296° sl. dec. (42); 171-173° at 19 mm. (43), 157-160° at 12 mm. (44). [From \bar{C} + benzoyl chloride on htg. (42) or with pyridine (44).]
- Φ β,β'-Dichloroisopropyl p-nitrobenzoate: m.p. 59-60° (32), 58-59° (33). [From C + p-nitrobenzoyl chloride with pyridine (94% yield) (33) or with quinoline in CHCl₃ (100% yield) (32).]
- Φ β,β' -Dichloroisopropyl 3,5-dinitrobenzoate: m.p. 129° (32). [From $\tilde{C}+3,5$ -dinitrobenzoyl chloride + quinoline in CHCl₃ in 100% yield (32).]
- Φ β,β'-Dichloroisopropyl benzenesulfonate: long colorless ndls. from C₆H₆, m.p. 50°
 (34). [From C̄ + benzenesulfonyl chloride + conc. aq. NaOH (34); for study of pyrolysis see (35).]
- Φ β,β'-Dichloroisopropyl N-(phenyl)carbamate: m.p. 73-74° (20) (38), 73° (39). [From C with phenyl isocyanate (20) (39); also indirectly from C by conv. to corresp. chloroformate and reacting with aq. aniline (38).] [This prod. htd. a few min. with conc. aq. KOH loses HCl and ring-closes alm. quant. to 5-chloromethyl-3-phenyloxazolidone-2, pr. from hot alc., m.p. 104-105° (39).]
- β,β'-Dichloroisopropyl N-(α-naphthyl)carbamate: m.p. 115° (38). [Prepd. indirectly from C by conv. to corresp. chloroformate and reacting with aq. annline (38).] [This prod. with conc. aq. alk. loses HCl and ring-closes to 5-chloromethyl-3-(α-naphthyl)-oxazolidone-2, m.p. 118° (38).]
- Φ β,β'-Dichloroisopropyl N-(β-naphthyl)carbamate: m.p. 101° (38). [Prepd. indirectly from Č by conv. to corresp. chloroformate and reacting with aq. aniline (38).] [This prod. with conc. aq. alk. loses HCl and ring-closes to 5-chloromethyl-3-(β-naphthyl)-oxazolidone-2, m.p. 107° (38).]

3:5985 (1) Markownikow, Ann. 208, 352-359 (1881). (2) Gibson, J. Soc. Chem. Ind. 50, 949-954; 970-975 (1931). (3) Lecat, Rec. trav. chim. 45, 622 (1926). (4) Gilchrist, Purves, J. Chem. Soc. 127, 2743 (1925). (5) Tornõe, Ber. 21, 1285 (1888). (6) Fairbourne, Gibson, Stephens, J. Soc. Chem. Ind. 49, 1021-1023; 1069-1070 (1930). (7) Timmerman, Bull. soc. chim. Belg. 30, 69 (1921). (8) Brash, J. Soc. Chem. Ind. 46, 481T (1927). (9) Posner, Rohde, Ber. 42, 3240 (1909). (10) Conant, Quayle, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 292-294 (1941); (1st. ed.) 286-288 (1932); 3, 29-31 (1922).

(11) Hill, Fischer, J. Am. Chem. Soc. 44, 2586-2588 (1922). (12) Britton, Heindel (to Dow Chem. Co.), U.S. 2,144,612, Jan. 24, 1939; Cent. 1939, II 525; C.A. 33, 2914 (1939). (13) Britton, Slagh (to Dow Chem. Co.), U.S. 2,198,600, April 30, 1940; C.A. 34, 5860 (1940). (14) Britton, Slagh (to Dow Chem. Co.), U.S. 2,279,509, April 14, 1942; C.A. 36, 5188 (1942). (15) I.G., French 844,375, July 24, 1939; Cent. 1939, II 4589; C.A. 34, 7297 (1940). (16) Reboul, Ann. Suppl. 1, 224-225 (1861). (17) Hübner, Müller, Ann. 159, 176 (1871). (18) Smith, Z. physik.

Chem. 81, 356-357 (1912); 92, 737-738 (1917). (19) Delaby, Ann. chim. (9) 26, 67-68 (1923). (20) Carré, Mauclere, Bull. soc. chim. (4) 49, 1151-1152 (1931); Compt. rend. 192, 1567-1569 (1931).

- (21) Delaby, Dubois, Bull. soc. chim. (4) 47, 573 (1930). (22) Sen, Barat, J. Indian Chem. Soc. 2, 79-81 (1925). (23) Braun, J. Am. Chem. Soc. 54, 1248-1250 (1932). (24A) Braun, Org. Syntheses, Coll. Vol. 2 (1st ed.) 256-258 (1943); 16, 30-32 (1936). (24B) Clarke, Hartmann, Org. Syntheses, Coll. Vol. 1 (1st ed.) 228-229 (1932); 3, 47-49 (1923). (25) Fairbourne, Gibson, Stephens, J. Chem. Soc. 1932, 1965-1972. (26) Drozdov, Cherntsov, J. Gen. Chem. (U.S.S.R.) 4, 1305-1309 (1936); Cent. 1936, I 4549. (27) Conant, Quayle, Org. Syntheses, Coll. Vol. 1 (2nd ed.) 211-213 (1943); (1st ed.) 206-208 (1932); 2, 13-15 (1922). (28) Aschan, Ber. 23, 1831 (1890). (29) Tornöe, Ber. 24, 2672 (1891). (30) Bert, Dorier, Bull. soc. chim. (4) 33, 1573-1575 (1926).
- (31) Hartenstein, J. prakt. Chem. (2) 7, 310-312 (1873). (32) Fairbourne, Foster, J. Chem. Soc. 1926, 3150-3151. (33) Conant, Quayle, J. Am. Chem. Soc. 45, 2771-2772 (1923). (34) Földi, Ber. 53, 1838-1839 (1920). (35) Földi, Ber. 60, 659-660 (1927). (36) Blanchard, Bull. soc. chim. (4) 41, 832 (1927). (37) Luttringhaus, Nawiasky, Ehrhardt (to I.G.), Ger. 451,122, Oct. 21, 1927; Cent. 1928, I 261. (38) Otto, J. prakt. Chem. (2) 44, 20 (1891). (39) Johnson, Langley, Am. Chem. J. 44, 357 (1910). (40) Malinovskii, J. Gen. Chem. (U.S.S.R.) 9, 832-839 (1939); C.A. 34, 375 (1940).
- (41) Rheinboldt, Tetsch, Ber. 70, 677-678 (1937). (42) Guth, Z. Biol. 44, 99; Beil. IX-112. (43) Fritsch, Ber. 24, 777 (1891). (44) Sabalitschka, Jeglinski, Arch. Pharm. 269, 241 (1931). (45) Sjöberg, Svensk Kem. Tud. 53, 454-457 (1941); Cent. 1942 II 25; C.A. 37, 4363 (1943).

CHAPTER XIV

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 1. D_4^{20} greater than 1.1500

(3:6000-3:6499)

3:6000 n-PROPYL DICHLOROACETATE
$$C_5H_8O_2Cl_2$$
 Beil. II - 204 $n_-C_3H_7.O.CO.CHCl_2$ II $_1$ — II $_2$ -(196)

B.P. 176.7-177° at 771 mm. (1)
$$D_4^{25} = 1.2006$$
 (4) $n_D^{25} = 1.4360$ (4) 176.0 -176.6° (2) $D_4^{20} = 1.2240$ (5) $n_D^{20} = 1.4398$ (5) 176°

[For prepn. (70% yield (3)) from anhydrous chloral (3:5210) in n-propyl alc. by treatment with 1.2 moles powdered KCN see (3); for prepn. (59% yield (4)) from cyclopropane + dichloroacetic ac. (3:6208) + BF₃ see (4).]

3:6600 (1) Schiff, Z. physik Chem. 1, 379 (1887)
(2) Cheng, Z. physik. Chem. B-24, 307 (1934).
(3) Chattaway, Irving, J. Chem. Soc. 1929, 1042.
(4) Dorris, Sowa, J. Am. Chem. Soc. 60, 358 (1938).
(5) Schjanberg, Z. physik. Chem. A-172, 229 (1935).

3:6010
$$\gamma$$
-CHLORO- n -PROPYL CHLOROFORMATE $C_4H_6O_2Cl_2$ Beil. S.N. 199 $(\gamma$ -Chloro- n -propyl chlorocarbonate) CH_2 CH_2 CH_2 CH_2 O -CO Cl

B.P. 177° (1)
$$D_{20}^{25} = 1.2946$$
 (1) $n_{\rm D}^{20} = 1.4456$ (1) 175–176° at 736 mm. (2)

Colorless liq.; insol. in aq. toward which it is relatively stable.

[For prepn. of Č from 3-chloropropanol-1 (trimethylene chlorohydrin) (3:8285) with phosgene (3:5000) in 80% yield see (1) (2).]

 \ddot{C} in quinoline begins to decompose into 1,3-dichloropropane (trimethylene (di)chloride) (3:5450) + CO_2 even at 35° (3) (for discussion see (4)).

 \bar{C} with primary arom. amines reacts as an acyl chloride yielding the corresp. γ -chloro-n-propyl N-arylcarbamates [e.g., \bar{C} with p-aminobenzenearsonic acid (arsanilic acid) gi res (92% yield (5)) γ -chloro-n-propyl N-(p-arsonophenyl)carbamate, m.p. 245-246° (5) cf. (6); for analogous reactions of \bar{C} with o-aminobenzenearsonic acid (5) (6), o-toluidine-5-arsonic acid (5), p-phenetidine (1), p-aminobenzoic acid (1), o-chloroaniline (1), or p-chloroaniline (1) see indic. refs.]; for simpler cases see below.

- —— γ-Chloro-n-propyl N-phenylcarbamate: pr. from alc., m.p. 38° (2), 35–36° (1). [From Č with aniline (2 moles) both diluted with dry ether (3 vols.) slowly mixed in flask surrounded by ice water, ether evaporated and prod. distilled, b.p. 160–170° at 5 mm. (2); this prod. in alc. on addn. of 1 N aq. NaOH ring-closes with loss of HCl giving (84% yield (2)) (1) 3-phenyl-tetrahydro-2-keto-1,3-oxazine, m.p. 96° (2), 94.0–94.5° (1).]
- \bigcirc γ -Chloro-n-propyl N-(o-tolyl)carbamate: ndls. from alc., m.p. 49° (2), 46.0–46.5° (1). [From $\bar{\mathrm{C}}$ with o-toluidine in dry ether as for preceding case (69% yield (2)); this prod. in alc. on addn. of 1 N aq. NaOH ring-closes with loss of HCl giving (60% yield (2)) (1) 3-(o-tolyl)-tetrahydro-2-keto-1,3-oxazine, m.p. 89° (1), 87.0–87.5° (2).]
 - γ -Chloro-n-propyl N-(p-tolyl)carbamate: oil, b.p. 188° at 4.5 mm., $D_{20}^{20} = 1.186$, $n_{D}^{18} = 1.494$ (1). [This prod. with alc. KOH (1 mole) refluxed 2 hrs. ring-closes with loss of HCl giving (1) 3-(p-tolyl)-tetrahydro-2-keto-1,3-dioxazine, m.p. 127.5-128° (1).]
- ① γ -Chloro-n-propyl N'-anilinocarbamate (γ -chloro-n-propyl N-phenylcarbazate): cryst. from C_6H_6 , m.p. 72° (7). [From \tilde{C} with phenylhydrazine (1 mole) in aqueous pyridine (62% yield (7)).]
- 3:8010 (1) Pierce, Adams, J. Am. Chem. Soc. 45, 791-794 (1923). (2) Dox, Yoder, J. Am. Chem. Soc. 45, 725-726 (1923). (3) Carré, Passedouet, Compt. rend. 201, 899 (1935). (4) Carré, Passedouet, Bull. soc. chm. (5) 3, 1073-1082 (1936). (5) Rodewald, Adams, J. Am. Chem. Soc. 45, 3102-3105 (1923). (6) Adams, Rodewald (to Abbott Laboratories), Brit. 255,971, Aug. 26. 1926, Cent. 1927, I 1744; C.A. 21, 2908 (1927) Cam. 254,983, Oct. 27, 1925; Cent. 1927, I 1744; C.A. 20, 424 (1926). (7) Dox, J. Am. Chem. Soc. 48, 1952 (1926).

3:6025
$$\beta,\beta'$$
-DICHLORODIETHYL ETHER $C_4H_8OCl_2$ Beil. I — (bis-(β -Chloroethyl) ether; ClCH $_2$ CH $_2$ O I_1 — I_2 -(335)

B.P. 177-178° cor. (1) M.P.
$$-24.5^{\circ}$$
 (2) $D_4^{20} = 1.2095$ (3) $n_D^{20} = 1.457$ (1) $80-82^{\circ}$ at $20-22$ mm. (3) $D_{20}^{20} = 1.213$ (1) 70° at 15 mm. (2) 66° at 12 mm. (2)

Colorless oil with pleasant ethereal odor. — [For data on surface tension and parachor see (4); for vapor-press. data see (5).]

[For prepn. from ethylene chlorohydrin (3:5552) see (1); for use in prepn. of di-(θ -chloroethyl) sulfate see (12).] [Note that \bar{C} forms with ethylene chlorohydrin (3:5552) a constboilg. mixt., b.p. 128.2°, contg. 8.2 mole % \bar{C} (15).]

The halogen atoms of \tilde{C} are very unreactive to most reagents; \tilde{C} is extremely resistant to hydrolysis, gives no Friedel-Crafts reaction with $C_6H_6+AlCl_3$, no reaction with KCN, and is unaffected by NaOH + As₂O₃ (2).

 \tilde{C} on htg. with solid KOH yields (6) (7) (9) (3) divinyl ether (1:7800) (accompanied by some β -chloroethyl vinyl ether (3:7464) q.v.), but \tilde{C} on htg. with dimethylaniline or quinoline fails to react at all, even to form quaternary salts (6).

 \tilde{C} on htg. with excess sodium alcoholates for 3-15 hrs. gives 36-45% yields of the corresponding liquid bis ethers (8); \tilde{C} in alc. refluxed overnight with an excess of Na phenolates yields corresponding bis ethers (9); e.g., \tilde{C} with Na α -naphtholate gives 52% yield bis $[\beta(\alpha$ -naphthoxy)ethyl] ether, m.p. 87° (9); \tilde{C} with Na β -naphtholate gives 56% yield bis- $[\beta$ -(β -naphthoxy)ethyl] ether, m.p. 122° (9).

 \tilde{C} on htg. with aniline (3 moles) for 2 hrs. at 200° gives (65% yield (9)) 4-phenylmorpholine, white flakes from 50% alc., m.p. 57-58° (1). [The crude prod. may also cont. bis-(\$\beta\$-anilinoethyl) ether, pl. from alc., m.p. 115.5° (9).] [For similar prepn. (77% yield (9)) of N-(\$p\$-tolyl)morpholine, m.p. 51° (8); N-(\$\alpha\$-naphthyl)morpholine (68% yield (9)), m.p. 83° (8); N-(\$\beta\$-naphthyl)morpholine (72% yield (9)), m.p. 90° (8), see (8) (9).] [For corresp. reaction of \tilde{C} with phenylhydrazine, p-phenylenediamine, and benzidine see (10); with ethylenediamine see (11).]

- $\beta_i \beta'$ -bis-(α -Naphthoxy)diethyl ether: m.p. 87° (16). [From $\ddot{C} + \alpha$ -naphthol (1:1500) + aq. NaOH in s.t. at 120° for 8 hrs. (16).]
- β,β' -bis- $(\beta$ -Naphthoxy)diethyl ether: m.p. 122° (16). [From $\tilde{C} + \beta$ -naphthol (1:1540) + aq. NaOH in s.t. at 120° for 8 hrs. (16).]
- bis-(β-Phthalimidoethyl) ether [Beil. XXI-470]: from C̄ on refluxing 3 hrs. with phthalimide + K₂CO₃ (13) or from C̄ + K phthalimide (2 moles) + trace of diethylamine on htg. 4 hrs. at 135-140° (55% yield) (9), cryst. from alc. (14), ndls. from 50% AcOH (13), m.p. 159° (9), 157° (13), 156.5° (14). [The half reaction prod., β-chloro-β-phthalimidodiethyl ether, ndls. from lt. pet., m.p. 72° (13), 69° (9), may be sepd. from the above bis-ether by its much greater solubility in pet. eth. (13).]
- 3:8025 (1) Kamm, Waldo, J. Am. Chem. Soc. 43, 2223-2227 (1921). (2) Gibson, Johnson, J. Chem. Soc. 1930, 2525-2530. (3) Gulyaeva, Dauguleva, Caoutchouc and Rubber (U.S.S.R.) 1937, No. 1, 49-52, Cent. 1937, II 558; C.A. 32, 3756 (1938). (4) Gallaugher, Hibbert, J. Am. Chem. Soc. 59, 2515 (1937). (5) Gallaugher, Hibbert, J. Am. Chem. Soc. 59, 2523 (1937). (6) Ruigh, Major, J. Am. Chem. Soc. 53, 2662-2271 (1931). (7) Lott, Smith, Christiansen, J. Am. Pharm. Assoc. 26, 203-208 (1937). (8) Cretcher, Pittenger, J. Am. Chem. Soc. 47, 163-166 (1925). (9) Cretcher, Koch, Pittenger, J. Am. Chem. Soc. 47, 1173-1177 (1925) (10) Axe, Freeman, J. Am. Chem. Soc. 56, 478-479 (1934).

(11) Hultquist, Northey, J. Am. Chem. Soc. 62, 447-448 (1940). (12) Suter, Evans, J. Am. Chem. Soc. 60, 536-537 (1938). (13) Baldwin, Robinson, J. Chem. Soc. 1934, 1266. (14) Gabriel, Ber. 38, 3413 (1905). (15) Snyder, Gilbert, Ind. Eng. Chem. 34, 1519-1521 (1942). (16) Dahlen, Black, Foohey (to du Pont Co.), U.S. 1,979,144, Oct. 30, 1934; Cent. 1935, I 3051; [C.A. 29, 177 (1935)].

3:6035 1,1,2,3-TETRACHLOROPROPANE H
$$C_3H_4Cl_4$$
 Beil. I - 107 $ClCH_2$ — C — $CHCl_2$ I_1 — I_2 — I_3 — I_4 — I_5 — I_5 —1.522 (1) 179° (3)

[For prepn. of \bar{C} from 1,2,3-trichloropropane (3:5840) + SbCl₅ at 150-190° see (2); from 1,1,2-trichloropropane (3:5630) + Cl₂ + AlCl₃ see (3); from 1,3-dichloropropene-1 (3:5280) + Cl₂ see (4); from 3,3-dichloropropene-1 (3:5140) + Cl₂ see (1); from ordinary 1,2-dichloroethylene (3:5030) with CH₂Cl₂ (3:5020) + AlCl₃ at 40° for 8 hrs. (24% yield) see (5).

3:6035 (1) Romburgh, Bull. soc. chim. (2) 36, 553-557 (1881). (2) Herzfelder, Ber. 26, 2435 (1893). (3) Mouneyrat, Bull. soc. chim. (3) 21, 621-623 (1899). (4) Hartenstein, J. prakt. Chem. (2) 7, 312-313 (1873). (5) Lehmann, Bayer (to I.G.), Ger. 715,069, Dec. 16, 1941; Cent. 1942, I 2584; C.A. 38, 2051 (1944).

B.P. 180-182° cor. at 718 mm. (1) 179-181° (3)

[See also 1,1,1,3-tetrachloropropanone-2 (unsym.-tetrachloroacetone) (3:6085).]

Colorless liq. with penetrating odor; produces blisters on skin. — Eas. sol. cold aq., alc., ether, C_6H_6 .

Č with aq. readily yields a crystn. tetrahydrate, m.p. $48-49^{\circ}$ (1) (6), 48° (2), $47-48^{\circ}$ (3) (4) (for crystallographic data see (2), for polymorphism see (5)); this tetrahydrate loses its aq. on distn., on stdg. over H_2SO_4 , or by actn. of dry HCl gas.

[For prepn. of C from phloroglucinol (1:1620) via conversion in AcOH with Cl₂ to 1,1,-3,3,6,6-hexachloro-2,4,6-triketocyclohexane ("hexachlorophloroglucinol") [Beil. VII-854, VII₁-(469)], and treatment of latter with water (yield is almost quant.) (dichloroacetic acid (3:6208) is also formed) see (6); from 2,4,6-triaminophenol [Beil. XIII-569, XIII₁-(211)] (2), from chloroanilic acid (3:4970) (1) (7), from 3,3,5-trichlorocyclopentanetrione-1,2,4 [Beil. VII-852] (4), or from 2,2,5-trichlorocyclopentanedione-3,4-ol-1-carboxylic acid-1 [Beil. X-985] (4) by oxidn. with KClO₃ + HCl (other by-products are also formed and yield is low, e.g., 7% (7)) see indic. refs.; for formn. of C from isopropyl alc. (1:6135) with Cl₂ (8), from chloroacetone (3:5425) with Cl₂ at 50-70° in light (9), or from 1,1-dibromo-3,3-dichloropropanone-2 [Beil. I-658] with alc. HgCl₂ in s.t. at 100° for several hours (3) see indic. refs.]

[\tilde{C} (as tetrahydrate) on reduction with Zn + H₂SO₄ yields (1) acetone (1:5400); \tilde{C} on reduction with Al(OEt)₃, Mg(OEt)₂, or EtOMgCl yields (10) 1,1,3,3-tetrachloropropanol-2 (3:9037).]

C with satd. aq. NaHSO3 readily yields a NaHSO3 cpd. (3).

Č with aq. alk. does not (3) yield chloroform; Č with alk. + aniline does not (3) give phenylisocyanide (carbylamine test). [Dif. from the isomeric unsym.-tetrachloroacetone (3:6085).]

 \bar{C} in abs. ether with dry NH₃ gas adds 1 NH₃ giving (92% yield (2)) 1,1,3,3-tetrachloro-2-aminopropanol-2 [Beil. I-656], ndls. from C₆H₆, m.p. 110-111° dec. with prev. sublimation; this prod. is eas. sol. in cold aq. but on warming the soln. dissociates into its components. — [The action of \bar{C} with aq. NH₄OH or with aniline has not been clarified cf. (3).]

[\bar{C} with excess conc. aq. HCN warmed at 50-60° soon dissolves and after 12 hrs. warming (2) ppts. $\beta,\beta,\beta',\beta'$ -tetrachloro- α -hydroxyisobutyronitrile [Beil. III-318], cryst. from C₆H₆, m.p. 112-114° (2); this prod. with AcOH/H₂SO₄ as directed (2) yields the corresp. $\beta,\beta,\beta',\beta'$ -tetrachloro- α -hydroxyisobutyramide, cryst. from C₆H₆, m.p. 156° (2).]

C with PCl₅ on htg. gives (2) mainly 1,1,2,2,3,3-hexachloropropane (3:6525) accompanied by some 1,1,2,3,3-pentachloropropene-1 (3:6075).

[\tilde{C} with diazotized aniline (4 moles) in pres. of NaOAc yields (11) dichloro-bis-(benzene-azo)methane, yel.-or. cryst. from hot alc., m.p. $81-82^{\circ}$ (11); \tilde{C} with diazotized p-toluidine (4 moles) in pres. of NaOAc yields (11) dichloro-bis-(p-tolueneazo)methane, orange cryst. from C_0H_6 , m.p. $159-160^{\circ}$ (11).] [These prods. are also similarly obtd. (11) from unsymdichloroacetone (3:6085).]

4-(Benzeneazo)-1-phenylpyrazole [Beil. XXV-535]: golden-yel. lfts. from dil. alc. or lgr., ndls. from AcOH, m.p. 126-127° cor. (2), 126° (6). [From Č in abs. alc. (2) or AcOH (6) with excess phenylhydrazine, refluxed for 5 min.]

3:8050 (1) Levy, Jedlicka, Ann. 249, 89-95 (1888). (2) Levy, Curchod, Ann. 252, 330-349 (1889). (3) Cloëz, Ann. chim. (6) 9, 182-186 (1886). (4) Hantzsch, Ber. 21, 2438 (1888). (5) Schaum, Schalling, Klausing, Ann. 411, 192 (1916). (6) Zincke, Kegel, Ber. 22, 1467-1477; 1478-1482 (1889). (7) Levy, Witte, Ann. 254, 86-88 (1889). (8) Buc (to Standard Oil Co.), U.S. 1,391,757, Sept. 27, 1921; Cent. 1922, IV 942. (9) I.G., French 816,956, Aug. 21, 1937; Cent. 1938, I 2216. (10) Meerwein, von Bock, Kirschnick, Lenz, Migge, J. prakt. Chem. (2) 147, 212, 225 (1936).

(11) Favrel, Bull. soc. chim. (5) 1, 988-989 (1934).

3:6055 o-DICHLOROBENZENE C|
$$C_6H_4Cl_2$$
 Bell. V - 201 $V_{1^-}(111)$ $V_{2^-}(153)$

B.P. F.P. 180.3° at 760 mm. (1) -16.7° (1) $D_4^{25} = 1.2965$ (3) 1.2934 (13) 180.2° at 757.4 mm. (1) -17.5° (10) $n_D^{25} = 1.5486$ (2) 1.5476 (13) 179-181° at 755 mm. (3) $n_D^{20} = 1.5518$ (1) 179.9-180.6° (4) -17.6° (10) $D_4^{20} = 1.3048$ (12) 179.5° at 745.2 mm. (1) $D_4^{20} = 1.3048$ (12) 179.5° at 745.2 mm. (1) $D_4^{20} = 1.5513$ (2) 1.549 (14) 179° cor. (7) $D_4^{20} = 1.5532$ (10) 178° at 762.5 mm. (8) 1.5524 (12) 178° at 758 mm. (8a) $D_4^{15} = 1.3104$ (12) 86° at 18 mm. (8) $D_4^{15} = 1.3104$ (12) $D_2^{20} = 1.3085$ (14) $D_{15}^{15} = 1.3112$ (1)

 \bar{C} when pure is colorless oil, volatile with steam. — Ord. comml. \bar{C} conts. also the isomeric p-dichlorobenzene (3:0980), even as much as 25% (16); and a comml. prod. sold as insecticide conts. 40% \bar{C} + 30% p-dichlorobenzene (3:0980) + 30% trichlorobenzene (17).

[For f.p./compn. data and diagram of system $\bar{C}+p$ -dichlorobenzene (3:0980) (cutectic, m.p. -23.4° , contg. 86.7% \bar{C}) see (10) (11); for f.p./compn. data and diagram of system $\bar{C}+m$ -dichlorobenzene (3:5960) (cutectic, m.p. -45.9° , contg. 48.7% \bar{C}) see (11); for f.p./compn. data on ternary system of all three dichlorobenzenes see (10).]

[For data on densities of solns. of \bar{C} in C_6H_6 (1:6400) and in *n*-hexane (1:8530) see (18); for data on D_{20}^{20} and n_{20}^{20} on system \bar{C} + diethylbenzene (and use of the mixt. in testing fractionating columns) see (19).]

[Č is very spar. sol. aq. (for study of this soly. over range 20-60° see (20).]

[For study and use of \bar{C} as cleaner for metals see (21); for use as solvent for fats and oils (16) and for detn. of oils in seeds (by use of density of resultant extract (22) see indic. refs.; for use for removal of tar or pitch from surfaces coated with cellulose esters see (23); for use as solv. in purification of anthraquinone see (24); for study of toxicity of \bar{C} see (25).]

[For prepn. of Č from o-chloroaniline [Beil. XII-597, XII₁-(297)] via diazotization and use of Cu₂Cl₂ reactn. (yields: 70% (26), 25% (27)) (1) (8) (28) see indic. refs.; from o-phenylenediamine [Beil. XIII-6, XIII₁-(5)] via tetrazotization in AcOH with nitrosylsulfuric acid followed by use of Cu₂Cl₂ reactn. (70.1% yield) see (29); from 1,2-dichlorobenzenesulfonic acid-4 (see below) by distn. from strong H₂SO₄ with superheated steam at 200-240° see (30).]

[For formn. of $\bar{\mathbf{C}}$ from 2-chlorophenol (3:5980) by htg. with PCl₅ (20% yield) see (7); from o-bromonitrobenzene [Beil. V-247, V₁-(131)] with PCl₅ in s.t. at 180° (31) or with NH₄Cl in s.t. at 320° (32) see indic. refs.; from o-dinitrobenzene [Beil. V-257, V₁-(135)] with conc. HCl in s.t. at 250-270° see (33).]

[For formn. of $\bar{\mathbf{C}}$ (together with m- and p-isomers in some cases) from $\mathbf{C}_0\mathbf{H}_0$ with \mathbf{Cl}_2 in pres. of \mathbf{I}_2 (7), AlCl₃ (34) (35), or SnCl₄ (36) see indic. refs.; from chlorobenzene (3:7903) with \mathbf{Cl}_2 + cat. at 600° (11) cf. (37) or with \mathbf{Cl}_2 in pres. of Al/Hg (38), AlCl₃ (gives 30% $\bar{\mathbf{C}}$ (11)) (34), FeCl₃ (gives 39% $\bar{\mathbf{C}}$ (11)), or with $\mathbf{Al}_2\mathbf{S}_2\mathbf{Cl}_3$ (i.e., 2AlCl₃ + $\mathbf{S}_2\mathbf{Cl}_2$) + SO₂Cl₂ (8a) see indic. refs.]

[C with Cl₂ in pres. of Al/Hg (38) or FeCl₃ (39) (40) (41) gives mainly 1,2,4-trichlorobenzene (3:6420), but 1,2,3-trichlorobenzene (3:0990) is also formed (41). — C with Cl₂ in s.t. at room temp. in sunlight as directed (42) adds 3Cl₂ yielding o-dichlorobenzene-hexachloride, m.p. 149° (42).] — [For study of photochem. chlorination of C see (43).]

[\bar{C} with Mg in dry ether does not react (44).] — [\bar{C} with CO + cat. at elev. temps. gives (45) benzoic acid, presumably through intermediate forms. of o-phthalic acid and subsequent loss of CO₂.]

[\bar{C} with isopropyl alc. (1:6135) + BF₃ + P₂O₅ under reflux gives (53% yield (87)) 3,4-dichlorocumene (3,4-dichloro-isopropylbenzene) (87).]

[\bar{C} with CH₃Cl (3:7005) + AlCl₃ yields (30) hexamethylbenzene (1:7265) + esotrichloromesitylene (3:8725). — \bar{C} (3+ moles) with CHCl₃ (1 mole) + AlCl₃ without solv. at 55° for 8 hrs. gives (15% yield on the CHCl₃ (46)) tris-(3,4-dichlorophenyl)methane, white pl., m.p. 160.5-162° (46). — \bar{C} with CCl₄ + AlCl₃ presumably yields 3,4,3',4'-tetrachlorobenzophenone dichloride (not isolated) since the reaction prod. with 95% alc. (46) or AcOH/H₂SO₄ (47) gives 3,4,3',4'-tetrachlorobenzophenone, cryst. from hot alc. or hot acetone, m.p. 141-142° (46), 142° (47) (accompanied in latter case (H₂SO₄) by some 3,4-dichlorobenzoic acid (3:4925), m.p. 203° (47).]

[\bar{C} with acetyl Cl (3:7065) + AlCl₃ gives (yields: 70% (49), 40% (48)) 3,4-dichloro-acetophenone, b.p. 135° at 12 mm. (48), m.p. 76° (48), 74° (49) (corresp. oxime, m.p. 107° (50)). — \bar{C} with chloroacetyl chloride (3:5235) + AlCl₃ gives (50) (85) 3,4-dichloro-phenacyl chloride (3,4, ω -trichloroacetophenone), m.p. 43° (50), 44° (85). — \bar{C} with β -chloro-n-butyric acid (3:0035) + AlCl₃ or cone. H₂SO₄ yields (51) by condens. and subsequent ring closure a mixt. of x,y-dichloro-3-methylindanone-1 cpds.]

[C with phthalic anhydride (1:0725) + AlCl₃ gives (yields: 80% (5), 73% (52) (53), 35% (54)) (55) o-(3,4-dichlorobenzoyl)benzoic acid, m.p. 194.5° cor. (54), 192.5° (5), 191.2° cor. (52), 190° (55); this prod. on ring closure with conc. H₂SO₄ gives a mixt. of two dichloroanthraquinones consisting of 87% (54) (5) 2,3-dichloroanthraquinone [Beil. VII₁-(413)], m.p. 271° cor. (54), 268° (5), and 13% (54) (5) 1,2-dichloroanthraquinone [Beil. VII₁-(411)], m.p. 196.5° cor. (54), 194.5° (5). Note that C reacts with phthalic anhydride much more readily than p-dichlorobenzene (3:0980); after making reactn. mixt. alk. any p-dichlorobenzene (as from use of crude \tilde{C}) may be distilled out with steam (use in sepn. of p-dichlorobenzene from C (86)); note also the claim (86) that under certain conditions C with phthalic anhydride + AlCl₃ is claimed to replace 1 chlorine atom by hydrogen so that an o-(x-chlorobenzoyl) benzoic acid results which on ring closure with 100% H₂SO₄ gives 80% yield 2-chloroanthraquinone (3:4922). — C with 4,5-dichlorophthalic anhydride (3:4830) + AlCl₃ gives (80% yield (56)) 2-(3,4-dichlorobenzoyl)4,5dichlorobenzoic acid, cryst. from C₆H₆, m.p. 183° (56); this prod. with conc. H₂SO₄ ringcloses giving mainly 2,3,6,7-tetrachloroanthraquinone, m.p. 348° (56), accompanied by a little 1,2,6,7-tetrachloroanthraquinone, m.p. 242° (56).]

[Č on partial hydrol. with aq. MeOH alk., alk. carbonates, or best alk. earths in pres. of Cu or Cu salts at elevated temps. under press. gives in excellent yields (57) (58) (59) (60)

(61) (62) (63) (64) (65) o-chlorophenol (3:5980) (some phenol (1:1420) is also formed (62)); if the hydrolysis of \tilde{C} is carried further, especially by use of aq. alk. in pres. of Ba or Sr salts and a reducing agt. (66), pyrocatechol (1:1520) is obtd. cf. (59) (61) (64).] — [For study of kinetics of reactn. of \tilde{C} with NaOMe/MeOH at 175° see (67) (68) (69).]

 $[\bar{C}$ with anhyd. NH₃ in alc. in pres. of CuCl₂ + Cu at 200° under press. yields (70) o-chloroaniline; \bar{C} with conc. aq. NH₄OH in pres. of CuO under press. at 150-200° (71) (72) or with Na in liq. NH₃ (73) gives o-phenylenediamine.] — $[\bar{C}$ with K diphenylamine gives by rearr. on htg. (74) (75) N,N,N',N'-tetraphenyl-m-phenylenediamine [Beil. XIII-42], m.p. 137.5-138° (74) (75).]

[\bar{C} on mononitration, e.g., at 0° with a mixt. of HNO₃ (D=1.52) + conc. H₂SO₄ (75) cf. (15) (4), gives (yields: 95% (15), 67% (75)) (7) (8) (76) mainly 1,2-dichloro-4-nitro-benzene [Beil. V-246, V₁-(131)], cryst. from alc., m.p. 43° (7) (8), 42.5° (4) (reactn. prod. with piperidine is 2-chloro-4-nitropiperidinobenzene, m.p. 47-48° (78)), accompanied by a little (5.2% at -30°, 7.2% at 0° (8)) 1,2-dichloro-4,5-dinitrobenzene (see below).] — [The only other possible mononitro-isomer, viz., 1,2-dichloro-3-nitrobenzene [Beil. V-245, V₁-(130)], m.p. 61°, has been obtd. only by indirect means (77) (76) although prob. present (4) in the oil from the main mononitration product.]

[\tilde{C} on dinitration, e.g., with 4 wt. pts. HNO₃ (D=1.52) + 6 wt. pts. conc. H₂SO₄ at 100° for 1 hr. (79) (28) cf. (80) (or the above 1,2-dichloro-4-nitrobenzene with HNO₃ (D=1.5) + fumg. H₂SO₄ (20% SO₃) 2 hrs. at 100° (78), gives 1,2-dichloro-4,5-dinitrobenzene [Beil. V-265], cryst. from dil. AcOH, m.p. 109-110° (78), 110° (28) (79) (reactn. prod. with piperidine is 1,2-dichloro-4-nitro-5-piperidinobenzene, m.p. 62-64° (78), accompanied (28) by a little 1,2-dichloro-3,5-dinitrobenzene [Beil. V₁-(138)], m.p. 56° (28).] – [All the other possible isomeric σ -dichlorodinitro cpds. are known but have been obtd. only by indirect means: 1,2-dichloro-3,4-dinitrobenzene [Beil. V-264], m.p. 53-55°, 1,2-dichloro-3,6-dinitrobenzene, m.p. 60°, and 1,2-dichloro-4,6-dinitrobenzene, m.p. 56°.]

[None of the four possible 1,2-dichloro-trinitrobenzenes appears to have been reported.] [\bar{C} on monosulfonation, e.g., with fumg. H_2SO_4 in s.t. at 210° for 8 hrs. (7), or at room temp. (30), or at 100° (10), or with H_2SO_4 . H_2O + fumg. H_2SO_4 (60% SO_3) in pres. of Hg at 100° for 1 hr. (81), gives mainly 1,2-dichlorobenzenesulfonic acid-4 [Beil. XI-55, XI₁-(16)] (Na salt less sol. aq. (81)) accompanied by a lesser amt. of 1,2-dichlorobenzenesulfonic acid-3 (Na salt more sol. aq. (81)) (some bis-(dichlorobenyl) sulfone, m.p. 173° (30), may also be formed during sulfonation).] — [\bar{C} sulfonates much more readily than p-dichlorobenzene (3:0980); for use in sepn. see (7) (30); for removal of chlorobenzene from mixt. with dichlorobenzenes via sulfonation of former with 95% H_2SO_4 see (11).]

₱ 1,2-Dichlorobenzenesulfonamide-4 (3,4-dichlorobenzenesulfonamide-1): cryst. from dil. alc., m.p. 134-135° u.c. (83). [From C by treatment as directed (83) with ClSO₂H followed by conv. of the intermediate 1,2-dichlorobenzenesulfonyl chloride-4, m.p. 18-19° (83), with (NH₄)₂CO₃ to the desired sulfonamide.] — [For formn. of 3,4-dichlorobenzenesulfonyl chloride with ClSO₃H and use in sepn. of C̄ from p-dichlorobenzene see (82); for prepn. of the sulfonamide and use as plasticizer see (84).]

3:6055 (1) Carswell, Ind. Eng. Chem. 20, 728 (1928). (2) Hurdis, Smyth, J. Am. Chem. Soc. 64, 2213 (1942). (3) Groves, Sugden, J. Chem. Soc. 1937, 1783. (4) Ruhoff, J. Am. Chem. Soc. 55, 3470-3471 (1933). (5) Groggins, Newton, Ind. Eng. Chem. 25, 1030-1033 (1933). (6) Dadieu, Pongratz, Kohlrausch, Monatsh. 61, 431 (1932). (7) Beilstein, Kurbatow, Ann. 176, 40-43 (1875); 182, 94-95 (1876). (8) Holleman, Reiding, Rec. trav. chim. 23, 358-359, 370-379 (1904). (8a) Silberrad, J. Chem. Soc. 121, 1019 (1922). (9) Bergmann, Engel, Sandor, Z. physik. Chem. B-10, 117 (1930). (10) Holleman, van der Linden, Rec. trav. chim. 30, 315-334 (1911).

(11) Wibaut, van de Lande, Wallagh, Rec. trav. chim. **56**, 65-70 (1937). (12) Narbutt, Ber. **52**, 1030-1031, 1034 (1919). (13) Philip, J. Chem. Soc. **101**, 1868 (1912). (14) von Auwers, Ann. **422**, 164, 168 (1921). (15) McMaster, Magill, J. Am. Chem. Soc. **50**, 3038-3041 (1928). (16)

Ehrlich, Oil & Fat Industries 8, No. 1, 19-20 (1931); C.A. 25, 1401 (1931). (17) Lipp, J. Econ. Entomol. 22, 268 (1929); C.A. 23, 3294 (1929). (18) Smyth, Morgan, Boyce, J. Am. Chem. Soc. 59, 1542 (1928). (19) Bragg, Richards, Ind. Eng. Chem. 34, 1088-1091 (1942). (20) Klemenc, Löw, Rec. trav. chrm. 49, 637 (1930).

(21) Groggins, Scholl, Ind. Eng. Chem. 19, 1029-1030 (1927). (22) Schwarz, Oil & Fat Industries 7, 335-336, 347 (1930); C.A. 24, 5519 (1930). (23) Soc. Chem. Ind. Basel, Flench 42,825, Nov. 4, 1933; Cent. 1934, I 1580. (24) Lewis (to National Aniline Co.), U.S. 1,429,514, Sept. 19, 1922; Cent. 1924, I 2824. (25) Cameron, Thomas, et al., J. Path. Bact. 44, 281-296 (1937); C.A. 31, 4399 (1937). (26) Haeussermann, Ber. 33, 939, Note (1900). (27) Haeussermann, Ber. 32, 1914-1915 (1899). (28) Holleman, Rec. trav. chim. 39, 446, 450-452 (1920). (29) Hodgson, Walker, J. Chem. Soc. 1935, 530. (30) Friedel, Crafts, Ann. chim. (6) 10, 413-424 (1887).

(31) Schmidt, Wagner, Ann. 387, 164-165 (1911). (32) Schmidt, Ladner, Bcr. 37, 4403-4404 (1904). (33) Lobry de Bruyn, van Leent, Rec. trav. chim. 15, 86 (1896). (34) Mouneyrat, Pouret, Compt. rend. 127, 1027 (1898). (35) Meunier, Bull. soc. chim. (4) 27, 696-697 (1920). (36) Marcs (to Monsanto Chem. Co.), U.S. 2,111,866, March 22, 1938, Cent. 1938, I 4719. (37) Imperial Chem. Ind. & Wheeler, Brit. 388,818, March 30, 1933; Cent. 1933, I 4037. (38) Cohen, Hartley, J. Chem. Soc. 87, 1361-1364 (1905). (39) Zil'bermann, Slobodnik, J. Applied Chem. (U.S.S.R.) 10, 1080-1085 (1937); Cent. 1938, II 1580; C.A. 32, 1664 (1938). (40) Slobodnik, Zil'bermann, Russ. 48,285, Aug. 31, 1936; Cent. 1937, II 288.

(41) Britton (to Dow Chem. Co.), U.S. 1,923,419, Aug. 22, 1933; Cent. 1933, II 3049; C.A. 27, 5086 (1933). (42) van der Linden, Ber. 45, 414-415 (1912). (43) Fisk, Noyes, J. Am. Chem. Soc. 58, 1707-1714 (1936). (44) E. L. St. John, N. B. St. John, Rec. trav. chrm. 55, 587 (1936). (45) Dieterle, Eschenbach, Arch. Pharm. 265, 192-193 (1927). (46) Wilson, Cheng, J. Org. Chem. 5, 223-226 (1940). (47) Böeseken, Rec. trav. chim. 27, 9 (1908). (48) Roberts, Turner, J. Chem. Soc. 1927, 1855. (49) Florence, Bull. sci. pharmacol. 40, 325-336 (1933); Cent. 1933, II 2123; C.A. 27, 4225 (1933). (50) Jastrzebski, Suszko, Roczniki Chem. 13, 293-297 (1933); Cent. 1933, II 1516; C.A. 27, 4531 (1933).

(51) I.G., Swiss, 126,404, June 16, 1928; 127,692-127,703, Sept. 1, 1928; 128,366, Oct. 16, 1928; Cent. 1929, I 1271-1272. (52) Phillips, J. Am. Chem. Soc. 49, 474-478 (1927). (53) Phillips, J. Am. Chem. Soc. 49, 2334 (1927). (54) Fierz-David, J. Am. Chem. Soc. 49, 2334 (1927). (55) M. Tanaka, N. Tanaka, Bull. Chem. Soc. Japan 3, 286-287 (1928); Cent. 1929, I 752, C.A. 23, 1408 (1929). (56) Barnett, Goodway, Watson, Ber. 66, 1884-1885 (1933). (57) Chemische Werke Ichendorf, Ger. 281,175, Dec. 15, 1914; Cent. 1915, I 180. (58) Boehringer und Söhne, Ger. 284,533, May 29, 1915; Cent. 1915, II 168. (59) Boehringer und Sohne, Ger. 286,266, July 30, 1915; Cent. 1915, II 566. (60) Lloyd. Kennedy, U.S. 1,849,844, March 15, 1932; Cent.

1932, I 2994.

(61) Vorozhtzov, Karlash, Russ. 30,690, June 30, 1933; Cent. 1934, I 767. (62) Vorozhtzov, Karlash, Compt. rend. acad. sci. U.R.S. 1933, 221-223; Cent. 1935, I 55; C.A. 28, 1991 (1934). (63) Bertsch (to Monsanto Chem. Co.), U.S. 1,966,281, July 10, 1934; Cent. 1935, I 959; C.A. 28, 5471 (1934). (64) Kiprianov, Ssytsch, Ukraine Chem. J. 7 (Wiss. Teil), 94-100 (1932); Cent. 1933, II 1339. (65) Lofton, Burroughs (to Pennsylvania Coal Prod Co.), U.S. 2,126,648, Aug. 9, 1938; Cent. 1938, II 3006; C.A. 32, 7925 (1938). (66) Downing, Clarkson (to du Pont Co.), U.S. 1,969,732, 1,970,363, Aug. 14, 1934; Cent. 1935, I 792-793; C.A. 28, 6160 (1934). (67) Holleman, de Mooy, Rec. trav. chim. 35, 27-28 (1915). (68) Holleman, Rec. trav. chim. 37, 203 (1917). (69) Clark, Crozier, Trans. Roy. Soc. Can., (3) 19, III, 153-154 (1925); Cent. 1926, C.A. 20, 388 (1926). (70) Hale, Cheney (to Dow Chem. Co.), U.S. 1,729,775, Oct. 1, 1929; Cent. 1930, I 2007; C.A. 23, 5474 (1929).

(71) Williams (to Dow Chem. Co.), U.S. 1,775,360, Sept. 9, 1930; Cent. 1931, II 1195. (72) Federal Phosphorus Co., Brit. 370,774, May 5, 1932; Cent. 1932, II 1237. (73) Kraus, White, J. Am. Chem. Soc. 45, 774 (1923). (74) Haeussermann, Bauer, Ber. 32, 1914-1915 (1899); Haeussermann, Ber. 33, 939-941 (1900); Ber. 34, 38-40 (1901). (75) Hodgson, Kershaw, J. Chem. Soc. 1929, 2922. (76) Kiprianov, Mikhailenko, Ukrain. Khem. Zhur. 5, Tech. Part, 225-239 (1930); Cent. 1931, II 425; C.A. 25, 5033 (1931). (77) Kremer, Bendich, J. Am. Chem. Soc. 61, 2659-2660 (1939). (78) LeFevre, Turner, J. Chem. Soc. 1927, 1117, 1119. (79) Blanksman, Rec. tran. chim. 21, 419 (1902). (80) Hartley, Cohen. J. Chem. Soc. 85, 867 (1904).

ma, Rec. trav. chim. 21, 419 (1902). (80) Hartley, Cohen, J. Chem. Soc. 85, 867 (1904). (81) Lauer, J. prakt. Chem. (2) 138, 89-90 (1933). (82) Imperial Chem. Ind. & Bennet, Brit. 440,205, Jan. 23, 1936; Cent. 1936, I 4367. (83) Huntress, Carten, J. Am. Chem. Soc. 63, 511-514 (1940). (84) Kyrides (to Monsanto Chem. Co.), U.S. 1,993,722, March 5, 1935; Cent. 1935, II 1446; C.A. 29, 2546 (1935). (85) Glynn, Linnell, Quart. J. Pharm. Pharmacol. 5, 480-485 (1932); Cent. 1933, I 605; C.A. 27, 1355 (1933). (86) Dodd, Sprent, & The United Alkali Co., Ltd., Brit. 204,528, Oct. 25, 1923; Cent. 1925, II 1228. (87) Vermillion, Hill, J. Am. Chem. Soc. 67, 2209 (1945).

3:6060 d,l-2,3-DICHLOROPROPANOL-1
$$CH_2Cl$$
 $C_3H_6OCl_2$ Beil. I - 356 (Glycerol α,β -dichlorohydrin; $H-C-Cl$ $I_1-(181)$ alcohol dichloride) CH_2OH

B.P. 182° at 760 mm. (1)
$$D_4^{20} = 1.3534$$
 (5) 182° (2) (3) (8) 179–181° sl. dec. (4) $D_0^{18} = 1.345$ (4) $n_D^{18} = 1.4875$ (4) 81–81.5° at 13.5 mm. (5) 75–77° at 15 mm. (6)

Colorless visc. liq.; spar. sol. cold aq., pet. ether; misc. with alc., ether, acetone, C_6H_6 . [For prepn. of \bar{C} from glycerol (1:6540) (together with other prods.) see (1); for prepn. from allyl alcohol (1:6145) with Cl_2 + aq. (2) (7) (8) (5) (20% yield) or with Cl_2 in CS_2 (40% yield (9)) see indic. refs.; from allyl chloride (3:7035) by addition of HOCl see (10) (11) (12); from the corresp. acetate (β , γ -dichloro-n-propyl acetate) (3:6220) by alcoholysis using MeOH + HCl (33% yield (4)) (6); from vinyl chloride (3:7004) by reactn. with formaldehyde (30% soln.) + HCl + CaCl₂ see (13).]

 \bar{C} with aq. alk. loses HCl yielding (14) 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358). [For studies of kinetics of this loss of HCl with aq. alk. see (15); for use of Ba(OH)₂ hydrol. as means of detn. of \bar{C} in pres. of 1,3-dichloropropanol-2 (" α -dichlorohydrin") (3:5985) see (16).]

Č with sodium phenolate does *not* give the expected 2,3-diphenoxypropanol-1 but instead (4) (presumably by intermediate formation of epichlorohydrin (3:5358)) the isomeric 1,3-diphenoxypropanol-2, [Beil. VI-149, VI₁-(86)], m.p. 79° (4).

 \bar{C} on oxidn. with conc. HNO₃ (D=1.47) yields (12) (17) (6) (18) α,β -dichloropropionic acid (3:0855), m.p. 50°. [\bar{C} on reductn. with P + HI at 180° yields (8) isopropyl iodide + isopropyl chloride.]

[\bar{C} with SOCl₂ at 100° gives (85% yield (19)) bis-(β,γ -dichloro-n-propyl) sulfite, b.p. 175° at 4 mm., D_0^{23} 7 = 1.501, n_D^{23} = 1.509 (19); \bar{C} with SO₂Cl₂ gives (75% yield (19)) 2,3-dichloropropane-sulfonyl chloride-1, b.p. 122-123° at 15 mm., $D_0^{20.5}$ = 1.582, n_D^{23} = 1.457 (19).]

[\bar{C} with PCl₅ yields (7) 1,2,3-trichloropropane (3:5840); \bar{C} with NaCN gives (20) (presumably by formation and subsequent reaction of epichlorohydrin) 25% yield γ -chloro- β -hydroxy-n-butyronitrile; for reactn. of \bar{C} with NH₃ see (21); for reactn. of \bar{C} with Na₂S, NaSH, etc., yielding thioglycerols see (22).]

- —— β,γ-Dichloro-n-propyl acetate: b.p. 192° (see 3:6220). [For general study of kinetics of esterification of C̄ see (3).]
- ---- $\beta_{,\gamma}$ -Dichloro-n-propyl benzoate: oil, b.p. 180-183° at 24 mm. (4).
- \mathfrak{D} β,γ -Dichloro-n-propyl p-nitrobenzoate: m.p. 37-38° (4), 35.5-37° (23). [From $\tilde{\mathbf{C}}$ + p-nitrobenzoyl chloride + pyridine (23).]
- —— $\beta_{,\gamma}$ -Dichloro-n-propyl 3,5-dinitrobenzoate: unreported.
- $\beta_{,\gamma}$ -Dichloro-n-propyl benzenesulfonate: unreported.
- ---- $\beta_{,\gamma}$ -Dichloro-n-propyl p-toluenesulfonate: unreported.
- $\mathfrak{G}_{,\gamma}$ -Dichloro-n-propyl N-phenylcarbamate: cryst. from lgr., m.p. 72-73° (24), 73-74° (25). [From $\ddot{\mathbf{C}}$ + phenyl isocyanate at 90° (24) or indirectly from $\beta_{,\gamma}$ -dichloro-n-propyl chloroformate with aniline (25).]
- Φ $\beta_{\gamma\gamma}$ -Dichloro-n-propyl $N-(\alpha$ -naphthyl)carbamate: ndls. from alc., m.p. 93° (25).

[Prepd. indirectly from β, γ -dichloro-n-propyl chloroformate with α -naphthylamine

① β,γ -Dichloro-n-propyl N-(β -naphthyl)carbamate: lfts. from alc., m.p. 99° (25). [Prepd. indirectly from β, γ -dichloro-n-propyl chloroformate with β -naphthylamine

3:6060 (1) Gibson, J. Soc. Chem. Ind. 50, 949-954; 970-975 (1931). (2) Tollens, Ann. 156, 164-166 (1870). (3) Kailan, Rosenblatt, Monatsh. 68, 109-170 (1936). (4) Delaby, Dubois, 164-166 (1870). (3) Kallan, Rosenblatt, Monatsh. 68, 109-170 (1936). (4) Delaby, Dubois, Bull. soc. chim. (4) 47, 572-573 (1930). (5) Read, Hurst, J. Chem. Soc. 121, 989-999 (1922). (6) Bockemuller, Hoffmann, Ann. 519, 189-190 (1935). (7) Hubner, Müller, Ann. 159, 179-183 (1871). (8) Tornoe, Ber. 24, 2672 (1891). (9) King, Pyman, J. Chem. Soc. 165, 1257 (1914). (10) von Gegerfelt, Ann. 154, 247-249 (1870); Ber. 6, 720-721 (1873). (11) Henry, Ber. 3, 352 (1870). (12) Henry, Ber. 7, 414 (1874). (13) I.G., Brit. 465,467, May 3, 1937; Cent. 1937, II 1445; C.A. 31, 7067; French 812,292, May 4, 1937; Cent. 1937, II

1445; C.A. 32, 952 (1938). (14) Münder, Tollens, Zeit. für Chemie 1871, 252. (15) Smith, Z. physik. Chem. 92, 739-740 (1917); 93, 83-85 (1919). (16) Smith, Z. physik. Chem. 95, 83-88 (1920). (17) Werigo, Melikoff, Ber. 10, 1499-1500 (1877). (18) Koelsch, J. Am. Chem. Soc. 52, 3365 (1930). (19) Levaillant, Compt. rend. 197, 335-337 (1933). (20) Braun, J. Am. Chem. Soc. 52, 3170 (1930).

(21) Lillienfeld, Brit. 390,516, Brit. 390,523, May 4, 1933; French 739,699, Jan. 16, 1933; Cent. 1933, II 1443. (22) Lillienfeld, Brit. 385,980, Feb. 2, 1933, Cent. 1933, II 1928; French 758,359, Jan. 15, 1934; Cent. 1934, I 3653. (23) Conant, Quayle, J. Am. Chem. Soc. 45, 2772 (1923). (24) Johnson, Langley, Am. Chem. J. 44, 360 (1910). (25) Otto, J. prakt. Chem. (2) 44, 21-22 (1891).

3:6075 1,1,2,3,3-PENTACHLOROPROPENE-1 Cl
$$C_3HCl_5$$
 Beil. I - 200 Cl_2C —C.CHCl₂ I_1 -(83) I_2 —B.P. 183° (1) $D_4^{34} = 1.6317$ (1) $n_D^{20} = 1.5313$ (1) 116° at 9 mm. (1)

 $\ddot{C} + Br_2$ in sunlight gives (1) 1,2-dibromo-1,1,2,3,3-pentachloropropane, m.p. 71° (1). Č with powdered KOH in toluene at 100° yields (1) a prod. C₆Cl₈, colorless ndls., m.p. 93-94° (1).

Č shaken with conc. H_2SO_4 , poured onto ice, yields 2,3,3-trichloropropen-2-al-1 $(\alpha,\beta,\beta$ trichloroacrolein) [Beil. I₁-(378)], b.p. 164° (1), m.p. 10° (1). [Oxime, m.p. 101°, converted on fusion into stereoisomer, m.p. 132° (1); phenylhydrazone, yel.-br. ndls., m.p. 97-98° dec. (1).

 \bar{C} with conc. H₂SO₄ for a longer time at 40-50°, poured onto ice, ppts. (1) α,β -dichloroacrylic ac. (3:2265), m.p. 86° (1).

3:6075 (1) Prins, J. prakt. Chem. (2) 89, 419-420 (1914).

3: 6085 1,1,1,3-TETRACHLOROPROPANONE-2
$$C_3H_2OCl_4$$
 Beil. I - 656 (unsym.-Tetrachloroacetone) CH_2 — C — CCl_3 I₁— I₂— B.P. 183° (1) $D_4^{15} = 1.624$ (1) $n_D^{18} = 1.497$ (1) 180–182° (2) 71–72° at 13 mm. (3)

[See also 1,1,3,3-tetrachloropropanone-2 (3:6050).]

Colorless limpid liq.; odor faint by itself but on warming or on dilution with ether shows

lachrymatory props. — \tilde{C} with aq. readily yields (1) (2) (3) (4) a crystn. tetrahydrate, m.p. 46° (1), 39° (2), 65° (3).

[For prepn. of C from isopropyl alc. (propanol-2) (1:6135) with Cl₂ in cold see (1); from acetone (1:5400) with Cl₂ see (2) (4) (5); from chloroacetone (3:5425) with Cl₂ at 50-70° in light see (6); from 1,1,1-trichloropropanone-2 (3:5620) with SOCl₂ at 180° see (3).]

Č reduces NH₄OH/AgNO₃, Fehling's soln., or aq. KMnO₄ instantly in cold (1) but does not give fuchsin-aldehyde test (1).

 $\ddot{\mathbf{C}}$ with NH₄OH (1) yields chloroform (3:5050) and chloroacetamide [Beil. II-199, II₁-(90), II₂-(193)], m.p. 116-117°.

C with aq. KOH yields (1) chloroform (3:5050) together with the salts of both chloroacetic acid (3:1370) and trichloroacetic acid (3:1150). [Dif. from the isomeric sym.tetrachloroacetone (3:6050).]

 $\ddot{\mathbf{C}}$ with aq. KOH + aniline yields (5) phenyl isocyanide (carbylamine reaction). [Dif. from the isomeric sym.-tetrachloroacetone (3:6050).]

3:685 (1) Brochet, Bull. soc. chim. (3) 13, 117-120 (1895); Ann. chim. (7) 10, 134-141 (1897); Compt. rend. 119, 1271 (1894). (2) Cloëz, Ann. chim. (6) 9, 180-182 (1886). (3) Arndt, Amende, Ender, Monatsh. 59, 215 (1932). (4) Bouis, Ann. 64, 316-319 (1848). (5) Bischoff, Ber. 8, 1340-1341 (1875). (6) I.G., French 816,956, Aug. 21, 1937; Cent. 1938, I 2216.

3:6090 ETHYL
$$d$$
, l - α , β -DICHLOROPROPIONATE $C_5H_8O_2Cl_2$ Beil. II - 252 CH_2 — CH — $COOC_2H_5$ II - II_2 — Cl Cl

B.P. 183-184° (1)
$$D_4^{20} = 1.2461$$
 (3) $n_D^{20} = 1.44815$ (3) 182-185° (3) 76-77° at 15 mm, (2)

[For prepn. of \bar{C} from α,β -dichloropropionic acid (3:0855) with abs. EtOH + dry HCl at 0° (74-78% yield (2)) (1) see indic. refs.; from α,β -dichloropropionyl chloride (3:9034) with EtOH see (4) (3) (5).]

 $\ddot{\mathbf{C}}$ is difficult to keep and readily loses HCl (3). — $\ddot{\mathbf{C}}$ on htg. with dimethylaniline, quinoline, or quinaldine at 100° for 10 min. under N₂ loses HCl yielding (4) ethyl α -chloro-acrylate (3:9242).

 \tilde{C} with Ba(OH)₂ both saponifies and loses HCl yielding (5) (6) α -chloroacrylic acid (3:1445), m.p. 65°.

Č reacts easily with alc. KCN, and after boilg. the resulting soln. with KOH yields (7) furnaric acid (1:0895) and d,l-malic acid.

 $\ddot{\mathbf{C}}$ on boilg. with 20% HCl hydrolyzes (4) yielding EtOH (1:6130) and α,β -dichloropropionic acid (3:0855) q.v.

3:6000 (1) Werigo, Melikov, Ber. **10**, 1500 (1877). (2) Yarnall, Wallis, J. Org. Chem. **4**, 287 (1939). (3) Brühl, Ann. **203**, 25 (1880). (4) Marvel, Dec, Cooke, Cowan, J. Am. Chem. Soc. **62**, 3495-3498 (1940). (5) Werigo, Werner, Ann. **170**, 167 (1873). (6) Otto, Beckurts, Ber. **18**, 243 (1885). (7) Werigo, Tanatar, Ann. **174**, 367-372 (1874).

B.P. 183-185° at 762 mm. (1)
$$D_4^{20} = 1.2527$$
 (1) $n_{20}^{20} = 1.4769$ (1) $n_{30}^{20} = 1.4865$ (1) $n_{30}^{20} = 1.4855$ (1) $n_{30}^{20} = 1.4855$ (1) $n_{30}^{20} = 1.4855$ (2) $n_{30}^{20} = 1.4753$ (2)

[For formn. of \bar{C} from 3-chloro-2-methylbutene-1 (3:7300) + Cl_2 + NaHCO₃ at 0° (30% yield \bar{C} + 40% 3-chloro-2-(chloromethyl)butene-1 (3:9210) + 25% 1,3-dichloro-2-methylbutene-2 (3:8170) (2)) or from 2-chloro-2-methylbutane (3:7220) or 2,3-dichloro-2-methylbutane (3:7975) + Cl_2 (1) (together with other prods.) see (1) (2).]

Č on distn. over KOH gives (1) 1,3-dichloro-2-methylbutene-2 (3:8170) + other prods. Č with 2 moles quinoline at 185-225° gives (30% yield (1)) 1-chloro-2-methylbutadiene-1.3 (3:9200).

3:6100 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1116-1132 (1936); Cent. 1937, I 573; C.A. 31, 1003 (1937). (2) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4222; C.A. 33, 4190 (1939).

3:6105 CHLOROFUMARYL (DI)CHLORIDE
$$C_4$$
HO₂Cl₃ Beil. II - 745 Cl—C—CO.Cl II₁-(303) II₂-(640)

(7)
•
(8)
(4)
(4)
-

[See also chloromaleyl (di)chloride (3:6158).]

Pale green oil (2).

[For prepn. of \bar{C} from d_il -tartaric acid (1:0550) or (less advantageously) d-tartaric acid (1:0525) with PCl₅ (large excess) at 100° (yield from d_il -tartaric acid 80% (1), from d-tartaric acid 48% (9)) (10) (11) (12) (3) see indic. refs. (note that care must be taken to ensure removal of all traces of phosphorus chlorides (9)); from acetylenedicarboxylic acid [Beil. II-801, II₁-(317), II₂-(670)] with PCl₅ in AcCl in s.t. shaken at room temp. for 45 hrs. (yield not stated (6)) or with PCl₅ directly (41% yield (5)) see indic. refs.]

[For formn. of \bar{C} to small extent from chloromaleyl (di)chloride (3:6158) on protracted boilg. see (2); for formn. of \bar{C} from succinyl (di)chloride (3:6200) during actn. of Cl_2 see (13); for formn. of \bar{C} (as an inseparable mixt. with BzCl) from dibenzoyl-d-tartaric anhydride with PCl₅ see (14).]

[Č with Cl₂ in pres. of Fe gives (16) dichloromaleyl (di)chloride (3:6197) q.v. — Č with Br₂ in dark does not react, but in direct sunlight for 5 hrs. adds 82% of theoretical amt. yielding (2) α -chloro- α , β -dibromosuccinyl (di)chloride, b.p. 116–118° at 10 mm. (2), which on hydrolysis with aq. gives (2) α -chloro- α , β -dibromosuccinic acid, hydrated pr. from HCl, m.p. 65–75°, which after drying over conc. H₂SO₄ gives anhydrous form, m.p. 139–140° (2).]

[\bar{C} with 3 N EtOH/KOH (large excess) in freezing mixt. loses HCl and hydrolyzes (or vice versa) and after acidification as directed gives K H acetylenedicarboxylate which with aq. at 100° for 1 hr. loses CO₂ giving (39% yield from \bar{C} (12)) propiolic acid [Beil. II-477, II₁-(208), II₂-(449).]

[C with MeOH under reflux yields (13) dimethyl chlorofumarate (3:6582); C with EtOH yields (1) (9) (15) diethyl chlorofumarate (3:6864); note that C reacts with MeOH or with aniline much more rapidly than the isomeric chloromaleyl (di)chloride (3:6158) (for details and graphs see (2)).]

C (1 mole) with chlorofumaric acid (3:4853) (1 mole) at 125° for 1 hr. gives (11) chloromaleic anhydride (3:0280), m.p. 33°.

[Č with AlCl₃ combines yielding a viscous oil, solidifying in freezing mixt. to yel. cryst., m.p. about 50°; this prod. with water regenerates Č but if first htd. at 100° for several hrs. and then treated with aq. gives (85-87% yield (2)) (3) chloromaleyl (di)chloride (3:6158).]

 $\ddot{\mathbf{C}}$ with excess conc. aq. NH₄OH reacts vigorously yielding (1) (11) chlorofumaric acid diamide, ndls. from alc., m.p. 187° (11).

[\tilde{C} in aq. AcOH (1:4) with hydrazine hydrate as directed gives hydrazine salt of N,N-bis (α -chloro- β -carboxyacryloyl)hydrazine (?), m.p. 218° (9); note that \tilde{C} with NH₂.NH₂.H₂O in ether, pet. eth., or AcOH gives only (9) resinous or amorphous yel. prods.]

Č (1 mole) with p-chloroaniline (4 moles) in dry ether reacts vigorously giving mainly (11) chlorofumaro-di-p-chloroanilide, pale yel. ndls. from alc., m.p. 223° (11), accompanied by a little N-(p-chlorophenyl)chloromaleimide, pl. from alc. mother liquor, m.p. 175° (11). Č on hydrolysis with aq. yields chlorofumaric acid (3:4853), m.p. 193°.

3:6165 (1) Perkin, J. Chem. Soc. 53, 695-697, 700 (1888). (2) Ott, Ann. 392, 258-259, 263-264, 278-285 (1912). (3) Dann, Davies, Hambly, Paul, Semmens, J. Chem. Soc. 1933, 15-21. (4) von Auwers, Schmidt, Ber. 46, 481 (1913). (5) Ruggli, Helv. Chrm. Acta 3, 569 (1920). (6) Diels, Thiele, Ber. 71, 1174-1175 (1938). (7) Gladstone, J. Chem. Soc. 59, 293 (1891). (8) von Auwers, Harres, Ber. 62, 1679 (1929). (9) Ruggli, Hartmann, Helv. Chrm. Acta 3, 512-514 (1920). (10) Perkin, Duppa, Ann 115, 105-107 (1860).

(11) Chattaway, Parkes, J. Chem. Soc. 125, 466-468 (1924). (12) Ingold, J. Chem. Soc. 127, 1202-1203 (1925). (13) Kauder, J. prakt. Chem. (2) 31, 24-38 (1885). (14) Zetsche, Hubacher, Helv. Chim. Acta 9, 292-293 (1926). (15) Claus, Ann. 191, 80-93 (1878). (16) Vandevelde, Bull. acad. roy. Belg. (3) 37, 680-700 (1899); Cent. 1900, I 404.

3:6110	DICHLOROACETALDEHYDI		$\mathbf{YDE} \qquad \qquad \mathbf{C_6H_{12}O_2Cl_2}$	Beil. I - 614
	DIETH	YLACETAL	$Cl_2.CH.CH(OC_2H_5)_2$	I ₁ -(328)
	(" Dichloroacetal ")			I ₂ -(677)
B.P. 1	85-186°	(1)	$D_{14}^{14} = 1.1383 \ (6$;)
1	83-184°	(2)		
1	82-184°	(3)	•	•
1	81-184°	(4)		
1	78-181°	at 760 mm. (5)		
6	6-71°	at 12 mm. (5)		

Č undergoes sl. decompn. on stdg. or distn. — [For use as insecticide see (7) (8).] [For prepn. of Č from acetaldehyde diethylacetal (1:0156) by actn. of Cl₂ (37% yield (5)) see (5) (17); from ethyl alcohol (1:6130) by actn. of Cl₂ (yield 75% (1), 40% (10),

Beil. II - 248

0% (5)) see (1) (10) (5) (6) (11); from α,β,β -trichlorodiethyl ether + Zn (78% yield (4)), or abs. alc. (3), or NaOEt (12), or even water (3); from α,β,β,β -tetrachlorodiethyl ether with Zn + abs. alc. (13).]

 \overline{C} on warming with conc. H_2SO_4 (14) (2) or on htg. at 150° with conc. HCl (15) or on htg. with benzoic anhydride + a little conc. H_2SO_4 gives (yield 81% (1), 78% (10), 71% (16)) dichloroacetaldehyde (3:5180), b.p. 90-91°.

 \bar{C} on htg. with alc. NaOH at 160–180° yields (17) glyoxal tetraethylacetal [Beil. I-760], b.p. 180° (17). — \bar{C} with K ter-butylate loses HCl yielding (5) chloroketene diethylacetal, b.p. 166° at 732–740 mm., $D_{15}^{15}=1.0534, n_{D}^{25}=1.4375$ (5).

C with PCl₅ yields (15) α,β,β-trichlorodiethyl ether [Beil. I-615].

3:6125 d,l-α-CHLOROPROPIONIC ACID

3:6110 (1) van de Walle, Bull. soc. chrm. Belg. 28, 308-309 (1914/18). (2) Pinner, Ann. 179, 33-34 (1875). (3) Oddo, Mameli, Gazz. chrm. vtal. 33, II 412-414 (1903). (4) Neher, Fleece, J. Am. Chem. Soc. 48, 2422-2423 (1926). (5) Magnani, McElvain, J. Am. Chem. Soc. 69, 2210-2213 (1938). (6) Lieben, Ann. 104, 114-115 (1857). (7) I.G., French 814,435, June 23, 1937; Cent. 1937, II 3066; C.A. 32, 1390 (1938). (8) Ger. 528,194, June 26, 1931, Cent. 1931, II 1910. (9) Fritsch, Ann. 279, 300 (1894). (10) Böeseken, Tellegen, Plusje, Rec. trav. chrm. 57, 75 (1938). (11) Chattaway, Backeberg, J. Chem. Soc. 125, 1101 (1924). (12) Jacobsen, Ber. 4, 217 (1871). (13) Neher, Foster, J. Am. Chem. Soc. 31, 414 (1909). (14) Paterno, Ann. 149, 373 (1869). (15) Krey, Jahresber. 1876, 475. (16) Wohl, Roth, Ber. 40, 217 (1907). (17) Pinner, Ber. 5, 148-151 (1872).

(2-Chloropropanoic acid)
$$CH_3$$
—CH.COOH II_{1-} (110) II_{2-} (226) II_{2-} (227) II_{2-} (228) II_{2-} (228) II_{2-} (228) II_{2-} (239) II_{2-} (24) II_{2-} (25) II_{2-} (26) II_{2-} (27) II_{2-} (28) II_{2-} (29) II_{2-} (29) II_{2-} (29) II_{2-} (20) $II_$

C₈H₅O₂Cl

Colorless liq. with weak odor suggestive both of acetic acid and butyric acid; misc. with aq. alc. or ether; volatile with steam; blisters skin.

[For prepn. of \bar{C} from propionic acid (1:1025) with Cl_2 (7) (8) or with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 (9) see indic. refs.; from α -chloropropionyl chloride (3:5320) by hydrolysis (1) (10) (11) (12) with water see indic. refs.; from α -chloropropionitrile by hydrolysis with conc. HCl see (5); from 2-chloropropanol-1 (3:7917) (4) or from 3-chlorobutanone-2 (α -chloroethyl methyl ketone) (3:7598) (13) (14) by oxidn. with HNO₃ or other oxidn. agts. see indic. refs.]

[\bar{C} on treatment with Cl₂ as specified (15) yields α,β -dichloropropionic acid (3:0855); \bar{C} with SOCl₂ yields (16) α -chloropropionyl chloride (3:5320), b.p. 111°; \bar{C} on reduction with Zn + HCl yields (10) propionic acid (1:1025) [for study of catalytic hydrogenation of \bar{C} or its salts see (17)]; \bar{C} with SO₃ at 170° yields (18) α -chloro- α -sulfopropionic acid [for reactn. of \bar{C} with sulfites see (2)]; \bar{C} with conc. aq. NH₄OH gives (43-46% yield (19)) d₃l-alanine (α -aminopropionic acid) [for behavior of \bar{C} with liq. NH₃ see (20) (21)].]

 \bar{C} on alk. hydrolysis gives (10) (22) lactic acid (1:0400) [for study of rate of hydrolysis of \bar{C} (23) or its sodium salt (24) see indic. refs.].

[C on htg. with pyridine at 100° loses CO₂ and yields (25) ethylpyridinium chloride.]

Č on conversion to salt, treatment with KCN, and subsequent acidification yields (26) methylmalonic acid, m.p. 132° (has been used for ident. of Č (26)).

 \tilde{C} with o-phenylenediamine in 5 N HCl refluxed 3 hrs. gives (yields: 61-64% (35), 55-60% (36)) 2 (α -chloroethyl)benzimidazole, ndls. from hot C_6H_6 , m.p. 134.7-135.4° cor. (35) 134-135° cor. (36).

- Methyl α -chloropropionate: b.p. 132°. (See 3:7908.)
- Ethyl α-chloropropionate: b.p. 147°. (See 3:8125.)
- Φ α-Chloropropionamide: m.p. 80° (27). [From ethyl α-chloropropionate (3:8125) with conc. aq. NH₄OH (27).]
- α-Chloropropion-anilide: lfts. from lgr., m.p. 92° (28) (9). [From α-chloropropionyl chloride (3:5320) + aniline in CHCl₃ (28).] [Note that the reactn. prod. of this compd. with more aniline, viz., α-anilinopropionanilide [Beil. XII-558], has m.p. 126°.]
- **D** Phenylhydrazine α -chloropropionate: m.p. 95° (30). [From \bar{C} + phenylhydrazine (30).]
- \bigcirc α -Phenoxypropionic acid: ndls. from aq., m.p. 115-116° (31), 115° (32). [From sodium α -chloropropionate + sodium phenolate on htg. and evapn. (33).] [Note that the opt. act. forms of this deriv. melt at 87° (32).]
- 3:6125 (1) Buchanan, Ann. 148, 170 (1868). (2) Backer, von Mels, Rec. trav. chim. 49, 177-194, 363-380 (1930). (3) Burkard, Kahovec, Monatsh. 71, 340 (1938). (4) Henry, Bull. acad. roy. Belg. 1903, 397-431; Cent. 1903, II 486. (5) Michael, Ber. 34, 4049-4050 (1901). (6) Schjanberg, Z. physik. Chem. A-172, 230 (1935). (7) Bass, Burlew (to Dow Chem. Co.), U.S. 1,993,713, March 5, 1935; Cent. 1935, II 1257; C.A. 29, 2550 (1935). (8) Bass (to Dow Chem. Co.), U.S. 2,010,685, Aug. 6, 1935; Cent. 1936, I 880; C.A. 29, 6608 (1935). (9) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940). (10) Ulrich, Ann. 109, 269-271 (1859).
- (11) Mazzara, Gazz. chim. ital. 12, 261 (1882). (12) Lovén, J. prakt. Chem. (2) 29, 367 (1884). (13) DeSimo, Allen (to Shell Development Co.), U.S. 2,051,470, Aug. 18, 1936; Cent. 1936, II 3468; C.A. 30, 6764 (1936). (14) N. V. de Bataafsche Petroleum Maatschappij, Brit. 447,876, May 27, 1936; French, 797,943, May 6, 1936; Cent. 1936, II 866; C.A. 30, 7124 (1936). (15) Röhm, Haas, Ger. 579,654, June 29, 1933; Cent. 1933, II 1587. (16) Leimu, Ber. 70, 1049 (1937). (17) Paal, Müller-Lobeck, Ber. 64, 2143-2147 (1931). (18) Backer, Mook, Bull. soc. chim. (4) 43, 544 (1928). (19) Tobie, Ayres, J. Am. Chem. Soc. 59, 850 (1937). (20) Cheronis, Spitzmueller, J. Org. Chem. 6, 349-375 (1941).
- (21) Sisler, Cheronis, J. Org. Chem. 6, 467-478 (1941). (22) Wichelhaus, Ann. 143, 4-5 (1867). (23) Kailan, Kunze, Monatsh. 71, 386 (1938). (24) Simpson, J. Am. Chem. Soc. 49, 678 (1918). (25) von Walther, Weinhagen, J. prakt. Chem. (2) 96, 53-54 (1917). (26) Bloomfeld, Farmer, J. Chem. Soc. 1932, 2076-2078. (27) Beckurts, Otto, Ber. 9, 1592 (1876). (28) Bischoff, Walden, Ann. 279, 80, 92 (1894). (29) Wolffenstein, Rolle, Ber. 41, 736 (1908). (30) Stempel, Schaffel, J. Am. Chem. Soc. 64, 470-471 (1942).
- (31) Bischoff, Ber. 33, 925-926 (1900). (32) Fourneau, Sandulesco, Bull. soc. chim. (4) 31, 992 (1922). (33) Saarbach, J. prakt. Chem. (2) 21, 152-153 (1880). (34) Vandewijer, Bull. soc. chim. Belg. 45, 255 (1936). (35) Roeder, Day, J. Org. Chem. 6, 31-35 (1941). (36) Skolnik, Miller, Day, J. Am. Chem. Soc. 65, 1856 (1943).

3:6135-3:6150

3:6135 n-PROPYL TRICHLOROACETATE
$$C_5H_7O_2Cl_3$$
 Beil. II - 209 $n^-C_3H_7O.CO.CCl_3$ II_1— II_2 — B.P. 186.9–187.1° (1) $D_4^{20}=1.3221$ (6) $n_D^{20}=1.4501$ (6) 186.5–187° at 763 mm. (2) 1.3213 (5) 1.4507 (5) 187° (3) $D_4^{15}=1.3170$ (4) $n_D^{15}=1.4508$ (4) 117–117.3° at 130 mm. (1) 69° at 10 mm. (4) 65.0–65.5° at 5 mm. (5)

[For prepn. (57% yield (4)) from *n*-propyl alc. (1:6150) + trichloroacetic ac. (3:1150) see (4).]

[For study of chlorination of \bar{C} see (4).]

For study of hydrolysis of C see (5).

3:6135 (1) Cheng, Z. physik. Chem. B-24, 307 (1934). (2) Schiff, Z. physik. Chem. 1, 379 (1887). (3) Clermont, Bull. soc. chrm. (2) 40, 302 (1883). (4) Gayler, Waddle, J. Am. Chem. Soc. 63, 3358-3359 (1942). (5) Palomaa, Salmi, Korte, Ber. 72, 797 (1939). (6) Schjanberg, Z. physik. Chem. A-172, 229 (1935).

3:6140 ISOBUTYL TRICHLOROACETATE
$$C_8H_9O_2Cl_8$$
 Beil. II - 209 (CH₃)₂CH.CH₂.O.CO.CCl₃ II₁— II₂—

B.P.
$$187-189^{\circ}$$
 (1) $D_4^{25} = 1.255$ (2) $n_D^{25} = 1.4456$ (2) $93-94^{\circ}$ at 24 mm. (2) $D_4^{20} = 1.2636$ (3) $n_D^{20} = 1.4483$ (3)

Colorless liq. of agreeable odor (1).

[For prepn. (82-89% yield (2)) from isobutyl alc. (1:6165) + trichloroacetic ac. (3:1150) see (2) (1).]

[For study of chlorination of C see (2).]

3:6140 (1) Judson, Ber. 3, 784 (1870). (2) Waddle, Adkins, J. Am. Chem. Soc. 61, 3361-3364 (1939). (3) Schlanberg, Z. physik. Chem. A-172, 229 (1935).

3:6150 1,2,3,4-TETRACHLOROBUTADIENE-1,3
$$C_4H_2Cl_4$$
 Beil. S.N. 12 (Liquid stereoisomer) $HC = C - C = CH$

$$Cl Cl Cl Cl$$

B.P.
$$188^{\circ}$$
 (1) $D_{15}^{15} = 1.516$ (1) $67-68^{\circ}$ at 10 mm. (1) 43° at 1 mm. (1)

[See also the solid stereoisomer (3:0870), m.p. 50°.]

Colorless strongly refractive liq. with agreeable honey-like odor; on stdg. turns brown and evolves HCl.

[For isolation of \bar{C} from the high-boilg, fractn. resulting in the preparation of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see {1}; for prepn. of \bar{C} from 1,1,2,3,4,4-hexachlorobutane (3:3155) with alc. KOH at room temp. see {1}.

C on saturation with Cl2 yields (1) the liquid stereoisomer of 1,1,2,3,4,4-hexachlorobutene-

2 (3:9046), b.p. 97° at 10 mm. (1). [Note that \tilde{C} does not (1) yield octachlorobutane (3:2000).]

C with Br₂ yields 1,4-dibromo-1,2,3,4-tetrachlorobutene-2, long colorless doubly refracting ndls., m.p. 105° (1).

C does not react with conc. HNO₃, but with fumg. HNO₃ or even with NO₂ gas C reacts vigorously pptg. 1,4-dinitro-1,2,3,4-tetrachlorobutene-2, colorless cryst. from AcOH, m.p. 131° (1). [Note that this prod. cannot be recryst. from alc. since it reacts yielding ethyl nitrite and a yel. viscous oil (1).]

3:6150 (1) Muller, Huther, Ber. 64, 589-600 (1931); C.A. 25, 3956 (1931).

B.P. M.P. 189.3° at 760 mm. (1) 12.7° (1)
$$D_4^{20} = 1.602$$
 (3) $n_D^{20} = 1.5126$ (3) 186.3° at 760 mm. (1) 11-12° (2) 185.2° at 730 mm. (1) $D_4^{18} = 1.6049$ (3) $n_D^{18} = 1.51362$ (3) 104.0-105° at 50 mm. (2) 82.2-82.5° at 26 mm. (3) $D_4^{17} = 1.6044$ (3) $n_D^{17} = 1.51375$ (3) 71.5° at 10 mm. (1)

[See also chlorofumaryl (di)chloride (3:6105).]

Č is generally formulated in the unsymmetrical structure shown above (for discussion see (1) (2)); note, however, that the position of the chlorine atom attached to the carbon bearing the double bond is frankly assumed and may be on the other such carbon.

Note also that \bar{C} appears to exist also in a labile form, m.p. 4.8° (1), which readily changes to the higher-melting (stable) variety; \bar{C} on supercooling and inoculation with the labile form cryst, in the latter.

Č from pet. ether cryst. as needles; Č has disagreeable odor (1) and is far more lachrymatory than the isomeric chlorofumaryl (di)chloride (3:6105) (2).

[For prepn. of \tilde{C} from chlorofumaryl (di)chloride (3:6105) by combination with AlCl₃, htg. at 100° for several hrs., and subsequently decomposing with ice water (yield as high as 85-87% but varies according to nature of AlCl₃ used) see (1) (2).]

[C on hydrogenation in dry ether in pres. of Pt black yields (4) n-butyric acid (1:1035) and other prods.]

[\tilde{C} with AlCl₃ gives a cpd., red-brown ndls., m.p. abt. 100° (1); on htg. at 180-225° this prod. decomposes yielding (1) α,β -dichloroacryloyl chloride (see under 3:2265), b.p. 147.3° at 733 mm., phosgene (3:5000), CO, HCl, and other prods.]

C on protracted boilg. is converted (1) to chlorofumaryl (di)chloride (3:6105).

[Č reacts with MeOH and with aniline much more slowly than the isomeric chlorofumaryl (di)chloride (3:6105) (for details and graphs see (1) cf. (2)).]

3:6158 (1) Ott, Ann. 392, 256-265, 278-285 (1912). (2) Dann, Davies, Hambly, Paul, Semmens, J. Chem. Soc. 1933, 15-21. (3) von Auwers, Schmidt, Ber. 46, 482 (1913). (4) Ott., Ber. 46, 2173-2175 (1913).

3:6162
$$\alpha,\alpha$$
-DICHLOROPROPIONIC ACID Cl $C_3H_4O_2Cl_2$ Beil. II - 250 II_1 — II_2 -(228) Cl_3 —C—COOH II_1 — II_2 -(228) Cl_3 —C C

Colorless liq. — Very eas. sol. aq. or alc.; from aq. solns. can be salted out with NaCl. — Volatile with steam without hydrolysis. — Insol. conc. HCl.

[For prepn. of \bar{C} from corresp. acid chloride, viz., α,α -dichloropropionyl chloride (3:5372), by hydrolysis see (3); from α,α -dichloropropionitrile monomer [Beil. II-251] (1) (4) (19), α,α -dichloropropionitrile dimer [Beil. II-252] (5), or α,α -dichloropropionitrile trimer [Beil. XXVI-38] (6) (7) by hydrolysis with H₂SO₄ see indic. refs.; from α,α -dichloropropionanilide (see below) by hydrolysis with conc. HCl in s.t. at 140° see (2); for formn. of \bar{C} from propionic acid with Cl₂ under certain conditions see (26).]

 \overline{C} is reduced by Zn + dil. H_2SO_4 giving (1) propionic acid (1:1025).

 \bar{C} on keeping gradually splits off some HCl (2). — \bar{C} with alc. KOH on boilg. either loses HCl giving (8) α -chloroacrylic acid (3:1445) or by some obscure mechanism gives (9) cf. (10) (11) β -ethoxyacrylic acid [Beil. III-369], m.p. 110°.

 \bar{C} as a monobasic acid forms corresp. salts; e.g., NH₄ \bar{A} (1); KA.6H₂O (1); Ca \bar{A}_2 .3H₂O (1); Ba \bar{A}_2 .H₂O (1); Zn \bar{A}_2 .H₂O (1) (12); Ag \bar{A}_3 , spar. sol. aq. (1); note that this dry Ag \bar{A}_3 at 60° decomposes violently giving (12) AgCl and a mixed anhydride of \bar{C} with pyruvic acid, viz., CH₃.C(Cl₂).CO.O.CO.CO.CO.H₃; however, Ag \bar{A}_3 on warming with aq. gives (12) AgCl + pyruvic acid (1:1040) and/or (1) α -chloroacrylic acid (3:1445).

 \tilde{C} with aq. Ag₂O or Ag₂CO₃ on protracted htg. gives (13) (12) pyruvic acid (1:1040), but use of excess Ag₂O (14) (1) cf. (15) leads to AcOH (1:1010) + CO₂ + H₂O. — \tilde{C} with aq. Ba (OH)₂ on boilg. or \tilde{C} with aq. in s.t. at 120–150° gives (14) (16) pyruvic acid (1:1040).

[\bar{C} with finely divided Ag in C_6H_6 on refluxing 40–70 hrs. gives (17) (18) (19) α,α' -dimethylmaleic anhydride [Beil. XVII-445], m.p. 95°, and α,α' -dichloro- α,α' -dimethylsuccinic acid [Beil. II-668], m.p. 185°.]

[$\bar{\mathbb{C}}$ (3 moles) with PCl₃ (1 mole) gives (3) (20) α,α -dichloropropionic acid anhydride [Beil. II-251], b.p. 196-200° (20), 190-192° (3). — $\bar{\mathbb{C}}$ (3 moles) with PCl₃ (2 moles) (3) or with SOCl₂ refluxed for 10 hrs. (21) gives α,α -dichloropropionyl chloride (3:5372).

C with alcohols in pres. of dry HCl gives (1) the corresp. esters (see also below).

- Methyl α,α-dichloropropionate: b.p. 144-146° (7), 143-144 u.c. (1). [From C with MeOH + dry HCl (1) (7); for study of kinetics of hydrolysis see (22).]
- Ethyl α,α-dichloropropionate: b.p. 160° (23), 156-157° (1) (6), 83-85° at 53 mm. (2).
 [From C with EtOH + dry HCl (1) or from α,α-dichloropropionyl chloride (3:5372) with EtOH (23); note that this ester with aq. in s.t. at 130° gives (16) (14) undergoes hydrolysis yielding pyruvic acid (1:1040) and ethyl pyruvate (1:3308) or with aq. Ag₂O gives (15) Ag acetate.]
- Φ α,α-Dichloropropionamide: lfts. from dil. alc., m.p. 117-118° (2) (24), 117° (12), 116-117° (3), 116° (23) (5) (20), 115-116° (4) (6) (7). [From ethyl α,α-dichloropropionate (above) (3) (23), from methyl α,α-dichloropropionate (above) (7), or from α,α-dichloropropionyl chloride (3:5372) (3) with conc. aq. NH₄OH.]
- D α.α-Dichloropropion-N-ethylamide: m.p. 51-52° (2). [From C with EtNH₂.]
- α,α-Dichloropropionanilide: m.p. 101° (2). [Reported only by indirect means (2).]
 α,α-Dichloropropion-p-toluidide: m.p. 84-86° (25). [Reported only by indirect means (25).]

3:6162 (1) Beckurts, Otto, Ber. 9, 1876-1881 (1876). (2) von Braun, Jostes, Münch, Ann. 453, 134-135 (1927). (3) Beckurts, Otto, Ber. 11, 386-391 (1878). (4) Beckurts, Otto, Ber. 9, 1593-1594 (1876). (5) Tróger, J. prakt. Chem. (2) 46, 362-363 (1892). (6) Beckurts, Otto, Ber. 10, 263-264 (1877). (7) Otto, Voigt, J. prakt. Chem. (2) 36, 84-85 (1887). (8) Otto, Beckurts, Ber. 18, 241-242 (1885). (9) Otto, Ber. 23, 1108-1110 (1890). (10) Claisen, Ber. 31, 1020 (1898).

(11) Tschitschibabin, J. prakt. Chem. (2) 73, 335 (1906). (12) Beckurts, Otto, Ber. 18, 228-235 (1885). (13) Beckurts, Otto, Ber. 10, 265-266 (1877). (14) Beckurts, Otto, Ber. 10, 2037-2039 (1877). (15) Klimenko, Ber. 7, 1405-1406 (1874). (16) Klimenko, Ber. 5, 477 (1872). (17) Beckurts, Otto, Ber. 10, 1503-1504 (1877). (18) Otto, Beckurts, Ber. 18, 826-830, 836, 847 (1885). (19) Otto, Holst, J. prakt. Chem. (2) 42, 78 (1890). (20) Otto, Holst, J. prakt. Chem. (2) 42, 78 (1890).

(21) Leimu, Ber. 70, 1050 (1937). (22) Burki, Helv. Chim. Acta 1, 244-245 (1918). (23) Klithenko, Ber. 3, 466-467 (1870). (24) Otto, Ann. 132, 183 (1864). (25) Bischoff, Walden, Ann. 279, 93 (1894). (26) Röhm and Haas, A.G., Ger. 579,654, June 29, 1933; Cent. 1933 II 1587; [C.A. 28, 1056 (1934)].

3:6165 1,1,2,3-TETRACHLORO-2-METHYLPROPANE C4H6Cl4 Beil. S.N. 10

B.P. M.P. 190.6-191.3° cor. (1) $D_4^{25} = 1.4393$ (1) $n_D^{20} = 1.4963$ (1)

[For form. of \bar{C} (together with other products) from ter-butyl chloride (3:7045) or from 1,3-dichloro-2-methylpropane (3:7960) + Cl_2 see (1).]

3:6165 (1) Rogers, Nelson, J. Am. Chem. Soc. 58, 1027-1029 (1936).

3:6180 β,β,β -TRICHLORO-ter-BUTYL ACETATE $C_0H_9O_2Cl_3$ Beil. II - 131 ("Acetone-chloroform" acetate; CH_3 II₁- (59) II₂- CCl_3 CCl₃- CCl_3 CCl₄- CCl_3 CCl₅- CCl_5 CCl₆- CCl_5 CCl₇- CCl_5 CCl₈- CCl_5 CCl₈- CCl_5 CCl₈- CCl_5 CCl₉- CCl_5 - CCl_5

B.P. 191° (1) 190–191° (2) 151–152° at 237 mm. (3)

Colorless mobile liq. with agreeable odor (1). Insol. aq.; eas. sol. alc., ether, acetone, $CHCl_3$, C_6H_6 (3). — Volatile with steam (3).

 \bar{C} on boilg. with 3-4 vols. conc. HNO₃ is rapidly hydrolyzed; after boilg. only a few min. addn. of aq. ppts. β,β,β -trichloro-ter-butyl alc. (3:2662), m.p. 78° (3). $[\bar{C}$ hydrolyzes only very slowly (108 hrs.) on boilg. with aq. alone; in pres. of dil. H₂SO₄ hydrolysis is more rapid (7 hrs.) and β,β,β -trichloro-ter-butyl alc. (chloretone) sublimes into condenser (3).

[For prepn. from β,β,β -trichloro-ter-butyl alc. (3:2662) + Ac₂O (1) or Ac₂O + NaOAc (3) see (1) (3).]

3:6180 (1) Willgerodt, Dürr, J. prakt. Chem. (2) 39, 285 (1889). (2) Taffe, Roczniki Farm. 2, 99-107 (1923); Cent. 1924, II 304. (3) Aldrich, J. Am. Chem. Soc. 37, 2720-2723 (1915).

3:6185-3:6195

B.P. 191° at 756 mm. (1)
$$D_{20}^{20} = 1.2505$$
 (1) 105° at 30 mm. (1)

 \bar{C} on distn. tends to decompose into 2-methylbutene-2 (1:8220) + trichloroscetic acid (3:1150) (1).

[For studies on prepn. from 2-methylbutene-2 (1:8220) + trichloroacetic acid (3:1150) see (2) (3) (4) (5) (6); for prepn. (84% yield (1)) from ter-amyl alc. (1:6160) and trichloroacetic ac. (3:1150) see (1).]

3:6185 (1) Liston, Dehn, J. Am. Chem. Soc. 60, 1264-1265 (1938). (2) Timofeev, Andreasov, J. chim. Ukraine 1, 107-110 (1925); C.A. 20, 2820 (1926). (3) Timofeev, Israilevich, Chaskes, J. chim. Ukraine 1, 576-580 (1925); C.A. 20, 2820 (1926). (4) Andreasov, Ukrain. Khem. Zhur. 3, Sci. pt. 209-218 (1928); C.A. 23, 322 (1929); Cent. 1929, I 3084. (5) Andreasov, Ukrain. Khem. Zhur. 3, Sci. pt. 467-470 (1928); C.A. 23, 3207 (1929); Cent. 1929, I 3084. (6) Andreasov, Ukrain. Khem. Zhur. 4, Sci. pt. 89-92 (1929); C.A. 23, 4439 (1929); Cent. 1929. II 2433.

TRICHLOROMETHYL TRICHLOROACETATE Cl₃C.COOCCl₃ Beil. III - 17

B.P. 191-192°

M.P. 34°

 $D_4^{35} = 1.67331$

See 3:0290. Division A: Solids.

3:6195 m-CHLOROANISOLE (m-Chlorophenyl methyl ether)

B.P. 193-194° (1)

$$D_{1}^{12.0} = 1.1759 (4)$$
 $C_{7}H_{7}OCl$

Beil. VI - 185

VI₁-(100)

193° (2) 191–192° at 728 mm. (3)

Oil. — Volatile with steam (3). — Odor like anisole (5). — Sol. alc., ether.

[For prepn. of \bar{C} from m-chlorophenol (3:0255) by htg. with KOH + MeI in MeOH (1) or Me₂SO₄ + alk. (7) see (1) (7); from m-chloroaniline by diazotization and warming with MeOH see (2); from m-aminophenyl methyl ether by diazotization and reactn. with CuCl see (3).]

 \bar{C} on nitration with 1 pt. fumg. HNO₃ (D=1.52) at -10 to $+25^{\circ}$ yields (6) a product, m.p. 81° (6), which may have been an impure form of the trinitro epd., 2,4,6-trinitro-3-chloroanisole, m.p. 86°, obtd. (61% yield (7)) by use of 5 pts. fumg. HNO₃ (D=1.51) + 5 pts. conc. H₂SO₄ at -15° . [The numerous possible mono- and di-nitration products of \bar{C} cannot be discussed here and, in any case, have not been reported by direct nitration of \bar{C} .]

[For a study of the reactn. kinetics of the splitting of C in acid soln. see (8).]

3:6195 (1) Gattermann, Ann. 357, 349 (1907). (2) Cameron, Am. Chem. J. 26, 238 (1898).
 (3) Reverdin, Eckhard, Ber. 32, 2626 (1899). (4) von Auwers, Z. physik. Chem. A-158, 418 (1932). (5) Holleman, Rec. trav. chim. 37, 104 (1918). (6) Reverdin, Phillip. Ber. 38, 3776 (1905); Bull. soc. chim. (3) 33, 1322 (1905). (7) Schlubach, Mergenthaler, Ber. 58, 2734 (1925).
 (8) Ghaswalla, Donnan, J. Chem. Soc. 1936, 1341-1346.

B.P.	unsym.	
192–194° (1)	(B) $D_4^{20} = 1.7091 (2)$	$n_{\rm He}^{20} = 1.51947 (2)$
190° at 743 mm. (2)	sym.	
86-89° at 11 mm. (3)	(A) $D_4^{20} = 1.6723$ (2)	$n_{\rm Hc}^{20} = 1.51572 (2)$

[See also dichloromaleic acid (3:3634) and dichloromaleic anhydride (3:3635).]

Colorless mobile lachrymatory liq. with penetrating camphoraceous odor but *not* fumg. in moist air. — Insol. aq. but volatile with steam without hydrolysis. — Soluble in org. solvents.

Although C has not been separated into the completely pure desmotropic forms (A) and (B), their presence is clearly evidenced (2). The relative proportion of the two forms varies with the age of the sample and other conditions, but the above data on density and refraction indicate the extremes so far realized (for much further detail see (2)).

[For prepn. of ord. \bar{C} (mixt. of (A) and (B)) from succinyl (di)chloride (3:6200) with Cl₂ at 145° in pres. of Fe (81% yield) see (2) (note that some dichloromaleic anhydride (3:3635) is also formed, that in absence of Fe the reactn. is very slow, and that use of I₂ in place of Fe lowers yield of \bar{C} to 54% (2)); from chlorofumaryl (di)chloride (3:6105) with Cl₂ in pres. of Fe see (1); from dichloromaleic anhydride (3:3635) with PCl₅ see (1); from dibromofumaryl (di)chloride [Beil. II₁-(303)] with AlCl₃ at 100° see (3).]

Ord. Č with 60% of its wt. of AlCl₃ spontaneously evolves ht.; after further htg. at 100° and pouring into aq. the ethereal extract yields (2) a prod. which reacts as substantially pure *unsym*. form (B).

Ord. \bar{C} is not affected by ord. treatment with boilg. aq. or boilg. aq. KOH (2), although it is attacked by alc. KOH (1). — \bar{C} on very protracted (168 hrs.) boilg. with aq. slowly dissolves giving (2) an acidic soln. which on extraction with ether followed by drying and evapn. of this solvent gives (80% yield) dichloromaleic anhydride (3:3635).

[For study of rate of reactn. of C with MeOH or with aniline see (2).]

[For condens. of \bar{C} with 1-aminoanthraquinone in prepn. of dyestuffs see (2) (4).]

Ord. \bar{C} (2 g.) in C_6H_6 (150 ml.) treated with 4 moles aniline (3.4 g.) in C_6H_6 (30 ml.) immediately ppts. aniline hydrochloride; after stdg. for $\frac{1}{2}$ hr., then removing this ppt., the filtrate leaves on evapn. a mixt. (m.p. 165-185°; yield 67-83% (2)) of two different dianilides, which can be separated by recrystn. from hot alc.: the dianilide from the sym. dichloride (A) is white, has m.p. 193°, and with alc. KOH is much more slowly hydrolyzed than its isomer and during such hydrolysis shows no transient color; the dianilide from the unsym. dichloride (B) is yellow, has m.p. 170°, and with hot 8% alc. KOH readily hydrolyzes with development of a transient cherry-red coloration. — Note that, although the white dianilide is somewhat more readily sol. in hot alc. than the yellow isomer, it also separates first on slow cooling; note also that on hydrolysis of the anilides with alc. KOH the presence of aniline is readily detected but (presumably because of further attack by the alkali) no dichloromaleic acid can be recovered in either case.

3:6197 (1) Vandevelde, Bull. acad. roy. Belg. (3) **37**, 680-700 (1899); Cent. **1900**, I 404. (2) Leder, J. prakt. Chem. (2) **130**, 255-288 (1931). (3) Ott, Ann. **392**, 271 (1912). (4) Leder, Ger. 558,248, Sept. 3, 1932; Cent. **1932**, II 3789.

Note that \tilde{C} may react in either sym. (above) or unsym. form acc. to circumstances. [For discussion of structure see (1) (5) (7) (9) (10); in the liquid only the sym. form (\tilde{C}) exists (9).] — \tilde{C} is sol. in C_6H_6 , but insol. in pet. ether (7).

[For prepn. of $\bar{\mathbb{C}}$ from succinic acid (1.0530) with PCl₅ (yield: 85% (8) (12)) (13) (14) (4) (5) see indic. refs. (note that neither PCl₃ + ZnCl₂ (8) nor SOCl₂ (16) give $\bar{\mathbb{C}}$); for prepn. of $\bar{\mathbb{C}}$ from succinic anhydride (1.0710) with PCl₅ (4) (6), with PCl₃ + Cl₂ (17), or with SOCl₂ + ZnCl₂ at 200-240° (18) (35) see indic. refs.; for formn. of $\bar{\mathbb{C}}$ from the trimer of β -aldehydopropionic acid with PCl₅ see (19).]

 $[\bar{C} \text{ with } Cl_2$ + Fe at 145° gives (81% yield (20)) dichloromaleyl dichloride (3:6197) cf. (21); \bar{C} with Br₂ yields (22) (23) mixt. of d_{ν} and $meso-\alpha_{\nu}\alpha'$ -dibromosuccinyl dichlorides; \bar{C} with Br₂ + Fe yields (24) dibromomaleic anhydride [Beil. XVII-435, XVII₁-(233)], m.p. 118°.]

[\bar{C} on reduction with Na/Hg + AcOH in ether (25) or with H₂ + Pd (26) (15) gives (54% yield (26)) γ -butyrolactone (1:5070), b.p. 206°.]

[\bar{C} with AlCl₃ + C₆II₆ yields (27) γ , γ -diphenyl- γ -butyrolactone [Beil. XVII-367], m.p. 90° (arising from reactn. of \bar{C} in the *unsym*. form), 1,2-dibenzoylethane [Beil. VII-773, VII₁-(401)], m.p. 144° (arising from reactn. of the *sym*. form), and β -benzoylpropionic acid [Beil. X-696, X₁-(330)], m.p. 116°.]

[\bar{C} on distn. or htg. with succinic acid (1:0530) (30) (31), or on htg. (31) with anhydrous oxalic acid (1:0535) or on protracted boiling with Na in xylene (32), or on htg. with diethyl succinate (1:3756) + $ZnCl_2$ (33), yields succinic anhydride (1:0710), m.p. 120°.]

 \ddot{C} with conc. aq. NH₄OH (7) or with NH₃ gas in C₆H₆ reacts mainly in the *unsym*. form (7) yielding the hygroscopic *unsym*. succindiamide [Beil. XVII-410] with at most 5% of sym.-succindiamide, m.p. 260°; \ddot{C} with aniline in C₆H₆ (7) (34), however, gives 90% yield (7) sym.-succindianilide, m.p. 230°.

[For behavior of C with diethyl sodio-malonate see (35) (36).]

Č on hydrolysis yields succinic acid (1:0530) q.v., m.p. 185°.

3:6200 (1) Ott, Ann. 382, 277 (1912). (2) Perkin, J. Chem. Soc. 53, 563-564 (1888). (3) Dann, Davies, Hambly, Paul, Semmens, J. Chem. Soc. 1933, 18. (4) Vorlander, Ann. 280, 183-184

(1894). (5) Garner, Sugden, J. Chem. Soc. 1927, 2878-2880. (6) von Auwers, Schmidt, Ber. 48, 478 (1913). (7) Morrell, J. Chem. Soc. 105, 1736-1739 (1914). (8) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (9) Martin, Partington, J. Chem. Soc. 1936, 1179-1181. (10) Purvis, Jones, Tasker, J. Chem. Soc. 97, 2289 (1910).

(11) Vorlander, Ber. 30, 2268-2269, Note (1897). (12) Curtius, Hechtenberg, J. prakt. Chem. (2) 105, 302, Note (1923). (13) Gerhardt, Chiosza, Ann. 87, 293-294 (1853). (14) Möller, J. prakt. Chem. (2) 22, 208 (1880). (15) Fröschl, Maier, Monatsh. 59, 264-268 (1932). (16) McMaster, Ahmann, J. Am. Chem. Soc. 50, 146 (1928). (17) Clemmensen, Miller (to Monsanto Chemical Co.), U.S. 1,974,845, Sept. 25, 1934; Cent. 1935, I 960; C.A. 28, 7265 (1934). (18) Kyrides (to Monsanto Chem. Co.), U.S. 1,951,364, March 20, 1934; Cent. 1934, II 333. (19) Carrière, Ann. chim. (9) 17, 91 (1922). (20) Leder, J. prakt. Chem. (2) 130, 269-271 (1931).

(21) Kauder, J. prakt. Chem. (2) 31, 1-36 (1895). (22) Ing, Perkin, J. Chem. Soc. 125, 1815, 1822 (1924). (23) Meyer, Marx, Ber. 41, 2465 (1908). (24) Vandevelde, Bull. acad. roy. Belg. 37, 680-700; Cent. 1900, I 404. (25) Saytzeff, Ann. 171, 261-272 (1874). (26) Fröschl, Danoff, J. prakt. Chem. (2) 144, 222 (1936). (27) Lutz, J. Am. Chem. Soc. 49, 1111 (1927). (28) Borsche, Ann. 526, 17 (1936). (29) Auger, Ann. chim. (6) 22, 312-317 (1891); Bull. soc. chim. (2) 49, 345-348 (1888). (30) Anschutz, Ber. 10, 1883 (1877).

(31) Anschütz, Ann. 226, 6, 16-17 (1884). (32) Pearl, Evans, Dehn, J. Am. Chem. Soc. 60, 2479 (1938). (33) Kyrides, Dvornikoff, J. Am. Chem. Soc. 55, 4630 (1933). (34) Dunlap, Cummer, J. Am. Chem. Soc. 25, 621 (1903). (35) Ruggli, Maeder, Helv. Chim. Acta 26, 1476-1498 (1943); C.A. 38, 2934 (1944). (36) Ruggli, Maeder, Helv. Chim. Acta 26, 1499-1511 (1943); C.A. 38, 2935 (1944).

3:6205 PENTACHLOROPROPANONE-2
$$C_3HOCl_5$$
 Beil. I - 656 (Pentachloroacetone) Cl_2CH —C—CCl₃ I_1 — I_2 —

B.P. F.P. 192° at 753 mm. (1) +2.1° (2) $D_{15}^{15} = 1.69$ (3) 97.5–98.5° at 40 mm. (2) $D_{-}^{14} = 1.576$ (1)

[See also hexachloropropanone-2 (3:6312).]

Colorless oil with odor suggesting chloral (3:5210); slightly sol. cold aq. (aq. at 0° dis. 0.1 vol. \bar{C} (1)) but on warming to 50-60° the soln. becomes turbid. — \bar{C} with aq. at 0° forms (1) (4) a crystn. tetrahydrate, m.p. 15-17° (4), 15° dec. (1). — \bar{C} is volatile with steam.

[For prepn. of \bar{C} from acetone (1:5400) with Cl_2 in sunlight see (1); from chloroacetone (3:5425) with Cl_2 at 50-70° in light see (5) cf. (3); from citric acid (1:0455) in aq. soln. at 100° with Cl_2 see (1); from chloranilic acid (3:4970) in aq. with Cl_2 in pres. of I_2 see (6); from isopropyl alcohol (1:6135) at 65° with Cl_2 see (7); for formn. of \bar{C} from citric acid, gallic acid, quinic acid, salicylic acid, indigo, etc., by distn. with $HCl + KClO_3$ see (4); note that in prepn. of \bar{C} some hexachloroacetone (3:6312) is frequently also obtd.]

 \bar{C} with PCl₅ in s.t. at 180° for 6–8 hrs. yields (8) 1,1,1,2,2,3,3-heptachloropropane (3:0200) b.p. 247–248°, m.p. 30°.

Č with dil. aq. KOH undergoes hydrolytic cleavage yielding (1) (3) chloroform (3:5050) and the K salt of dichloroacetic acid (3:6208).

Č with aniline in dil. AcOH yields (1) (3) chloroform (3:5050) and dichloroacetanilide [Beil. XII-244, XII₁-(193)], cryst. from aq., C₆H₆, or ether/alc., m.p. 117°. — Č with alc. NH₄OH yields (1) chloroform (3:5050) and dichloroacetamide [Beil. II-205, II₁-(92), II₂-(196)], cryst., m.p. 98°.

3:6265 (1) Closs, Ann. chim. (6) 9, 187-194 (1886). (2) Edwards, Evans, Watson, J. Chem. Soc. 1937, 1944-1945. (3) Fritsch, Ber. 26, 598 (1893); Ann. 279, 317-318 (1894). (4) Städeler, Ann. 11, 293-301 (1859). (5) I.G., French 816,956, Aug. 21, 1937; Cent. 1938, I 2216. (6) Levy, Jedlicka, Ann. 249, 87-89 (1888). (7) Buc (to Standard Oil. Co. of N.J.), U.S. 1,391,757, Sept. 27, 1921; Cent. 1932, IV 942. (8) Fritsch, Ann. 297, 314 (1897).

86-89° at 12 mm. (7) 88-89° at 11 mm. (1) 58° at 2.5 mm. (3)

105-110° at

[See also ethyl γ -chloroacetoacetate (3:6375).]

30 mm. (6)

Colorless oil with penetrating odor; vapor is strong lachrymator. — \bar{C} can be preserved for some time but on very long stdg. (several years) decomposes (8) with formn. of oxalic acid (1:0445). — \bar{C} is spar. sol. aq., eas. sol. alc., ether.

[For prepn. of \bar{C} from ethyl acetoacetate (1:1710) with SO₂Cl₂ (yields: 85% (7), 55% (6)) (2) or with Cl₂ in diffused light at room temp. (75% yield (9)) or in gas phase at 76–102° and 7 mm. press. (68% yield (40)) see indic. refs.; from the copper enolate of ethyl acetoacetate in CHCl₃ with Cl₂ (67% yield (10)) cf. (11); from ethyl sodioacetoacetate with *p*-toluenesulfonyl chloride in dry ether or lgr. (12); or from ethyl β -(chlorimino)-*n*-butyrate [Beil. III-656] on distillation with dil. H₂SO₄ (13) see indic. refs.]

[\bar{C} can be further chlorinated: e.g., \bar{C} (1 mole) with SO₂Cl₂ (1 mole) gives (1) (2) ethyl α,α -dichloroacetoacetate [Beil. III-663, III₁-(233), III₂-(427)], b.p. 205-207° at 726 mm., 91° at 11 mm. (1), $D_{16,5}^{16} = 1.293$ (14), $n_{17}^{17} = 1.4492$ (1).]

 \bar{C} on hydrolysis with boilg. dil. H_2SO_4 undergoes ketonic splitting yielding (15) chloro-acetone (3:5425) + CO_2 + EtOH (note that this does not distinguish \bar{C} from ethyl γ -chloro-acetoacetate (3:6375) which yields same prods.)

[\bar{C} with alc. NaOC₂H₅ yields (9) ethyl acetate (1:3015), ethyl α -ethoxyacetoacetate, and traces of ethyl chloroacetate (3:5700); \bar{C} with sodium phenolate (free from alc. or aq.) on htg. gives (16) ethyl α -phenoxyacetoacetate (not further described) which in cold conc. H₂SO₄ loses H₂O and ring-closes to 2-carbethoxy-3-methylcoumarone [Beil. XVIII-309], tbls. from C₆H₆, m.p. 51°, b.p. 290° (16); note dif. in behavior of \bar{C} with these reagents as compared with ethyl γ -chloroacetoacetate (3:6375).]

[$\ddot{\mathbf{C}}$ with diethyl sodiomalonate yields in alc. (7) ethyl acetate (1:3015), ethyl chloroacetate (3:5700), triethyl ethane-1,1,2-tricarboxylate [Beil. II-813, II₁-(321), II₂-(681)], and tetraethyl propane-1,2,2,3-tetracarboxylate [Beil. II-862, II₁-(333), II₂-(701)] but in toluene yields (7) triethyl 3-hydroxybuten-2-tricarboxylate-1,1,2 [Beil. III₂-(509)]; note dif. from behavior of ethyl γ -chloroacetoacetate (3:6375).]

[For behavior of Cwith KCN see (4); with ethyl sodiocyanoacetate see (17); with NH₃ in dry ether see (18).]

Note that \tilde{C} is capable of displaying keto enol tautomerism as is shown in the following reactions.

C with FeCl₃ soln. gives intense violet coloration (10) (4).

Č forms a series of metallic salts of the enolic form; these are in general insol. aq. but sol. in org. solvents: e.g., Č in ether on shaking with aq. Cu(OAc)₂ (19) or NH₄OH/CuSO₄ (20) gives Cu(C₆H₃O₂Cl)₂, green tbls. from C₆H₆, m.p. 169-170° (19) (note that this m.p. is

alm. ident. with corresp. deriv. from the isomeric ethyl γ -chloroacetoacetate (3:6375)); for corresp. Mg, Cu, or Ni enolates see (20).

[$\bar{\mathbf{C}}$ with phenols in pres. of conc. $\mathbf{H}_2\mathbf{SO}_4$ or $\mathbf{P}_2\mathbf{O}_5$ undergoes condensation and ring closure with loss of $\mathbf{H}_2\mathbf{O}$ giving the corresp. substituted coumarins: e.g., $\bar{\mathbf{C}}$ with *m*-cresol (1:1730) in conc. $\mathbf{H}_2\mathbf{SO}_4$ at 0° gives (6) 3-chloro-4,7-dimethylcoumarin, ndls. from alc., m.p. 135° (6); $\bar{\mathbf{C}}$ with *p*-cresol (1:1410) similarly (6) (or m small yield (21) with $\mathbf{P}_2\mathbf{O}_5$) gives 3-chloro-4,6-dimethylcoumarin, ndls. from AcOH, m.p. 160° (6), 158° (21): for corresp. reactn. of $\bar{\mathbf{C}}$ with α -naphthol (1:1500) (22) (6), with β -naphthol (1:1540) (23), with 6-chloro-m-cresol (4-chloro-3-methylphenol) (3:1535) (24) see indic. refs. — This type of condensation also occurs with polyhydric phenols: e.g., $\bar{\mathbf{C}}$ with resorcinol (1:1530) + conc. $\mathbf{H}_2\mathbf{SO}_4$ at 0° (25) or with $\mathbf{P}_2\mathbf{O}_5$ in alc. (26) gives 3-chloro-7-hydroxy-4-methylcoumarin, cryst. from alc. with $\mathbf{P}_2\mathbf{V}_5$ in alc. (26) gives 3-chloro-7-hydroxy-4-methylcoumarin, cryst. from alc. with $\mathbf{P}_2\mathbf{V}_5$ in alc. (26) gives 3-chloro-7-hydroxy-4-methylcoumarin, cryst. from alc. with $\mathbf{P}_2\mathbf{V}_5$ in alc. (26) gives 3-chloro-7-hydroxy-4-methylcoumarin, cryst. from alc. with $\mathbf{P}_2\mathbf{V}_5$ in corresp. behavior of $\bar{\mathbf{C}}$ with orcinol (1:1525) (22) (25), with pyrogallol (1:1555) (22) (25), see indic. refs.; many other cases are known. — Note, however, with particular care that $\bar{\mathbf{C}}$ with sodium salts of these phenols reacts in a different manner yielding substituted coumarone derivs. (cf. case of sodium phenolate in fifth paragraph).]

 \bar{C} with aq. solns. of diazonium salts behaves quite differently from the isomeric ethyl γ -chloroacetoacetate (3:6375): e.g., \bar{C} in alc. with aq. benzenediazonium sulfate in pres. of NaOAc (2 moles) yields (27) (28) (4) ethyl α -chloro- α -(phenylhydrazono)acetate [Beil. XV-270], yel. lfts. or pl. from alc., m.p. 80-81° (28) (4), 70-71° (27) (for use of this reactn. on mixts. of \bar{C} with the isomer see (4)).

 \tilde{C} with excess hydrazine hydrate is reduced with evolution of N₂ (1); \tilde{C} with phenylhydrazine (2 moles) condenses and ring-closes yielding (29) (30) 4-(benzeneazo)-3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-328, XXIV₁-(319)], or.-red. ndls. from alc., AcOH, or CHCl₃, m.p. 156-157° (note, however, that in pres. of other the reactn. with phenylhydrazine takes a different course yielding (31) ethyl β -(benzeneazo)-crotonate [Beil. XVI-27], red ndls. from alc., m.p. 50-51°).

[\bar{C} with thioacetamide on warming yields (32) 5-carbethoxy-2,4-dimethylthiazole [Beil. XXVII-318], cryst. from ether, m.p. 50-51° (32). — \bar{C} with NH₄SCN (33) or better Ba-(SCN)₂ (34) in alc. gives (55% yield (34)) 5-carbethoxy-2-hydroxy-4-methylthiazole [Beil. XXVII-338], lfts. from alc., m.p. 128° (33), 127-129° (34); note that this prod. may be regarded as merely the isomeric ethyl α -(thiocyano)acetoacetate (35). — \bar{C} with NH₄dithiocarbamate (from NH₄OH + CS₂) in alc. eliminates NH₄Cl giving an intermediate, m.p. 115-121°, according to mode of htg. (38) but which on fusion ring-closes with loss of aq. to 5-carbethoxy-2-mercapto-4-methylthiazole [Beil. XXVII-339], ndls. from alc., m.p. 150° (38), 141° (39).]

[Č with urea in alc. contg. a little aq. HCl gives on stdg. 5 months (36) 5-carbethoxy-2-hydroxy-4-methylimidazole [Beil. XXV-216], ndls. from aq. or tbls. from alc., m.p. 218° (36). — Č (1 mole) with thiourea (1 mole) at 90° reacts vigorously eliminating H₂O and giving (alm. quant. yield (37)) as the hydrochloride 2-amino-5-carbethoxy-4-methylthiazole [Beil. XXVII-338]; addn. of alk. sets free the base, ndls. from ether/alc., m.p. 175° (37) (13).]

3:6267 (1) Macbeth, J. Chem. Soc. 123, 1125 (1923). (2) Allihn, Ber. 11, 567-570 (1878). (3) Milone, Gazz. chim. idal. 65, 342 (1935). (4) Favrel, Prevost, Bull. soc. chim. (4) 49, 243-261 (1931). (5) Haller, Held, Bull. soc. chim. (2) 65, 888-892 (1887). (6) Dey, J. Chem. Soc. 107, 1646 (1915). (7) Gault, Klees, Bull. soc. chim. (4) 39, 889-905 (1926); Compt. rend. 179, 600 (1924). (8) von Konek-Norwall, Ber. 51, 393-398 (1918). (9) Mewes, Ann. 245, 58-60, 66-69 (1888). (10) Schönbrodt, Ann. 253, 170-174 (1889).

Michael, Carlson, J. Am. Chem. Soc. 58, 353-364 (1936).
 yon Meyer, von Findeisen, J. prakt. Chem. (2) 65, 529-532 (1902).
 Behrend, Schreiber, Ann. 318, 381 (1901).
 Conrad, Ann. 186, 234 (1877).
 Peratoner, Gazz. chim. ital. 22, II 40-41 (1892).
 Hantssch, Ber. 19, 1292-1293 (1886).
 Chassagne, Bull. soc. chim. (4) 1, 914-916 (1907).

(18) Genvresse, Ann. chim. (6) 24, 64-65 (1891). (19) Wislicenus, Stoeber, Ber. 35, 542-543 (1902). (20) Allihn, Ber. 12, 1298-1300 (1879).

(21) Robertson, Sandrock, J. Chem. Soc. 1932, 1180, 1183-1184. (22) Chakravarti, J. Indian Chem. Soc. 8, 407-411 (1931). (23) Dey, J. Chem. Soc. 107, 1629 (1915). (24) Dey, Dalal, J. Chem. Soc. 123, 3390 (1923). (25) von Pechmann, Hanke, Ber. 34, 357-360 (1901). (26) Chakravarti, J. Indian Chem. Soc. 8, 136 (1931). (27) Bowack, Lapworth, J. Chem. Soc. 87, 1859 (1905). (28) Favrel, Compt. rend. 134, 1313 (1902). (29) Schönbrodt, Ann. 253, 188-193 (1889). (30) Buchka, Sprague, Ber. 22, 2548-2550 (1889).

(31) Bender, Ber. 20, 2747-2752 (1887). (32) Hantzsch, Ann. 250, 269 (1888). (33) Hantzsch, Weber, Ber. 20, 3131-3132 (1887). (34) Zürcher, Ann. 250, 282-283 (1888). (35) Wohmann, Ann. 259, 298 (1890). (36) Behrend, Ann. 229, 16 (1885). (37) Zürcher, Ann. 250, 289-290 (1888). (38) Levi, Gazz chim. ital. 61, 723-724 (1931). (39) Miolati, Gazz. chim. ital. 23, I 577 (1893). (40) Ubaldini, Chimica e industria (Italy) 25, 113-114 (1943); Cent. 1943, II 1951; C.A. 38, 5799 (1944).

```
3:6208 DICHLOROACETIC ACID
                                                          C_2H_2O_2Cl_2
                                                                            Beil. II - 202
                                                                                 II<sub>1</sub>-( 90)
                                           нс—соон
                                                                                 \Pi_{2}-(194)
  B.P.
                                  M.P.
  195°
                         (1) (62) 13.25° (17)
                                               D_4^{25} = 1.5579 (28)
  194.5-195°
                                  13.00° (18)
                         (2)
                                  12.15° (17)
                                               D_{25}^{25} = 1.5604 (4)
  194.42° at 760 mm.
                         (3)
  194.0-194.5° cor.
                                  11°(19) (20)
                         (4)
                         (5) (6) 10.85^{\circ} (21) D_{22}^{22} = 1.5594 (14) n_{\rm D}^{22} = 1.4659
  194°
  193.5-193.9°
                         (7)
                                  10.8° (22)
                                                D_4^{20} = 1.5648 (28) n_D^{20} = 1.46582 (27)
  192.5° at 763 mm. (28)
                                  10°
                                          (23)
                                                        1.5642 (27)
                                          (28)
  192-193° cor., dec. (8)
                                                        1.5634 (8)
                                          (24)
                                          (25)
  191°
           at 760 mm. (9)
                                  5–6°
                                          (14)
                                   -4.1° (24)
                                                D_{20}^{20} = 1.5666 (8)
  190°
                        (10)
  189-191°
                                  -4°
                                          (26)
                        (11)
                                                D_4^{19} = 1.5691 (29) n_D^{19} = 1.4667 (29)
                                  See Note 2.
                                                D_4^{\bar{1}5} = 1.5717 (28)
                                                 D_{15}^{15} = 1.5707 (27)
  144°
                                                See Note 3.
                                                                      See Note 3.
           at 164 mm. (12)
  140°
            at 142 mm. (12)
  129°
            at 88 mm. (12)
                                    Note 1. The b.p. of C at normal press. is not very
  125°
            at 71 mm. (12)
  111.5°
                                  significant, some decompn. to dichloroacetyl chloride
            at 36 mm. (12)
  105°
            at 25 mm. (13)
                                  (3:5290), phosgene (3:5000), and tarry products always
           at 24 mm. (12)
                                  occurring (8).
  102.5°
  99°
            at 21 mm. (12)
                                    Note 2. C apparently can exist in at least two crystn.
  102° cor. at 20 mm. (8) (14) modifications (24); no clear-cut study of the matter, how-
  102°u.c. at 20 mm. (16)
                                  ever, has been reported.
                                    Note 3. For values of D_{20}^{20} and n_{\rm D}^{20} for ag. solns. of
  95-96° at 17 mm. (8)
  91-92° at 12 mm. (15)
                                  Č see (27).
```

[See also chloroacetic acid (3:1370) and trichloroacetic acid (3:1150).]

See Note 1.

C when pure is a colorless liq. which does not fume in moist air and which dissolves in

aq. without opalescence. — Ordinary comml. samples of Č may contain also chloroacetic acid (3:1370) and trichloroacetic acid (3:1150) as well as decompn. products from these or from Č itself, cf. (30) (31).

MISCELLANEOUS PHYSICAL PROPERTIES OF C

Adsorption of \tilde{C} . [For studies of adsorption of \tilde{C} by activated carbon, charcoal, etc., see (32) (33) (34) (35) (36) (39); by silica gel see (33); by cellulose (viscose) see (37); by hide powder see (38).]

Distribution of \tilde{C} between solvents. [For studies and data on distribution of \tilde{C} between aq. + ether at 25° (40) (41); $aq. + C_6H_6$ at 15° (42) (43) (44) (45); aq. + nitrobenzene (43); aq. + toluene (43); aq. + c-nitrotoluene (43) (47); $aq. + CHCl_3$ (3:5050) (43); $aq. + CCl_4$ (3:5100) (43) (46); aq. + EtBr (43) (46); aq. (contg. $MgSO_4$) + di-n-butyl ether (1:7950) (48); aq. + clive oil (49); acetone + glycerol (50) see indic. refs.]

Binary systems contg. \tilde{C} . [For f.p./compn. data on systems \tilde{C} + trichloroacetic acid (3:1150) (25); \tilde{C} + AcOH (1:1010) (25); \tilde{C} + crotonic acid (1:0425) (25); \tilde{C} + benzoic acid (1:0715) (25); \tilde{C} + o-toluic acid (1:0690) (25); \tilde{C} + m-toluic acid (1:0705) (25); \tilde{C} + p-toluic acid (1:0705) (25); \tilde{C} + phenylacetic acid (1:0665) (25); \tilde{C} + cinnamic acid (1:0735) (25); \tilde{C} + 2,6-dimethylpyrone (24); \tilde{C} + azobenzene (19); \tilde{C} + urea (51); \tilde{C} + ethyl carbamate (urethane) (51) see indic. refs.]

PHYSIOLOGICAL BEHAVIOR OF C

[For study of toxicity of C see (52); for action of C on human skin see (53) (54).]

PREPARATION OF C

FROM VARIOUS CHLORO COMPOUNDS

From chloral hydrate. [For prepn. of \bar{C} from chloral hydrate (3:1270) with aq. NaCN + CaCO₃ (yields: 88–92% (55), 90% (15)) or with aq. NaCN (60–65% yield (16)) or with K₃Fe (CN)₆ (63) see indic. refs.; cf. also (56) (57); note here also the closely related matter of conversion of anhydrous chloral (3:5210) with alcohols + KCN (58) to the corresponding alkyl dichloroacetates, e.g., with MeOH to methyl dichloroacetate (3:5655) or with EtOH to ethyl dichloroacetate (3:5850), etc.; also conversion of chloral hydrate (3:1270) in ether with KCN + conc. aq. NH₄OH to (65–78% yield (59)) cf. (58) α,α -dichloroacetamide (see also below).]

From trichloroacetic acid. [For prepn. of \bar{C} from trichloroacetic acid (3:1150) by partial reduction with Zn + aq. (13), with Cu powder in aq. (80% yield (14)) or C_6H_6 + aniline (75-85% yield (8)) cf. (60), or by electrolytic reduction (80% yield (61)) see indic. refs.]

From chloroacetic acid. [For prepn. of \bar{C} from chloroacetic acid (3:1370) with Cl_2 (1), or Cl_2 in pres. of I_2 (62), see indic. refs.]

From dichloroacetaldehyde. [For prepn. of C from dichloroacetaldehyde (3:5180) by oxidn. with HNO₃ see (2).]

From other misc. chloro compounds. [For formn. of \bar{C} from ethyl dichloroacetate (3:5850) with HCl gas (100% yield (11)); from dichloroacetyl chloride (3:5290) by hydrolysis or by disproportionation with AcOH (acetyl chloride (3:7065) also being formed (64)); from β,β,β -trichloro- α -hydroxypropionic acid (trichlorolactic acid) [Beil. III-286, III₁-(111), III₂-(210)] or its ethyl ester with excess aq. Ba(OH)₂ (65); from β,β -dichloro- α -acetoxyacrylonitrile [Beil. III₁-(135), III₂-(254)] with boilg. aq. (66) or from α,β,β -trichloro- α -acetoxypropionitrile [Beil. III-288, III₁-(112)] with 33% H₂SO₄ (66); from 2,2,4,4,6,6-hexachlorocyclohexantrione-1,3,5 (hexachlorophloroglucinol) [Beil. VII-854,

 VII_1 -(469)] with aq. (sym.-tetrachloroacetone (3:6050) is also formed) (67); from unsym.-dichloroacetone (3:5430) by oxidn. with HNO₃ + air (68); from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) with air in ultra-violet light in pres. of water (21) cf. (69); from pentachloroethane (3:5880) by partial hydrolysis with 88-97% $\rm H_2SO_4$ at 168° (90% yield (70)) see indic. refs.]

From miscellaneous non-chlorinated compounds. [For formn. of \tilde{C} from AcOH with Cl₂ (71) in presence of I_2 (62) see indic. refs.; from acetylene with HOCl at 75-80° see (72); from ethyl acetoacetate (1:1710) with aq. bleaching powder (yield 60%) see (73); from phloroglucinol (1:1620) with aq. Cl₂ see (74) (75); from pyrrole with NaOCl see (76).]

CHEMICAL BEHAVIOR OF C

BEHAVIOR AS AN ACID

Acid strength of $\bar{\mathbf{C}}$. $\bar{\mathbf{C}}$ in aq. soln. is a strong acid (ionization const. at 25° is $K=5.14\times 10^{-2}$ (77) cf. (78) (18), at 18° $K=5.15\times 10^{-2}$ (45); for studies of activity coefficient of $\bar{\mathbf{C}}$ in aq. and in salt solns, see (18) (48). — For tests on corrosion of metals by $\bar{\mathbf{C}}$ see (16)].

[Studies of acid strength of \tilde{C} in other solvents include the following: in aq. MeOH (79) (81), in aq. EtOH (79) (80), in abs. EtOH (82), in n-BuOH (5) (83), in C₆H₆ (84), in chlorobenzene (85), in formamide (86), in acetonutrile (87).]

 \bar{C} on titration gives Neut. Eq. = 129.

Salts of C. This topic cannot be exhaustively treated here but following examples are cited.

Salts with inorganic bases. [NH₄ \bar{A} (88); hydroxylamine salt, HONH₃ \bar{A} , cryst. from C₆H₆/EtOH, m.p. 116.0–116.5° (89); Na \bar{A} (on electrolysis gives (90) H₂, CO₂, CO, and also (91) dichloromethyl dichloroacetate; K \bar{A} , lfts. from alc. (11), on dry distn. gives (92) \bar{C} + KCl + CO₂ + carbon; Ca \bar{A} ₂, ndls. from abs. alc. (93); Ca \bar{A} ₂.3H₂O (93); Cu \bar{A} ₂ (88); Cu \bar{A} ₂.4H₂O (88); Cd \bar{A} ₂.H₂O (94); Mn \bar{A} ₂.1½ H₂O (94); Co \bar{A} ₂.3H₂O (94); note that all the foregoing salts are sol. aq.]

[Inorg. salts of \bar{C} which are sparingly sol. aq. include the following: AgA (93); Th(OH)₂ \bar{A}_2 (96); (UO) \bar{A}_2 .2H₂O (97).]

Salts with organic bases (amines). [Aniline dichloroacetate, m.p. 122-123° (8) (98) cf. (30) (159) (note that this prod. or its components at 140° for 24 hrs. gives (98) dichloroacetanilide, m.p. 118°). — o-Toluidine dichloroacetate, m.p. 132.5° (98), 140° (99) (note that this prod. or its components at 140° for 18 hrs. gives (98) dichloroaceto-o-toluidide, m.p. 133°, but depressing m.p. of the salt to as low as 112°). — p-Toluidine dichloroacetate, m.p. 138° (98) (note that this prod. or its components on htg. gives (98) dichloroaceto-p-toluidide, m.p. 154°). — Piperazine bis-(dichloroacetate), m.p. 181° cor. (100). — Semicarbazide dichloroacetate, m.p. 108° (101). — For salts of C with other org. amines see (30) (99).]

Esterification of \tilde{C} . [For this see the text of methyl dichloroacetate (3:5655), ethyl dichloroacetate (3:5850), n-propyl dichloroacetate (3:6000), isopropyl dichloroacetate (3:5890); for study of direct esterification of \tilde{C} with various butyl and amyl alcs. without cat. see (102).]

Conversion of \tilde{C} to corresp. acid chloride. \tilde{C} with PCl₃ (103), with HCl gas + P_2O_5 (104), with SOCl₂ (poor yield apparently due to much forms. of dichloroacetic acid anhydride (3:6430) (105) (106) (107) (108), with BzCl (3:6240) (73% yield (111)), or with benzotrichloride (3:6540) (109) (110) gives dichloroacetyl chloride (3:5290), b.p. 108°.

Addition reactions of \tilde{C} with org. cpds. \tilde{C} in pres. of suitable cat. adds to olefins yielding corresp. esters [e.g., \tilde{C} with propylene + BF₃ as directed gives (39.5% yield (112)) isopropyl dichloroacetate (3:5890); \tilde{C} with 2-methylbutene-2 (trimethylethylene) (1:8220) at 18°

shows slight tendency toward forms. of corresp. ester in C₆H₆, CHCl₃ or CS₂ but none in alc. or ether (113)].

[\bar{C} with ethylene oxide (1:6105) in dry ether at 0° gives (15% yield (114)) cf. (115) β -hydroxythyl dichloroacetate (3:9107).]

BEHAVIOR OF C AS DICHLORO COMPOUND

Reduction. [\tilde{C} in alc. KOH soln. with $H_2 + Pd/CaCO_3$ splits off all its halogen as HCl (116). — \tilde{C} with Zn + water on htg. is slowly reduced to chloroacetic acid (3:1370) but reaction is much less energetic than that of trichloroacetic acid (3:1150) under same conditions (13).]

Hydrolysis of halogen atoms of \bar{C} or its salts. [\bar{C} with aq. in s.t. at 100° is slowly or in pres. of NaOH or Ba(OH)₂ rapidly decomposed (93) cf. (117). — For study of kinetics of hydrolysis of \bar{C} see (118) (119). — Note, however, that Ag \bar{A} on htg. with aq. (93), or \bar{C} (or its salts) on hydrolysis at elevated temp. and press. (120), or salts of \bar{C} htd. with aq. solns. of NaOAc or NaOBz (121), gives glyoxylic acid, OHC—COOH [Beil. III-594, III₁-207, III₂-(385)], m.p. 98°, very sol. aq. — For a method of detn. of \bar{C} in pres. of chloroacetic acid (3:1370) and trichloroacetic acid (3:1350) based on this hydrolysis see (1221.)

Behavior of \tilde{C} with alkoxides. $[\tilde{C} \text{ (as KA)}]$ with excess MeOH/NaOMe refluxed under H₂, and the solution then further esterified with MeOH/HCl, gives (62% yield (123)) cf. (124) methyl dimethoxyacetate, b.p. 60-61° at 12 mm., $D_4^{18} = 1.0962$, $n_D^{18} = 1.4045$ (124); this ester upon alk. hydrolysis gives (85.7% yield (124)) dimethyoxyacetic acid (glyoxylic acid dimethylacetal) as a sirup.]

[C with excess EtOH/NaOEt under reflux followed by acidification and esterification as above gives (50% yield (125)) (126) ethyl diethoxyacetate [Beil. III-601, III₁-(210), III₂-(389)], b.p. 199° (127), 94-98° at 19 mm. (125), 83-85° at 13 mm. (125).]

[Č in excess EtOH/NaOEt with Na phenolate refluxed 14 hrs., then acidified and esterified as above, gives (61% yield (128)) ethyl diphenoxyacetate [Beil. VI-170], oil, b.p. 240° at 53 mm. (129), 166-168° at 0.8 mm. (128). — However, Č with phenol in aq. NaOH on htg. and acidification gives (130) (131) diphenoxyacetic acid, ndls. from pet. ether or aq. AcOH, m.p. 91° (129) (130).]

Condensation with hydrocarbons. \bar{C} with aromatic hydrocarbons on htg. condenses with elimination of 2 HCl giving diarylacetic acids [e.g., \bar{C} with naphthalene at 180° for 60–100 hrs. gives {132} di-(α-naphthyl)acetic acid [Beil. IX-720, IX₁-(313)], cryst. from CCl₄, m.p. 224° (133), 223° u.c. (134); for analogous behavior of \bar{C} with other hydrocarbons see {132}].

Behavior of \tilde{C} with RMgX compounds. [\tilde{C} with C_6H_6MgBr (large excess) in ether soln. followed by usual hydrolysis gives (34% yield (135)) α,α,β -triphenylethylene glycol, ndls. from C_6H_6 , m.p. 163° (135).]

Behavior of \tilde{C} with hydroxylamine. [\tilde{C} (1 mole) with NH₂OH.HCl (1 mole) + aq. KOH (4 moles) at 60° for 4 hrs. gives (136) isonitrosoacetic acid (glyoxylic acid oxime) [Beil. III-599, III₁-(208), III₂-(389)], cryst. from dry ether, m.p. 138° (136) (note that this prod. forms with water a monohydrate, m.p. about 70° (137)).]

Behavior of C with aromatic amines. (See also salt formation above.)

With aniline. The products of reaction of \bar{C} on htg. with aniline are disputed [on one hand \bar{C} (1 mole) with aniline (4 moles) at 100°, then evapd. with NaOAc, is claimed (138) (139) to give 4,4'-diaminodiphenylacetic acid [Beil. XIV-540, XIV₁-(625)], m.p. about 195° (140); on the other hand, the prod. is regarded by some (141) (142) as a mixt. of two stereoisomeric forms of 2,2'(?)-diaminostilbene- α , α '-dicarboxylic acids [Beil. XIV-573]].

With o-toluidine. [C (1 mole) with o-toluidine (4 moles) at 100° gives (140) (143) 4,4′-diamino-3,3′-dimethyldiphenylacetic acid [Beil. XIV-543, XIV₁-(627)], ndls. from alc.,

m.p. 239-240° (143) dec. (140), accompanied by some 7-methylisatin-3-(o-tolylimide) [Beil. XXI-512], yel. lfts. from alc., m.p. about 225° dec. (138).]

With p-toluidine. [Č (1 mole) with p-toluidine (4 moles) at 100° in aq. or alc. soln. gives (144) (145) 5-methylisatin-3-(p-tolylimide) [Beil. XXI-510, XXI₁-(401)], goldenyel. ndls. or lfts. from alc., m.p. 259° (144) (145).]

Behavior of \tilde{C} with urea. \tilde{C} with urea (2 moles) in pres. of NaOEt condenses to give (146) 5-ureidohydantoin (allantoin) [Beil. XXV-474, XXV₁-(692)], m.p. by ord. htg. in cap. tube is 228-230° (147), by rap. htg. in bath already at 228° is 233-234° (147).

Behavior of \bar{C} with arythydrazines. \bar{C} with arythydrazines in alc. KOH yields a mixt. of the two stereoisomeric arythydrazones of glyoxylic acid [e.g., \bar{C} with phenylhydrazone in dil. alc. KOH refluxed 2 hrs. gives (148) a mixt. of the α -glyoxylic acid phenylhydrazone, m.p. abt. 138° with decompn. at 142–143°, and the β -glyoxylic acid phenylhydrazone, m.p. 128–129° dec. (rap. htg.) (148); for analogous behavior of \bar{C} with other arythydrazines see (148)].

- Color test with NH₄OH/Cu₂Cl₂ reagent.
 C on shaking in filled stoppered bottle with conc. aq. NH₄OH contg. Cu₂Cl₂ gives dark blue color within 3 min. (149); note, however, that the same behavior is shown by trichloroacetic acid (3:1150).
- Methyl dichloroacetate: oil, b.p. 143° (see 3:5655).
- --- Ethyl dichloroacetate: oil, b.p. 158° (see 3:5850).
- Benzyl dichloroacetate: oil, b.p. 179° at 60 mm. (150). [From C with benzyl alcohol (1:6480) with HCl gas (150).]
- —— Phenyl dichloroacetate [Beil. VI-153, VI₁-(87)]: m.p. 48° (151), b.p. 247.5° cor. (151). [From dichloroacetyl chloride (3:5290) + AlCl₃ in CS₂ (prod. m.p. 33° was probably impure (152)).]
- ---- p-Tolyl dichloroacetate: m.p. 58° (151). [Prepd. indirectly from α,β-dichlorovinyl ethyl ether (3:5440) with p-cresol (1:1410) (151).]
- --- p-Nitrobenzyl dichloroacetate: oil, unsuitable as (160) (161).
- ---- Phenacyl dichloroacetate: oil (153).
- --- p-Chlorophenacyl dichloroacetate: m.p. 93.0-93.8° (153).
- --- p-Bromophenacyl dichloroacetate: m.p. 98.2-99.3° (153).
- --- p-Iodophenacyl dichloroacetate: unreported.
- --- p-Phenylphenacyl dichloroacetate: unreported.
- © S-Benzylthiuronium dichloroacetate: m.p. 178-179° (154). [Note that for corresp. salts from chloroacetic acid (3:1370) and from trichloroacetic acid (3:1150) the values are respectively 159-160° and 148-149° (154).]
- S-(p-Chlorobenzyl)thiuronium dichloroacetate: unreported.
- --- S-(p-Bromobenzyl)thiuronium dichloroacetate: unreported.
- α,α-Dichloroacetamide: cryst. from C₆H₆, m.p. 99.4° (155), 98.5-99° (58), 98.5° (156), 97.5-99.5° (59). [From ethyl dichloroacetate (3:5850) with aq. NH₄OH (155) or in other indirect ways, e.g., from chloralammonia with KCN + aq. NH₄OH (93% yield (58)), or from chloral hydrate (3:1270) with KCN + aq. NH₄OH (65-78% yield (59)).] [Note that dichloroacetamide forms with bromo-chloro-acetamide or with chloro-iodo-acetamide an unbroken series of mixed crystals.]
- \bigcirc α,α-Dichloroacetanilide: colorless ndls. from alc. or by sublimation, m.p. 118° (98), 117.7° (156). [From \ddot{C} with aniline at 140° for 24 hrs. (98) or from dichloroacetyl chloride (3:5290) with aniline in C_6H_6 (157) or acetone (157).] [Note that this prod. forms with α-bromo-α-chloroacetanilide, m.p. 116.8° (157), a series of mixed cryst. and with α-chloro-α-iodoacetanilide, m.p. 142.3°, a cutectic, m.p. 105.2° (157).] [Note also that aniline dichloroacetate (see also above) has m.p. 122–123° (98).]

- \bigcirc α, α -Dichloroacet-o-toluidide: cryst. from 50% alc. or by sublimation, m.p. 133° (98). [From \ddot{C} + o-toluidine at 140° for 18 hrs. (98); note that the salt o-toluidine dichloroacetate has same m.p. 132.5° as the α, α -dichloroacet-o-toluidide but that the m.p. of a mixture of the two compds. is depressed to below 112° (98).]
- α,α-Dichloroacet-p-toluidide: pl. from alc. or by sublimation, m.p. 154° (98).
 [From C + p-toluidine at 148° for 18 hrs. (98); note that the corresp. salt, p-toluidine dichloroacetate, has m.p. 138° (98).]
- ---- α,α-Dichloroacet-N-benzylamide: m.p. 96.2° (156), 94.8-95.6° cor. (158), 94.2-95.0° u.c. (158). [From ethyl dichloroacetate (3:5850) (158) cf. (162) or dichloroacetyl chloride (3:5290) (156) with benzylamine; note, however, that the corresp. derivs. from chloroacetic acid (3:1370) and from trichloroacetic acid (3:1150) have almost the same m.p.'s, viz., 93.0-93.6° cor. and 93.6-94.4° cor., respectively (158).]
- 3:6208 (1) Maumené, Ann. 133, 154-156 (1865); Bull. soc. chim. (2) 1, 417-422 (1864); Compt. rend. 59, 84 (1864). (2) Paterno, Gazz. chim. ital. 49, II, 348-350 (1919). (3) Louginine, Ann. chim. (7) 27, 117-118 (1902). (4) Perkin, J. Chem. Soc. 65, 422 (1894). (5) Wooten, Hammett, J. Am. Chem. Soc. 57, 2291 (1935). (6) Backer, van Mels, Rec. trav. chim. 49, 183, 189-190, (1930). (7) Kohlrausch, Kóppl, Pongratz, Z. physik. Chem. B-21, 254-255 (1933). (8) Doughty, Black, J. Am. Chem. Soc. 47, 1091-1094 (1925). (9) Landee, Johns, J. Am. Chem. Soc. 63, 2892 (1941). (10) Senderens, Compt. rend. 204, 211 (1937).
- (11) Wallach, Ber. 9, 1213 (1876). (12) Patterson, Ber. 38, 213 (1905). (13) Doughty, Lacoss, J. Am. Chem. Soc. 51, 852-855 (1929). (14) Doughty, Derge, J. Am. Chem. Soc. 53, 1594-1596 (1931). (15) Délepine, Bull. soc. chim. (4) 45, 827-833 (1929). (16) Pucher, J. Am. Chem. Soc. 42, 2251-2259 (1920). (17) Schreiner, Z. anorg. allgem. Chem. 122, 206 (1922). (18) Randall, Failey, Chem. Revs. 4, 302-318 (1927). (19) Kremann, Zechner, Monatsh. 46, 171-172. 175 (1925). (20) yon Auwers, Wissebach. Ber. 56, 733 (1923).
- 171-172, 175 (1925). (20) von Auwers, Wissebach, Ber. 56, 733 (1923).
 (21) Müller, Luber, Ber. 65, 985-987 (1932). (22) Pickering, J. Chem. Soc. 67, 675, 677 (1895).
 (23) Rabinowitsch, Z. physik. Chem. 119, 64 (1926). (24) Kendall, J. Am. Chem. Soc. 36, 1230 (1914).
 (25) Kendall, J. Am. Chem. Soc. 36, 1727-1728 (1914).
 (26) Ciamician, Silber, Ber. 18, 1764 (1885). (27) Hantzsch, Dürigen, Z. physik. Chem. 136, 15 (1928). (28) Jaeger, Z. anorg. allgem. Chem. 101, 65 (1917). (29) Vanderstichele, J. Chem. Soc. 123, 1228 (1923). (30) Wheeler, Jennings, J. Am. Chem. Soc. 49, 1091-1093 (1927).
- (31) Rugely, Johnson, J. Am. Chem. Soc. 47, 2998 (1925). (32) Jermolenko, Ginsburg, Colloid J. (U.S.S.R.) 5, 263-270 (1939); Cent. 1939 II 3556; not in C.A. (33) Swearingen, Dickinson, J. Phys. Chem. 36, 534-545 (1932). (34) Sabalitschka, Pharm. Ztg. 74, 382-384 (1929); Cent. 1929, I 2288; C.A. 23, 2627 (1920). (35) Namasivayam, J. Indian Chem. Soc. 4, 449-458 (1927). (36) Alekseevski, J. Russ. Phys.-Chem. Soc. 55, 401-432 (1924); Cent. 1925, II 642; C.A. 19, 2634 (1925). (37) Brass, Frei, Kolloid-Z. 45, 248-249 (1928). (38) Kubelka, Taussig, Kolloid-Beihefte, 22, 150-190 (1926). (39) Freundlich, Z. physik. Chem. 57, 433 (1907). (40) Dermer, Markham, Trimble, J. Am. Chem. Soc. 63, 3524-3525 (1941).
- (41) Smith, J. Phys. Chem. 25, 621 (1921). (42) Bell, Z. physik. Chem. A-150, 24-25 (1930). (43) Kolossowsky, Kulikow, Z. physik. Chem. A-169, 462-464 (1934). (44) von Georgievics, Z. physik. Chem. 90, 55 (1915); Monatsh. 36, 400-401 (1915). (45) Drucker, Z. physik. Chem. 49, 567, 578-579 (1904). (46) Kolosovski, Kulikov, J. Gen. Chem. (U.S.S.R.) 5, 63-68 (1935); Cent. 1936, II 2880; C.A. 29, 4652 (1935). (47) Kolosovskii, Kulikov, J. Gen. Chem. (U.S.S.R.) 4, 1370-1377 (1934); Cent. 1936, II 1511; C.A. 29, 3898 (1935). (48) Randall, Failey, J. Am. Chem. Soc. 49, 2679 (1927). (49) Bodansky, Meigs, J. Phys. Chem. 36, 816 (1932). (50) Smith, J. Phys. Chem. 25, 730 (1921).
- (51) Puschin, Rikovsky, Monatsh. 60, 441-442, 446 (1932). (52) Woodard, Lange, Nelson, Calvery, J. Ind. Hyg. Toxicol. 23, 78-82 (1941). (53) Roberts, Brit. J. Dermatology, Syphilis, 38, 323-334; 375-391 (1926); Ber. ges. Physiol. expll. Pharmakol. 40, 847-848; Cent. 1927, II 2207; not in C.A. (54) Menschel, Arch. expll. Pathol. Pharmakol. 110, 1-45 (1925); Cent. 1926, II 50; C.A. 20, 1090-1091 (1926). (55) Cope, Clark, Connor, Org. Syntheses, Coll. Vol. 2 (1st ed.), 181-183 (1943); 19, 38-39 (1939). (56) Wallach, Ber. 10, 2120-2128 (1877). (57) Wallach, Ann. 173, 288-302 (1874). (58) Chattawsy, Irving, J. Chem. Soc. 1929, 1038-1048. (59) Clark, Shibe, Connor, Org. Syntheses 20, 37-39 (1940). (60) Doughty, Freeman, J. Am. Chem. Soc. 44, 640-645 (1922).
- (61) Brand, Ger. 246,661, May 6, 1912; Cent. 1912, I 1742; C.A. 6, 2496 (1912). (62) Müller, Ann. 133, 156-161 (1865). (63) Wallach, Ber. 10, 1526-1527 (1877). (64) Mugdan, Wimmer

(to Consortium für Elektrochem. Ind.), Ger. 549,725, April 30, 1932; Cent. 1932, II 122; [C.A. 26, 4828 (1932)]. (65) Pinner, Ber. 18, 757-758 (1885). (66) Kötz, J. prakt. Chem. (2) 103, 231-232, 237-238 (1921/22). (67) Zincke, Kegel, Ber. 22, 1470-1475 (1880). (68) deSimo, Allen (to Shell Development Co.), U.S. 2,051,470, Aug. 18, 1936; Cent. 1936, II 3469; [C.A. 30, 6764 (1936)]. (69) Muller, Ehrmann, Ber. 69, 2207-2210 (1936). (70) Compagnie Produit Chim. Metallurg. Alais, Froges, Camargue, U.S. 2,036,137, March 31, 1936; [C.A. 30, 3442 (1936)]; not in Cent.: Brit. 424,047, Feb. 13, 1935; [C.A. 29, 4380 (1935)]; not in Cent.; Ger. 610,317, March 7, 1935; [C.A. 29, 3691 (1935)]; not in Cent.: French 773,623, Nov. 22, 1934; Cent. 1935, I 2895, C.A. 29, 1437 (1935).

Amstutz (to Dow Chem. Co.), U.S. 1,921,717, Aug. 8, 1933; Cent. 1933, II 2455; C.A. 27, 5084 (1933).
 Wittorf, J. Russ. Phys.-Chem. Soc. 32, 112 (1900); Cent. 1960, II 30.
 Hurd, Thomas, J. Am. Chem. Soc. 55, 1648 (1933).
 Hasiwetz, Habermann, Ann. 155, 132-135 (1870).
 Zincke, Kegel, Ber. 22, 1470-1477 (1889).
 Ciamician, Silber, Ber. 18, 1763-1764 (1885).
 Otamician, Silber, Ber. 18, 1763-1764 (1886).
 Otamician, Silber, Ber. 19, 1764 (1886).
 Otamician, Silber, Silb

(81) Goldschmidt, Aas, Z. physik. Chem. 112, 434-436 (1924).
(82) Larsson, Z. physik. Chem. A-169, 209 (1934).
(83) Mason, Kilpatrick, J. Am. Chem. Soc. 59, 572-578 (1937).
(84) LaMer, Downes, J. Am. Chem. Soc. 55, 1840-1864 (1933).
(85) Griffiths, J. Chem. Soc. 1938, 818-823.
(86) Verhoek, J. Am. Chem. Soc. 58, 2577-2584 (1936).
(87) M. Kilpatrick, M. L. Kilpatrick, Chem. Revs., 13, 131-137 (1933).
(88) Bateman, Comad, J. Am. Chem. Soc. 37, 2553-2560 (1915).
(89) Jones, Werner, J. Am. Chem. Soc. 39, 418 (1917).
(90) Troeger, Ewers, J. prakt. Chem. (2) 58, 125-127 (1898).

(91) Kaufler, Herzog, Ber. 42, 3870 (1909). (92) Friedrich, Ann. 206, 254-256 (1880). (93) Beckurts, Otto, Ber. 14, 578-583, 585 (1881). (94) Fogel, Rubinsztein, Tauman, Roczniki Chem. 9, 348-353 (1929); Cent. 1930, II 227; C.A. 23, 3900 (1929). (95) Morgan, Cahen, J. Chem. Soc. 91, 477-478 (1907). (96) Karl, Z. anorg. allgem. Chem. 68, 59 (1910); Ber. 43, 2070 (1910). (97) Lobanow, Roczniki Chem. 5, 444 (1925); Cent. 1926, II 1390; C.A. 20, 3139 (1926). (98) Doughty, J.; Am. Chem. Soc. 47, 1095-1098 (1925). (99) Wheeler, Smith, J. Am. Chem. Soc. 45, 1994-1998 (1923). (100) Adelson, Pollard, J. Am. Chem. Soc. 58, 532 (1936).

(101) Michael, J. Am. Chem. Soc. 41, 415 (1919). (102) Liston, Dehn, J. Am. Chem. Soc. 60, 1264-1265 (1938). (103) Otto, Beckurts, Ber. 14, 1618-1619 (1881). (104) Frankland, Patterson, J. Chem. Soc. 73, 187 (1898). (105) Bösseken, Rec. trav. chim. 29, 99-100 (1910). (106) Blaise, Bull. soc. chim. (4) 15, 729 (1914). (107) Carré, Libermann, Compt. rend. 199, 1423 (1934). (108) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III, 97-103 (1933). (109) Mills (to Dow Chem. Co.), U.S. 1,921,767, Aug. 8, 1933; Cent. 1933, II 2595; C.A. 27, 5085 (1933). (110) Mills (to Dow Chem. Co.), U.S. 1,965,556, July 3, 1934; Cent. 1934, II 2899; C.A. 28, 5474 (1934).

(111) Brown, J. Am. Chem. Soc. 60, 1325-1328 (1938). (112) Dorris, Sowa, Nieuwland, J. Am. Chem. Soc. 56, 2689-2690 (1934). (113) Andreasov, Ukrain. Khem. Zhur. 4, Sci. pt. 93-94 (1929); Cent. 1929, II 2175; C.A. 23, 4438 (1929). (114) Allen, Hibbert, J. Am. Chem. Soc. 56, 1399 (1934). (115) Hibbert, Greig, Can. J. Research, 4, 254-263 (1931). (116) Busch, Stöve, Ber. 49, 1063-1068 (1916). (117) Petrenko-Kritschenko, Opotzky, Ber. 59, 2137 (1926). (118) Kailan, Kunze, Monatsh. 71, 379-380 (1938). (119) Kunze, Z. physik. Chem. A-188, 99-108 (1941). (120) Mugdan, Wimmer (to Consortium für Elektrochem. Ind.), Ger. 672,481, March 4, 1939; Cent. 1939, II 228; C.A. 33, 3817 (1939).

(121) I.G., French 772,860, Nov. 7, 1934; Cent. 1935, I 3850; C.A. 29, 1437 (1935). (122) Pool, Pharm. Weekblad 42, 165-168 (1904); Cent. 1905, I 1006. (123) Helferich, Russe, Ber. 56, 762 (1923). (124) Scheibler, Schmidt, Ber. 69, 14 (1936). (125) Johnson, Cretcher, J. Am. Chem. Soc. 37, 2147-2148 (1915). (126) Wohl, Lange, Ber. 41, 3612-3614 (1908). (127) Traube, Ber. 40, 4949 (1907). (128) Scheibler, Baumann, Ber. 62, 2060 (1929). (129) Auwers, Haymann, Ber. 27, 2795-2796 (1894). (130) van Alphen, Rec. trav. chim. 46, 148 (1927). (131) Philipp (to Chem. Fabrik von Heyden), Ger. 561,281, Oct. 12, 1932; Cent. 1933, I 2280;

(131) Philipp (to Chem. Fabrik von Heyden), Ger. 501,281, Oct. 12, 1932; Cent. 1938, I 2280; [C.A. 27, 1008 (1933)]. (132) Wolfram, Schörnig, Hausdorfer (to I.G.), Ger. 562,391, Nov. 1, 1932; Cent. 1933, I 849; C.A. 27, 734 (1933); Brit. 330,916, July 17, 1930; Cent. 1930, II 2054; [C.A. 24, 6031 (1930)]; French 688,964, Sept. 1, 1930; Cent. 1931, I 2677; [C.A. 25, 971 (1931)]. (133) Burtner, Cusic, J. Am. Chem. Soc. 65, 265 (1943). (134) Schmidlin, Massini, Ber. 42, 2386 (1909). (135) Boyle, McKenzie, Mitchell, Ber. 70, 2159 (1937). (136) Hantssch, Wild, Ann. 289, 294–295 (1896). (137) Inglis, Knight, J. Chem. Soc. 93, 1596 (1908). (138) Ostromyslensky, Ber. 40, 4978–4979 (1907). (139) Ostromysslensky, Ber. 41, 3022–3026 (1908). (140) Heller, Ann. 375, 262–284 (1910).

(141) Heller, Ann. 332, 268-275 (1904). (142) Heller, Ann. 358, 349-373 (1908). (143) Meyer, Ber. 16, 924-926 (1883). (144) Meyer, Ber. 16, 2262-2264 (1883). (145) Duisberg,

Ber. 18, 190-193 (1885). (146) Zeller, Stevens (to Merck and Co., Inc.), U.S. 2,158,098, May 16, 1939; Cent. 1939, II 4355; [C.A. 33, 6350 (1939)]. (147) Hartmann, Moffett, Dickey, Org. Syntheses, Coll. Vol. 2 (1st ed.), 22 (1943); 13, 3 (1933). (148) Busch, Achterfeldt, Seufert, J. prakt. Chem. 92, 1-40 (1915). (149) Doughty, J. Am. Chem. Soc. 41, 1130 (1919). (150) Seubert, Ber. 21, 283 (1888).

(151) Crompton, Triffitt, J. Chem. Soc. 119, 1875 (1921). (152) Kunckell, Johannsen, Ber. 31, 171 (1898). (153) Lundqvist, J. Am. Chem. Soc. 60, 2000 (1938). (154) Veibel, Ottung, Bull. soc. chim. (5) 6, 1435 (1939). (155) Taylor, Forscey, J. Chem. Soc. 1930, 2276. (156) McKie, J. Chem. Soc. 123, 2214-2217 (1923); 125, 1076-1079 (1924). (157) Votocek, Burda, Ber. 48, 1005-1006 (1915). (158) Buehler, Mackenzie, J. Am. Chem. Soc. 59, 421-422 (1937). (159) Beamer, Clarke, Ber. 12, 1067 (1879). (160) Lyons, Reid, J. Am. Chem. Soc. 39, 1742 (1917).

(161) Lundqvist, J. Am. Chem. Soc. 60, 2000 (1938). (162) Dermer, King, J. Org. Chem. 8,

168-173 (1943).

----- TRICHLOROACETIC ACID Cl₃C.COOH C₂HO₂Cl₃ Beil. II - 206 II₁-(92) II₂-(196)

B.P. 196°

M.P. 57°

See 3:1150. Division A: Solids.

3:6210 ACETALDEHYDE bis- $(\beta$ - $C_6H_{12}O_2Cl_2$ Beil. S.N. 79 CHLOROETHYL)ACETAL $CH_3.CH(O.CH_2.CH_2Cl)_2$ $(\alpha,\alpha$ -bis- $(\beta$ -Chloroethoxy)ethane)

B.P. 194-196° dec. (2) $D_{19}^{19} = 1.1712$ (2) $n_{D}^{10.2} = 1.4532$ (2) 109-110° at 30 mm. (1)

106-108° at 17 mm. (2)

106-107° at 14 mm. (3)

Colorless liq. with odor resembling dichloroacetal dehyde diethylacetal (3:6110). [For prepn. of $\tilde{\mathbf{C}}$ from ethylene chlorohydrin (3:5552) with a cetaldehyde (1:0100) +

[For prepn. of C from ethylene chlorohydrin (3.5552) with acetaldchyde (1:0100) + dry HCl (36% yield (2)) see (2) (1); with acetylene + BF₃ (71% yield) see (3).]

3:6210 (1) Street, Adkins, J. Am. Chem. Soc. 50, 162-167 (1928). (2) Grignard, Purdy, Bull. soc. chim. (4) 31, 985-986 (1922). (3) Nieuwland, Vogt, Foohey, J. Am. Chem. Soc. 52, 1018-1024 (1930).

3:6215 2-CHLORO-4-METHYLPHENOL OH C₇H₇OCl Beil. VI - 402 (2-Chloro-p-cresol) Cl VI₁— VI₂-(383)

B.P. 195-196° at 760 mm. (2) $D_2^{47} = 1.1785$ (10) $n_D^{27} = 1.5200$ (10) 197-198° at 738 mm. $D_{25}^{25} = 1.2106$ (1) . . .

Clear odorless liq. with characteristic disagreeable persistent odor. — Slightly sol. aq.; sol. alc., ether, C_6H_6 .

[For prepn. from 2-chloro-4-methylaniline via diazo reaction see (3); from sodium p-cresolate in CS₂ see (1); from p-cresol with Cl₂ in CCl₄ (4) or with SO₂Cl₂ (77% yield (10)) see indic. refs.]

 \bar{C} in 5 pts. AcOH and treated with 2 pts. conc. HNO₃ (D=1.4), or \bar{C} dislyd. in 10 pts.

AcOH and grad. treated with powd. NaNO₂ (5), yields on pptn. with aq. 2-chloro-4-methyl-6-nitrophenol [Beil. VI-413], golden-yel. ndls. from dil. alc. or dil. AcOH, m.p. 65° (5). [Note that addition of $\tilde{\mathbf{C}}$ to fumg. HNO₃ (D=1.5) leads to its oxidn. (evoln. of nitrous fumes), nitration, and wandering of methyl group (6).]

The methyl ether of $\bar{\mathbb{C}}$ [Beil. VI-403], 2-chloro-4-methylanisole, b.p. 215-218° cor. at 760 mm., has been prepd. only indirectly.

- ② 2-Chloro-4-methylphenyl benzoate: pl. from pet. eth., m.p. 71-72° (7). [This benzoate htd. with 0.7 of its wt. of AlCl₃ for 10 min. at 140° gives by Fries rearrangement 92% yield (8) of 2-hydroxy-3-chloro-5-methylbenzophenone, yel. lfts. from MeOH, m.p. 71° (8) cf. (9).]
- S:6215 (1) Schall, Dralle, Ber. 17, 2528-2529 (1884). (2) Klarmann, Shternov, Gates, J. Am. Chem. Soc. 55, 2585 (1933). (3) Cain, Norman, J. Chem. Soc. 89, 24 (1906). (4) Zincke, Ann. 328, 277 (1903). (5) Zincke, Ann. 328, 311-312 (1903). (6) Zincke, Ann. 328, 314 (1903). (7) von Auwers, Ber. 44, 801 (1911). (8) Rosenmund, Schnurr, Ann. 460, 86 (1928). (9) von Auwers, Mauss, Ann. 464, 310 (1928). (10) Sah, Anderson, J. Am. Chem. Soc. 63, 3165 (1941).

3:6220
$$\beta, \gamma$$
-DICHLORO- n -PROPYL ACETATE (Glycerol α, β -dichlorohydrin (GH₂Cl) (

[For prepn. of \bar{C} from 2,3-dichloropropanol-1 (" β -dichlorohydrin") (3:6060) with Ac₂O see (3); from glycerol α,α' -diacetate with PCl₅ or S₂Cl₂ see (2); from allyl chloride (3:7035) with acetyl hypochlorite see (6).]

 \bar{C} on keeping decomposes, perhaps by hydrolysis (2). [For study of hydrolysis with N/10 HCl see (1).] — \bar{C} with MeOH + trace HCl gives by alcoholysis (5) (6) 2,3-dichloropropanol-1 (3:6060) + MeOAc.

3:6220 (1) Bancroft, J. Am. Chem. Soc. 41, 425 (1919) (2) Wegscheider, Zmerzlikar, Monatsh. 34, 1074-1079 (1913). (3) de la Acena, Compt. rend. 139, 868 (1904). (4) Gibson, J. Soc. Chem. Ind. 50, 950 (1931). (5) Delaby, Dubois, Bull. soc. chim. (4) 47, 572 (1930). (6) Bockemüller, Hoffmann, Ann. 519, 189-190 (1935).

```
3:6230 \beta-CHLOROETHYL CHLOROACETATE C_4H_6O_2Cl_2 Beil. II -198 II_1— II_2—

B.P. 197–198° (1) D^- = 1.317 (1)
```

94-95° at 12 mm. (3)

[For prepn. from ethylene chlorohydrin (3:5552) + chloroacetyl chloride (3:5235) see (1); for prepn. from ethylene oxide (1:6105) + chloroacetyl chloride see (3).]

 \bar{C} on boiling with aq. hydrolyzes to β -chloroethanol (3:5552) and chloroacetic ac. (3:1370).

3:6230 (1) Henry, Bull. soc. chim. (2) 42, 260 (1884). (2) Mulder, Bremer, Ber., 11, 1960 (1878). (3) Altwegg, Landrivon, U.S. 1,393,161, Oct. 11, 1921; Cent. 1922, IV 947.

MISCELLANEOUS PHYSICAL PROPERTIES OF C

BINARY SYSTEMS CONTAINING C

 $\ddot{\mathbf{C}}$ + inorganic compounds. \ddot{C} + $AlCl_3$: m.p. 93° (22), 95° (26); for prepn. from $\ddot{\mathbf{C}}$ + $AlCl_3$ in CS₂ see (26); for thermal anal. (eutectic with $\ddot{\mathbf{C}}$ has m.p. -7.5° and conts. 87.3 wt. % $\ddot{\mathbf{C}}$) see (22); for conductivity of AlCl₃ in $\ddot{\mathbf{C}}$ see (27); for study of mol. wt. in C₆H₆ see (28).

 $\bar{C} + AlBr_3$: m.p. 90° (22); for thermal anal. (eutectic with \bar{C} has m.p. -5° and conts. 77.8 wt. % \bar{C} while eutectic with AlBr₃ has m.p. abt. 7–8° and conts. 21 wt. % \bar{C}) see (22); see also (30).

 $-\bar{C} + FeCl_3$: scarlet red hygroscopic ndls. (31); for conductivity see (28).

 $\ddot{C} + SbCl_3$: for thermal anal. (eutectic with \ddot{C} has m.p. -23° and conts. 55 wt. % \ddot{C}) see (32).

 $\bar{C} + SbCl_5$: for prepn. see (34); for conductivity in liq. SO₂ see (33).

 $\bar{C} + SbBr_3$: for thermal anal. (eutectic with \bar{C} has m.p. -6° and conts. 68 wt. % \bar{C}) see (32).

 $\ddot{\mathbf{C}}$ + organic compounds. \ddot{C} + C_6H_6 : for thermal anal. (eutectic has m.p. -26.8° and conts. 63.6 wt. % $\ddot{\mathbf{C}}$) see (35). — \ddot{C} + p-xylene: for thermal anal. (eutectic has m.p. -18.5° and conts. 67.2 wt. % $\ddot{\mathbf{C}}$) see (35). — \ddot{C} + mesitylene: for thermal anal. (eutectic has m.p. abt. -70° and conts. abt. 20 wt. % $\ddot{\mathbf{C}}$) see (35). — \ddot{C} + biphenyl: for thermal anal. (eutectic has m.p. -8° and conts. 81.8 wt. % $\ddot{\mathbf{C}}$) see (35). — \ddot{C} + diphenylmethane: for thermal anal. (eutectic has m.p. -15° and conts. 66.7 wt. % $\ddot{\mathbf{C}}$) see (35).

 \ddot{C} + chlorobenzene: for thermal anal. (eutectic has m.p. -54.2° and conts. 19.3 wt. % \ddot{C}) see (35). $-\ddot{C}$ + nitrobenzene: for thermal anal. (eutectic has m.p. -20.5° and conts. 50 wt. % \ddot{C}) see (35).

PREPARATION OF C

Note that comml. \bar{C} is often contaminated with various chlorobenzoyl chlorides (e.g., o-chlorobenzoyl chloride (3:6540), m-chlorobenzoyl chloride (3:6550), p-chlorobenzoyl chloride (3:6550), etc.), with traces of benzaldehyde (1:0195), or with benzoic acid (1:0715) + HCl from hydrolysis. For removal of BzOH + HCl from \bar{C} by shaking its C_6H_6 soln. with cold aq. 5% NaHCO₃ see (12); by treatment with metallic oxides or carbonates see (36).

From benzoic acid. [For prepn. of \tilde{C} from benzoic acid (1:0715) with PCl₅ (70% yield (37)) (10) (38), with PCl₃ (39) (40) in pres. of ZnCl₂ (77% yield (37)) or in pres. of a little aq. at 100° under press. (41), with SOCl₂ (90% yield (37)) (42), with SCl₂ in CS₂ (43), with SiCl₄ directly (23% yield (44)) or in C₆H₆ (77% yield (44)), with POCl₃ + alkali chloride at elev. temp. (45), or with dry HCl + P₂O₅ at 200° (46) see indic. refs.]

[For prepn. of \bar{C} from benzoic acid (1:0715) with NaCl + Na or K pyrosulfate at 200° (47), or with Na chlorosulfonate (48) cf. (49), see indic. refs.]

[For prepn. of \bar{C} from benzoic acid (1:0715) with other organic acyl chlorides such as carbonyl chloride (phosgene) (3:5000) at 140-200° (50) or in pres. of tertiary bases (such as pyridine) or their salts (51), with oxalyl (di)chloride (3:5060) (98% yield (15)), with p-toluenesulfonyl chloride in pyridine (52), or with α,β -dichloroethyl ethyl ether (3:5640) (53), see indic. refs.]

From salts of benzoic acid. Note that with salts of benzoic acid more or less forms. of benzoic anhydride (1:0595) may occur.

[For prepn. of \bar{C} from NaOBz with POCl₃ (2) (54), with SCl₂ at room temp. (55) cf. (43), with SO₂ + Cl₂ (56), with Na chlorosulfonate (48) cf. (49), or with benzenesulfonyl chloride (57) see indic. refs.]

[For prepn. of C from AgOBz with carbonyl chloride (3:5000) in s.t. at 100° see (58).]

From dibenzoyl peroxide. [For prepn. of \bar{C} from dibenzoyl peroxide (1:4930) with oxalyl (di)chloride (3:5060) refluxed in dark for 24 hrs. (70% yield (59)), with PCl₅ in pet. ether (60), with AlCl₃ in CHCl₃ at 0° (61) or in C₆H₆ at 100° (62), or with FeCl₃ in C₆H₆ at 100° (62) see indic. refs.]

From other benzoic acid derivatives. [For formn. of \bar{C} from benzamide with dry HCl or AcCl at 140° see (63); from methyl benzoate (1:3586) with PCl₅ at 160-180° (64) or from ethyl benzoate (1:3721) with PCl₅ in s.t. at 140° (65) see indic. refs.; from α,β -dichloroethyl benzoate or from α -chloroethyl benzoate on htg. in pres. of traces of ZnCl₂ see (66); from benzoic anhydride (1:0595) with PCl₃ + Cl₂ (67) or with carbonyl chloride (3:5000) (68) see indic. refs.]

From benzaldehyde. [For formn. of \bar{C} from benzaldehyde (1:0195) with SO₂Cl₂ (5 moles) on distn. (69), with S₂Cl₂ in s.t. at 150° (107), with POCl₃ in C₆H₆ (70), with NOCl (71), with EtOCl (3:7022) (72), with ter-AmOCl (3:9287) (8.5% soln. in CCl₄) at room temp. for 15 hrs. (73), or with Cl₂ (91) (105) (106) see indic. refs.]

From benzotrichloride. [For prepn. of \bar{C} from benzotrichloride (3:6540) by partial hydrolysis with limited amt. of aq. in pres. of H₂SO₄ or FeCl₃ (74), with aq. vapor over tin phosphate at 240° (75), with ord. comml. ZnCl₂ at 120° (76) in pres. of limited aq. (77) (note that pure ZnCl₂ fails to react but addn. of 1 mole aq. or initial use of tech. ZnCl₂ gives \bar{C} (76)), with pure ZnO at 100° (76), with BzOH in boilg. nitrobenzene (78) or in pres. of ZnCl₂ (80), with NH₄OBz at 200–210° as directed (79), or with EtOH in pres. of FeCl₃ or Fe (81) see indic. refs.]

Note that benzotrichloride (3:6540) on heating with carboxylic acids or anhydrides, especially in pres. of ZnCl₂, is often employed to prepare a mixture of \bar{C} with the acid chloride corresponding to the acid or anhydride so employed, particularly in cases where the two acyl chlorides are readily separable. [E.g., note that benzotrichloride (3:6540) with phthalic anhydride (1:0725) (81) (82) or phthalic acid (1:0820) (83) + ZnCl₂ at 110-120° gives (96% yield (82)) \bar{C} + (93% yield (82)) sym.-phthalyl (di)chloride (3:6900); benzotrichloride with AcOH (1:1010) in pres. of an acid cat. gives (84) (85) (86) (87) \bar{C} + acetyl chloride (3:5295), for other examples see under chloroacetyl chloride (3:5235), dichloroacetyl chloride (3:5290), trichloroacetyl chloride (3:5235), fumaryl (di)chloride (3:575), and terephthalyl (di)chloride (3:2205). Similarly, benzotrichloride (3:6540) with salts of sulfonic acids yields \bar{C} + the corresp. arylsulfonyl chlorides; e.g., benzotrichloride with sodium β -naphthalenesulfonate gives (88) 90% yield \bar{C} + 80% yield β -naphthalenesulfonyl chloride.]

From benzal (di)chloride. [For formn. of \tilde{C} from benzal (di)chloride (3:6327) with O_2 in u.v. light (89), with air in pres. of Ni at 160° (90), or with BzOH (1:0715) + Cl_2 at 125-175° (91) see indic. refs.]

From miscellaneous sources. [For formn. of \bar{C} from benzyl alc. (1:6480) with Cl₂ (92) or with SOCl₂ at 180° (103), from benzyl acetate (1:3751) with Cl₂ at 150–170° (104), from thiobenzoyl chloride + O₂ at 100–120° (93), from benzonitrile with NOCl at 180° (94), from tolan (diphenylacetylene) with NOCl at 150–200° (95), from dibenzoyltartaric anhydride + PCl₅ (3 moles) in s.t. at 130° for 3 hrs. (note that chlorofumaryl dichloride is also formed) (96), from N,N-dibenzoylaniline (dibenzanilide) with dry HCl at 250–270° (note that benzanilide is also formed) (97), from α -chloro- α -nitro-phenylacetamide on dry htg. (98), from phthalic anhydride (1:0725) + HCl gas + CrCl₃ or ZnCl₂ at 290–300° under press. (99), or from C₆H₆ (1:7400) with carbonyl chloride (phosgene) (3:5000) + AlCl₃ (100) (101), or with oxalyl (di)chloride (3:5060) + AlCl₃ (102) see indic. refs.]

CHEMICAL BEHAVIOR OF C

Pyrolysis. [\bar{C} in N₂ through porcelain tube at 550-600° (108) or over Ni at 420° (109) cf. (110) gives CO, chlorobenzene (3:7903), and other products; \bar{C} over finely divided Cu at 420-450° gives (110) benzoic anhydride (1:0595) + HCl; \bar{C} over BaCl₂ at 420-450° gives (110) benzoic anhydride (1:0595) and other products. For study of effect of radium radiation at 2-12° over 7-8 month period see (13).]

Reduction. [C with H_2 in boilg. xylene in pres. of PtO_2 + trace of thiourea (111), $Pd/BaSO_4$ (112), or powd. Ni (112), or \tilde{C} over Pd at 200-230° (113) cf. (114) gives (yields: 96% (111), 87-89% (113)) benzaldehyde (1:0195); for study of purification of xylene as solvent for cat. reduction of \tilde{C} see (115); for study of influence of various other solvents see (116) (112).]

[\bar{C} with H_2 in pres. of NiCl₂ at 270-280° gives (110) benzene, toluene, biphenyl + HCl; \bar{C} with copper hydride is claimed (117) to yield benzaldehyde but this could not be confirmed (118). \bar{C} with chromous acetate in 50% KOH gives (very small yield (119)), benzyl alc. (1:6480), while \bar{C} with LiH in high-boilg. pet. ether at 130° gives (presumably by subsequent condensation of the intermediate benzaldehyde) 65% yield (120) benzyl benzoate (1:4422).]

[$\tilde{\mathbf{C}}$ with Na/Hg + stream of dry HCl gives (121) benzyl alc. (1:6480); $\tilde{\mathbf{C}}$ with Na/Hg in dry ether gives (122) (123) (124) benzyl alc. (1:6480), benzoic acid (1:0715), benzil (1:9015), α,α' -dibenzoxystilbene ("isobenzil") [Beil. IX-138], and α,α' -dibenzoxydibenzyl [Beil. IX-136]; $\tilde{\mathbf{C}}$ with Na in moist ether gives (125) benzyl alc. (1:6480), benzoic acid (1:0715), and benzyl benzoate (1:4422).]

Oxidation. [C on oxidn in pres. of hydrocarbon peroxides and various oxidn cat. is claimed (126) to give dibenzoyl peroxide (1:4930); see also below under behavior of C with Na₂O₂.

Chlorination. [\bar{C} on monochlorination with Cl₂ at 35° in pres. of FeCl₃ gives (10) cf. (127) mainly a mixt. of chlorobenzoyl chlorides [83.5% m- (3:6590) + 14.5% o- (3:6640) + 2.0% p- (3:6550)] accompanied by a small amt. of dichlorobenzoyl chlorides; for extensive study of effect of using higher proportion of Cl₂ under otherwise same conditions see (128). Note, however, that \bar{C} with 3 moles Cl₂ in s.t. gives (129) (130) a mixt. of addn. products, such as 1,2,3,4,5,6-hexachlorohexahydrobenzoyl chloride, substitution products, and materials formed by both addition and substitution (130).]

Sulfonation. [C cannot be sulfonated without accompanying hydrolysis of the acyl chloride function (131) (132) (133) (134) (137); the end prod. of these sulfonation processes is, therefore, not m-sulfobenzoyl chloride (apparently still unknown cf. (135)) but rather m-sulfobenzoic acid [Beil. XI-384, XI₁-(98)]. However, C added to conc. H₂SO₄ at 0-40° gives (136) a cryst. addn. prod. C.H₂SO₄ which on stdg. loses HCl forming benzoyl hydrogen sulfate [Beil. IX₁-(94)] but shows no transformation into m-sulfobenzoic acid even after 6 months over dry alkali even though HCl is lost completely (136). At 100° conversion of benzoyl hydrogen sulfate occurred very slowly and the prod. consisted of o-sulfobenzoic acid (not meta) (136).]

BEHAVIOR OF C WITH OTHER INORGANIC REAGENTS

 \bar{C} with HF. [\bar{C} with HF as directed (138) (139) or with dry KHF₂ in Cu retort (140) (141) (142), with ZnF₂ at 195° (11) (143), with AgF in s.t. at 190° for 6 hrs. (144), or with 3 moles SbF₃ (145) gives (yields: 67-80% (140), 76% (145), 69% (11)) benzoyl fluoride, b.p. 161.5° at 745 mm. (142), 159° (139), 156° (146), 155-156° at 760 mm. (11), 155° (138), 154-155° (143), 151° u.c. at 736 mm. (141), 145° (144). Note, however, that \bar{C} with KF in anhydrous formic acid gives (147) formyl fluoride, b.p. 26° at 750 mm. (147), while \bar{C} with KF in AcOH gives (147) acetyl fluoride, b.p. 20-22° (147).]

 $\ddot{\mathbf{C}}$ with HBr. [$\ddot{\mathbf{C}}$ with dry HBr gas at 100° gives (148) benzoyl bromide [Beil. IX-195, IX₁-(95)], b.p. 218-219° cor. at 760 mm. (149), 215.0° at 741 mm. (150), 90-91° at 12 mm. (16), m.p. +8.1° (150), $D_{2}^{40}=1.5461$ (150), $n_{D}^{20}=1.5900$ (150).]

 \bar{C} with HI. [\bar{C} with excess HI at ord. temp. (148) (16), or \bar{C} with Mg + I₂ in dry ether (151), gives benzoyl iodide [Beil. IX-195, IX₁-(95)], b.p. 109-109.5° at 10 mm. (148) cf. (16). Note that \bar{C} with KI does not (152) give benzoyl iodide.]

 \bar{C} with metals. $[\bar{C}$ with Na in dry ether stood 10 days at room temp. gives (86% yield (153)) (154) ethyl benzoate (1:3721) but \bar{C} with Na/Hg in dry ether causes the reaction to take a more complicated course (see above under reduction of \bar{C}). \bar{C} with Na vapor gives (155) cf. (154) benzil (1:9015). \bar{C} with K in xylene refluxed 2 days gives (153) benzoic anhydride (1:0595).]

[For behavior of \bar{C} with Zn in dry ether or in di-isoamyl ether at 20–32° see (156). For behavior of \bar{C} with finely divided Cu or Ni at elevated temps. see above under pyrolysis of \bar{C} .]

C WITH VARIOUS METAL OXIDES OR SALTS

 \bar{C} with Na₂O₂. [\bar{C} with Na₂O₂ in water at 5° (157) cf. (159) or \bar{C} with 30% H₂O₂ + aq. NaOH (158) cf. (159) gives (yields: 91% (157), 60–70% (158)) benzoyl hydrogen peroxide

(perbenzoic acid) [Beil. IX-178, IX₁-(93)], m.p. 42°. For other methods for prepn. of perbenzoic acid such as from dibenzoyl peroxide with NaOCH₃ in MeOH/CHCl₃ (160) or with NaOC₂H₅ in EtOH/toluene (161), or from benzaldehyde in acetone with air (162), see indic. refs. For study of Na perbenzoate (157) and its use in purification (163) of perbenzoic acid see indic. refs.]

[Č with Na₂O₂ in aq. at 0° (164) (165) or in aq. acetone (166), or \tilde{C} with aq. H₂O₂ + NaOH (167) or aq. H₂O₂ + iron-free Ca(OH)₂ (168), or \tilde{C} with aq. BaO₂.8H₂O (169) (170) (171), or \tilde{C} with perbenzoic acid (see preceding paragraph) + aq. NaHCO₃ (172) gives dibenzoyl peroxide [Beil. IX-179, IX₁-(93)], m.p. 105°. For review of prepn. and properties of this prod. see also (173).]

 \bar{C} with misc. salts. \bar{C} on warming with various inorganic salts yields benzoic anhydride. [E.g., \bar{C} with NaNO₂ (174) cf. (175) (176), with KNO₃ (177), with Pb (NO₃)₂ (178), with nitrates of other heavy metals (179), with Na₃PO₄.12H₂O in aq. soln. at 60° (180), with K₂S₂O₅ in pyridine (181), with Na₂SO₃ in pyridine (183) in pres. of C₆H₆ (181) cf. (182), or with BaO at 140–150° (184) gives benzoic anhydride (1:0595), m.p. 42°. For other methods of conversion of \bar{C} to benzoic anhydride see above under pyrolysis of \bar{C} and below under behavior of \bar{C} with organic acids and their salts.]

 $\tilde{\mathbf{C}}$ with NaN₃. [$\tilde{\mathbf{C}}$ with NaN₃ in aq. acetone at 0° (185), or in dry ether (186), gives (54.6% yield (185)) benzoyl azide (benzazide) [Beil. IX-332], m.p. 32° (185). Note that although this prod. readily explodes on htg. (187) (188) yet in inert solvents such as C_6H_6 (194) it smoothly decomposes into N₂ and phenyl isocyanate (for study of mechanism see (189)); under certain circumstances the latter may be hydrolytically split to aniline cf. (190). For studies on decomposition of benzoyl azide by ultrasonic waves see (185) (193).]

Hydrolysis of C

 \bar{C} with cold aq. is slowly and with warm aq. rapidly hydrolyzed (105) to benzoic acid (1:0715) and HCl. [For study of rate of hydrolysis of \bar{C} in ether with aq. at 20-22° (195) or at 0° (148), in 50% aq. acetone at 0° in pres. of H₂SO₄ (196) cf. (198), in various other organic solvents immiscible with aq. (197) or with BaBr₂.2H₂O at 158° (199) see indic. refs.]

 \bar{C} with aq. alkali on warming readily yields (105) alkali benzoate + alkali chloride. Note that \bar{C} in 50% aq. pyridine hydrolyzes much faster than in aq. NaOH or aq. Na₂CO₃ (39) (use in determination of atomic weight of carbon by hydrolysis of \bar{C} and pptn. of AgCl (39)). Note that rate of hydrolysis of \bar{C} is 2000 times as fast (200) as that of benzyl chloride (3:8535).

[Note that \tilde{C} in Ac₂O soln. behaves as an acid (201) and can be titrated (202) with NaOAc in Ac₂O.]

BEHAVIOR OF C WITH VARIOUS INORGANIC SULFUR COMPOUNDS

With H_2S . [The behavior of \bar{C} with H_2S is disputed; on one hand \bar{C} in dry pyridine treated with H_2S at 5° and subsequently acidified is claimed (203) to give thiolbenzoic acid, C_6H_6 .CO.SH [Beil. IX-419, IX₁-(169)] (see next paragraph); on the other hand \bar{C} refluxed in dry pyridine in stream of H_2S is claimed (204) to yield dithiobenzoyl oxide (C_6H_6 .CS)₂O, colorless cryst. from hot alc., m.p. 112°.]

With KSH. [Č with cold alc. KSH (from satn. of alc. KOH with H_2S) gives (205) (206) (207) (209) (8) salt of thiolbenzoic acid, C_0H_5 .CO.SH [Beil. IX-419, IX₁-(169)], m.p. 24° (207) (208), b.p. 98.0–98.6° at 11–12 mm. (8), 61.0–61.3° at 0.05 mm. (8). Note, however, that this product is readily oxidized (dehydrogenated) to dibenzoyl disulfide (see below) by air or mild oxidizing agents, e.g., I₂ (209). \ddot{C} with NaSH (35% aq. soln.) in stream of air followed by H_2O_2 as directed (210) (211), with alc. Na₂S₂ at 5–10° (212), with $K_2S.5H_2O$

in acetone followed by I_2/KI oxidn. (213), or with HSMgBr followed by air oxidn. (208) gives (65-70% yield (210)) dibenzoyl disulfide [Beil. IX-424], cryst. from 1,2-dichloroethane (3:5130) (210) (211) (212), m.p. 128-129° (210) (211) (212); this prod. has considerable pharmaceutical interest as an antipruritic; for hydrolysis to benzoic acid as method of detn. see (210) (214).]

Behavior of C with Various Inorganic Nitrogen Compounds

With NH₃. [C̄ with conc. aq. NH₄OH (215), with dry NH₃ (105), with liq. NH₃ (216), with solid (NH₄)₂CO₃ (217), or with KNH₂ in dry ether (218) gives benzamide [Beil. IX-195, IX₁-(96)], m.p. 130°; note that either the (NH₄)₂CO₃ (219) or KNH₂ (218) methods may give also small amounts of N-benzoylbenzamide (dibenzamide) [Beil. IX-213, IX₁-(104)], m.p. 148°, and/or N,N-dibenzoylbenzamide (tribenzamide) [Beil. IX-214, IX₁-(104)], m.p. 207-208°. However, C̄ with NH₃ gas over Al₂O₃ at 490-500° gives (220) benzonitrile [Beil. IX-275, IX₁-(121)], b.p. 191°, m.p. -13°.]

With NH₂OH. [C in C₆H₆ with free NH₂OH (221), or C in C₆H₆ with NH₂OH.HCl + pyridine (221), or C in ether with NH₂OH.HCl + Na₂CO₃ (221), gives benzohydroxamic acid (N-benzoylhydroxylamine) [Beil. IX-301, IX₁-(128)], cryst. from EtOAc, m.p. 128°. Note that C with aq. NH₂OH solns. (222) also gives side reactions which diminish yield and increase difficulty of purification of prod.; also that C with NH₂OH.HCl in toluene gives (222) benzohydroxamic acid benzoate (dibenzohydroxamic acid) [Beil. IX-303, IX₁-(128)] and other products. For alternative method of prepn. of benzohydroxamic acid from ethyl benzoate (1:3721) with NH₂OH.HCl + MeOH/KOH see (223); for review of utility of hydroxamic acids in org. qual. anal. see (224); for study of formn. of benzohydroxamic acid and its FeCl₃ color reaction as method of detn. of hydroxylamine see (230).]

With NH₂.NH₂. [\ddot{C} (1 mole) with N₂H₄.H₂O (2 moles) in ether gives (225) benzhydrazide (N-benzoylhydrazine) [Beil. IX-319, IX₁-(129)], m.p. 112°, but this prod. is usually better obtd. from reaction of N₂H₄.H₂O with MeOBz (1:3586) (226) or EtOBz (1:3721) (227) (225). \ddot{C} (1 mole) with N₂H₄.H₂SO₄ (0.5 mole) + aq. NaOH (2.3 moles) as directed gives (66-75% yield (228)) N,N'-dibenzoylhydrazine [Beil. IX-324, IX₁-(131)], ndls. from AcOH (228) or EtOH (229), m.p. 237-238° (229).]

BEHAVIOR OF C WITH ORGANIC REACTANTS

BEHAVIOR OF C WITH HYDROCARBONS

With cycloalkanes. [\bar{C} with cyclohexane (1:8405) + AlCl₃ gives (19% yield (231)) phenyl 2-methylcyclopentyl ketone, b.p. 160-162° at 36 mm., $D_4^{18} = 1.0255$, $n_D^{18} = 1.5380$, accompanied by much benzaldehyde (1:0195) presumably formed from \bar{C} by the hydrogen corresp. to coupling of 2 moles of cyclohexane.]

With alkenes. [\bar{C} with ethylene + AlCl₃ in special apparatus as directed gives (87–92% yield (232)) phenyl β -chloroethyl ketone (β -chloropropiophenone) (3:1115); cf. also (233).]

With cycloalkenes. [\bar{C} with cyclohexene (1:8070) + AlCl₃ in CS₂ gives by addition phenyl 2-chlorocyclohexyl ketone (234), which on dehydrochlorination in the pres. of AlCl₃ (234) or with alc. KOH (235) gives (40% yield (235)) phenyl cyclohexenyl ketone (tetrahydrobenzophenone), b.p. 147° at 8 mm., $D_{42}^{22} = 1.070$, $n_{D}^{22} = 1.5595$ (235).]

With alkynes. [For behavior of C with heptyne-1 (1:8085) in pres. of AlCl₃, ZnCl₂, SnCl₄, BF₃, etc., see (236).]

With aromatic hydrocarbons. [\bar{C} with C_6H_6 in pres. of AlCl₃ gives (yields: 74% (237), 71–74% (238)) (240) (241) (242) (243) (244) (245) benzophenone (1:5150), but best (239) prepn. of latter is from $C_6H_6+CCl_4$ (3:5100) + AlCl₃. — For studies of substitution for

AlCl₃ of FeCl₃ (237) (238) (246) (247) (248), FeCl₃ + AlCl₃ (249), GaCl₃ (250), TlCl₃ (251), WCl₆ (252), UCl₄ (252), ZrCl₄ (253), Cr powder (254), ZnCl₂ (238), SbCl₃ (255) (256), or SbBr₃ (257) see indic. refs. — \bar{C} with C₆H₆ in liq. HCl at 200° and 250 pounds press. (258) or in pres. of P₂O₅ in s.t. at 180-200° (259) (260) gives small yield of benzophenone (1:5150). — \bar{C} with C₆D₆ + AlCl₃ in CS₂ gives (261) phenyl pentadeuterophenyl ketone, b.p. 160° at 15 mm. (corresp. oxime, m.p. 140°, does *not* depress m.p. of ordinary benzophenone oxime).]

[C with toluene in pres. of AlCl₃ gives (262) (263) (264) mainly phenyl p-tolyl ketone (1:5160) together with some phenyl o-tolyl ketone [Beil. VII-439, VII₁-(234)]. For studies of substitution for AlCl₃ of FeCl₃ (263), FeCl₃ + AlCl₃ (265), or SbCl₃ (255) (256) see indic. refs.]

[For reaction of C in pres. of AlCl₃ with o-xylene (1:7430) (262), m-xylene (1:7420) (262) (266) (267), p-xylene (1:7415) (262), ethylbenzene (268) (266) (269), see indic. refs.] [Č with biphenyl (1:7175) in pres. of AlCl₃ gives (yields: 75% (270), 60% (271)) (272) (273) (274) (275) (276) (242) phenyl p-xenyl ketone (p-phenylbenzophenone) [Beil. VII-521, VII₁-(290)], scales from alc., m.p. 106° cor. (270), 106° (272) (273), 102-103° (275), 102° (271), 101-102° (242), 101° (276); b.p. 413° at 758 mm. (271), 419-420° at 744 mm. (274), 258° at 10 mm. (276) (corresp. oxime exists in two stereoisomeric forms (277), m.p. 200° and 173°, usual mixt. having m.p. 193-194° (278), 186-187° (271); corresp. 2,4-dinitrophenylhydrazone, m.p. 217-217.5° (271); for use of P₂O₅ (instead of AlCl₃) in prepn. of p-phenylbenzophenone (above) see (279). Note that the isomeric o-phenylbenzophenone, m.p. 86-87°, has been prepared indirectly (280)]

[\bar{C} with naphthalene (1:7200) in pres. of AlCl₃ in CS₂ (281) (282) (283) (284) (285) (286) or without solvent at 150° (286), or in liq. SO₂ (287), or \bar{C} with naphthalene in pres. of ZnCl₂ at 125° (286) cf. (288) (289) or of P₂O₅ (289) (279) (259) (260), gives (yields: 85% (282), 52% (287)) mainly phenyl α -naphthyl ketone (1-benzoylnaphthalene) [Beil. VII-510, VII₁-(283)], pr. from alc., m.p. 75.5-76° (276), 75.5° (282), 75-76° (281), 75° (283), b.p. 386° at 764 mm. (284), 222° at 8 mm. (276); note that this prod. is usually accompanied by some phenyl β -naphthyl ketone (2-benzoylnaphthalene) [Beil. VII-511, VII₁-(283)], ndls. from alc., m.p. 82° (276) (289), 81-83° (281), b.p. 398° at 754 mm. (284), 225° at 8 mm. (276).]

[For reaction of \tilde{C} with anthracene (1:7285) + AlCl₃ in CS₂ (277) (290) (291) (292) (293), or in nitrobenzene at -10° (294), or without AlCl₃ in boiling nitrobenzene (295) giving (yields: 85% (277), 78% (290)) 9-benzoylanthracene (α -anthraphenone) [Beil. VII-538], cryst. from EtOAc, m.p. 145.5-146° (277), see indic. refs.; note, however, that for prepn. of this prod. use of benzoic anhydride (1:0595) (rather than \tilde{C}) is preferred (296). — For reaction of \tilde{C} with phenanthrene (1:7240) + AlCl₃ in CS₂ (297) (298) or in nitrobenzene (298) see indic. refs.]

With heterocyclic parent nuclei. The behavior of \tilde{C} with furan (1:8015) in the pres. of Friedel-Crafts cat. has apparently not been reported [however, the prod. to be expected, viz., phenyl α -furyl ketone [Beil. XVII-348, XVII₁-(186)], b.p. 285° at 759 mm. (299), 186° at 46 mm. (299), 164° at 19 mm. (299), $D_{-}^{20} = 1.1732$ (300), $D_{10}^{19} = 1.1839$ (299), $D_{-}^{20} = 1.6055$ (299), 1.5798 (300), has been obtd. (49% yield (301)) from benzoic anhydride (1:0595) with furan (1:8015) + SnCl₄ in C₆H₆, and from furoyl chloride (3:8515) with C₆H₆ in pres. of AlCl₃ (299).]

[Č with thiophene in pres. of AlCl₃ (302), SnCl₄ (303) (304), P_2O_5 (305), or α -thienyl-mercuric chloride (306) cf. (307) (308) gives (yields: 89-90% (302), 82.5% (304)) phenyl α -thienyl ketone [Beil. XVII-348, XVII₁-(187)], m.p. 56° (305) (307), 55.5-56° (306), 55-56° (302), 55° (303) (304).]

BEHAVIOR OF C WITH ORGANIC HYDROXYL COMPOUNDS

Č with organic OH or SH compounds (or their metallic salts) gives in general the corresponding benzoates. With phenols, however, there is also the additional possibility (according to the conditions employed) of either direct nuclear benzoylation or Fries rearrangement of the benzoate esters to give phenolic ketones.

Esterification of alcohols or phenols with \bar{C} in presence of aqueous alkali comprises a general procedure first discovered by Lossen (309) and later developed and extended by Schotten, Baumann, and others. The reaction is not restricted to the use of benzoyl chloride but covers acid haldes in general, e.g., acetyl chloride, p-nitrobenzoyl chloride, 3,5-dinitrobenzoyl chloride, benzenesulfonyl chloride, etc.

For detailed quantitative study of the influence of conditions on the Schotten-Baumann reaction see (310); for study of its application to p-nitrobenzoyl chloride (311) or of 3,5-dinitrobenzoyl chloride (312) in the derivatization of alcohols in dilute aqueous solution see indic. refs.; for study of substitution of the acyl halide by the corresponding anhydride see (313).

Note that in general the yield of ester is improved by use of low temperature (0°-25°) (310), by use of relatively concentrated solutions of both the hydroxyl compound and the alkali (310), and sometimes by additions of NaOAc or other salts. (311).

With monohydric alcohols. C with monohydric alcs. gives the corresponding alkyl benzoates.

[E.g., \bar{C} with MeOH (1:6120) gives methyl benzoate (1:3586), b.p. 199.6°, m.p. -12.5° (for study of rate of reaction at 0° and 25° see (18)). $-\bar{C}$ with EtOH (1:6130) gives ethyl benzoate (1:3721), b.p. 213.2°, m.p. -34.2° (for study of rate of esterification at 0° (17) or at 25° in various solvents (314) see indic. refs. $-\bar{C}$ with n-PrOH (1:6150) gives n-propyl benzoate (3:3917), b.p. 231°. $-\bar{C}$ with isopropyl alc. (1:6135) gives isopropyl benzoate (1:3766), b.p. 218.5° (for study of rate of esterification at 25° (6) or at 30° (11) (315) see indic. refs.).

[Č with n-BuOH (1:6180) gives n-butyl benzoate (1:4104), b.p. 250.3°, m.p. -22.4° . — Č with isobutyl alc. (1:6165) gives isobutyl benzoate (1:4006), b.p. 242.2° cor. — Č with sec-BuOH (1:6155) gives (yields: 75% (316), 66% (317), 20% (318)) sec-butyl benzoate [Beil. IX-112, IX₁-(63)], b.p. 234.5–235.5° cor. at 757 mm. (317), 148–151° at 50 mm. (317), 115–117° at 20° (319), 112–116° at 14 mm. (318), $D_4^{25} = 0.9945$ (°17), $D_1^{21.3} = 1.4933$ (319). — Č with ter-BuOH (1:6140) in pres. of pyridine gives (yields. 86% (320), 80% (321) (322)) ter-butyl benzoate [Beil. IX₁-(64)], b.p. 112° at 18 mm. (321), 91–92° at 8 mm. (323), 91.3° at 7.5 mm. (320), 96° at 2 mm. (322); $D_4^{25} = 0.9928$ (322); $D_2^{25} = 1.4896$ (322) (321), $D_2^{25} = 1.4910$ (320).]

[$\tilde{\mathbf{C}}$ with n-AmOH (1:6205) gives n-amyl benzoate [Beil. IX₁-(64)], b.p. 138-139° at 15 mm. (316), 137-138° at 15 mm. (324). — $\tilde{\mathbf{C}}$ with isoamyl alc. (1:6200) gives isoamyl benzoate (1·4166), b.p. 262.3° cor. at 760 mm. — $\tilde{\mathbf{C}}$ with neopentyl alc. (1:5812) gives (325) neopentyl benzoate, b.p. 235-237° at 740 mm., 110-111° at 10 mm., $D_{25}^{25} = 0.9817$, $n_{D}^{25} = 1.4875$ (325).]

C reacts with other alcohols and thiols similarly, but details cannot be tabulated here.

With phenols. \bar{C} can react with phenols in either or both of two modes; on one hand it can benzoylate the phenolic OH yielding the corresponding phenol benzoates (a list of the melting points of 88 phenols of Order 1 is given on page 638 of Vol. I of this series (326); for study of effect of structure on rate of benzoylation of various monohydric phenols see (329)); on the other hand \bar{C} may under certain conditions effect the direct nuclear benzoylation of phenols. Since the phenolic ketones thus formed may also be more or less readily obtained by catalyzed rearrangement of the phenol benzoates, the chemistry of the phenol

benzoates and their rearrangement products is so voluminous that it cannot here be given detailed discussion. [For extensive reviews of the Fries rearrangement (327) (328) of phenol esters (including the benzoates) see indic. refs.]

With enols (or their metallic derivatives). With methyl acetoacetate. [\bar{C} with the Na enolate of methyl acetoacetate (1:1705) gives (330) methyl α -benzoylacetoacetate, b.p. 136-137° at 2 mm. (corresp. Cu enolate, blue-green ndls. from dioxane, m.p. 226-228°; corresp. semicarbazone, prepd. by indirect means, m.p. 166° (331)).]

With ethyl acetoacetate. [\bar{C} with the Na enolate of ethyl acetoacetate (1:1710) gives (yields: 74.8% (332), 67% (333), 63–75% (334) cf. (335) (337) ethyl α -benzoylacetoacetate [Beil. X-817, X₁-(396)], b.p. 202° at 50 mm. (335), 177–181° at 20 mm. (334), 175–176° sl. dec. at 12 mm. (337), 169° sl. dec. at 11 mm. (338), 165–167° at 10 mm. (333) (corresp. Cu enolate, m.p. 224° (336), 221–222° (339)). Note that this prod. upon cleavage of the acetyl group, e.g., with aq. NH₄OH + NH₄Cl, gives (77–78% yield (334)) (332) ethyl benzoylacetate (1:1778), for alternative prepn. of which see (340). — Note, however, that two forms of the isomeric ethyl O-benzoylacetoacetate are known (341); a liq. form, b.p. 153–155° at 3 mm., prepd. from ethyl acetoacetate (1:1710) with \bar{C} + pyridine, and a solid form, m.p. 42°, prepd. from the Cu enolate of ethyl acetoacetate (1:1710) with \bar{C} in ether (for much further detail see (341)).]

With acetylacetone. [C with the Na enolate (342) or K enolate (343) of acetylacetone (1:1700) in ether gives (50% yield (343)) C-benzoylacetylacetone (α -benzoyl- α -acetylacetone) [Beil. VII-865, VII₁-(474)], m.p. 35° (342), 34-35° (343), b p. 167° at 22 mm. (342), accompanied by some of the higher-melting form, m.p. 103° (342), 102-103° (343), of its benzoate [Beil. IX-156]; note that the lower-melting form, m.p. 66-67° (344), is obtd from α -benzoyl- α -acetylacetone (above) with \bar{C} in pyridine (344).]

With benzoylacetone. [Č with Na enolate of benzoylacetone (1:1450) under various conditions gives (345) (346) (347) cf. (348) α,α -dibenzoylacetone [Beil. VII-872, VII₁-(480)] (q.v. for constants of various enol and keto forms) and/or the corresp. benzoate [Beil. IX-157], m.p. 87-88° (349).]

With dibenzoylmethane. [C with Na enolate of dibenzoylmethane (1:1480) gives (45% yield (350)) (351) (352) (353) tribenzoylmethane [Beil. VII-877, VII₁-(485)] (q.v. for constants of various forms) and/or the corresp. benzoate [Beil. IX-158], m.p. 121-122° (351).]

BEHAVIOR OF C WITH ETHERS

With aliphatic ethers. Acyl chlorides with aliphatic ethers do not react even at elevated temperatures (354) although acid bromides (e.g., acetyl bromide (355)) or acyl iodides (e.g., benzoyl iodide (356)) are able to effect cleavage into alkyl halides and alkyl esters. However, when acyl chlorides are heated with aliphatic ethers in the presence of certain metallic salts, cleavage of the ethers is more or less readily effected. Although the topic cannot here be pursued exhaustively, several examples are cited in the following text.

[Č with diethyl ether (1:6110) on htg. in pres. of ZnCl₂ (354) (357) (358) (359) (360), SnCl₄ (358), ZrCl₄ (358), TiCl₄ (358) (362), SbCl₅ (358), FeCl₃ (358) (361), AlCl₃ (358) (362), or SbCl₅ (358) gives ethyl benzoate (1:3721); note, however, that use of BF₃, CuCl₂, and SnCl₂ gives only traces while SiCl₄, PCl₅, PCl₅, BCl₃, AsCl₃, or MgCl₂ achieves no cleavage (358) of the ether. Note that by extension of the ZnCl₂ method to use of 3,5-dinitrobenzoyl chloride a procedure for the identif. of ethers as the corresp. alkyl 3,5-dinitrobenzoates has been described (363) cf. (364).]

With phenol ethers. With phenol ethers where no phenolic OH remains to interfere, C reacts in the pres. of suitable cat. in the Friedel-Crafts sense. Although the topic cannot here be pursued exhaustively, several examples are cited in the following text.

[\bar{C} with methyl phenyl ether (anisole) (1:7445) + AlCl₃ in CS₂ solution (81% yield (365)) (366) (367) cf. (368) (360) or without other solvent (369) gives mainly p-anisyl phenyl ketone (p-methoxybenzophenone) (1:5170), m.p. 62° (366) (367) (370), 61-62° (365) (369), 61° (371), b.p. 354-355° at 729 mm. (371); this prod. is accompanied by some o-anisyl phenyl ketone (o-methoxybenzophenone) (1:5142), m.p. 39°, which is separable from the main prod. only by repeated recrystallization from lgr. (b.p. 40-60°) and alc. (369).]

[\bar{C} with ethyl phenyl ether (phenetole) (1:7485) + AlCl₃ in CS₂ soln. (yields: 83% (372), 73% (374)) (369) (366) (373) or without other solvent (369) gives mainly p-phenetyl phenyl ketone (p-ethoxybenzophenone) [Beil. VIII-159, VIII₁-(569)], m.p. 47-48° (374), 47° (369) (372), 46.5° (373), 38-39° (366), b.p. 245-250° at 25 mm. (374), 227° at 21 mm. (373), 215-225° at 15 mm. (373) (corresp. oxime, m.p. 135-136° (374)), accompanied by some o-phenetyl phenyl ketone (o-ethoxybenzophenone) which (although not further characterized) is liq. and readily separable.]

[\bar{C} with diphenyl ether (1:7125) + AlCl₃ in CS₂ (375) (376) (374), or \bar{C} with diphenyl ether (1:7125) + HgCl₂ at 150–160° (377) (27% yield), or \bar{C} with phenyl 4-chloromercuriphenyl ether at 150° (377), gives (yields: 97% (375), 95% (374), 70% (377)) p-phenoxy-benzophenone [Beil. VIII-159], m.p. 71° cor. (375), 70–71° (374), 66° (377) (corresp. oxime, m.p. 124° (374)); for further benzoylation of this prod. to bis-(p-benzoylphenyl) ether, m.p. 163–164°, see (376).]

[Č with methyl α -naphthyl ether (1:7630) + AlCl₃ in CS₂ (378) or in nitrobenzene (379) gives (84% yield (379)) 4-benzoyl-1-methoxynaphthalene, m.p. 82–83° (378), 81–82° (379); for high-press. hydrogenation of this prod. giving (84–86% yield) 4-benzyl-1-methoxynaphthalene, m.p. 83–84°, see (379). — Č with methyl β -naphthyl ether (1:7180) + AlCl₃ in CS₂ gives (85% yield (380)) 1-benzoyl-2-methoxynaphthalene, m.p. 125° cor.; not that use of 1,1,2,2-tetrachloroethane as solvent is much less satisfactory (381). — Č with ethyl α -naphthyl ether (1:7635) + AlCl₃ in CS₂ gives (366) (382) 4-benzoyl-1-ethoxynaphthalene [Beil. VIII-207, VIII₁-(586)], m.p. 74–75° (366), accompanied (383) by some 4-benzoylnaphthol-1 and other products. — The presumably analogous reaction of Č with ethyl β -naphthyl ether (1:7135) + AlCl₃ appears not to have been studied, and the expected 1-benzoyl-2-ethoxynaphthalene is unreported.]

Behavior of \bar{C} with Acids (or Their Salts)

With sodium formate. [C with NaOOCH on htg. (384) gives BzOH (1:0715), CO, + HCl.]

With acetic acid. [\bar{C} with AcOH (1:1010) refluxed in pres. of charcoal (385), or in pres. of a tertiary base (386) even at ord. temp., or \bar{C} with NaOAc on warming (387) cf. (388) (389) gives the mixed anhydride, CH₃.CO.O.CO.C₆H₅ [Beil. IX-163], accompanied by various other products. Note, however, that \bar{C} with AcOH (1:1010) at 100° for 3 hrs. gives (70% yield (147)) acetyl chloride (3:7065) while \bar{C} with Ac₂O (1:1015) at 100° for 1 hr. gives (77% yield (147)) acetyl chloride (3:7065) accompanied by benzoic anhydride (1:0595). For prepn. of acetic-benzoic anhydride by other means, e.g., from benzoic acid (1:0715) with ketene (390), and for study of its use in Friedel-Crafts type reactions (391), see indic. refs.]

With benzoic acid. [C with benzoic acid (1:0715) in s.t. at 160-200° for 12 hrs. (392), or at 220° under reduced press. (397), or with pyridine (389) (393), or C with NaOBz shaken with aq. (394) or htd. at 130° (395), gives benzoic anhydride (1:0595), m.p. 42°, b.p. 360°; for other modes of formn. of this prod. from C see above under behavior of C with various inorganic salts; for prepn. (72-74% yield) of benzoic anhydride (1:0595) from benzoic acid (1:0715) by use of acetic anhydride (1:1015) see (396).]

With HCN. [Č with dry HCN in pyridine + ether (398) (399) cf. (406), or Č with HgCN (400) (401) (403) (404), AgCN (402), or CuCN (12), gives (yields: 78% (399), 60-65% (12)) benzoyl cyanide (phenylglyoxylic acid nitrile) [Beil. X-659, X₁-(314)], m.p. 34° (401), 32.5-34° (403), 32-33° (12), b.p. 208-209° at 745 mm. (12), 207-210° (402), 206-208° (404), 123° at 42 mm. (401), 99° at 19 mm. (405). Note that by the HCN/pyridine method (398) (399) (406) or by reaction of Č with aq. KCN (402) dimeric benzoyl cyanide [Beil. XIX-362], m.p. 99-100° (402), 95-96° (406), is also formed; further that benzoyl bromide with AgCN gives (402) a trimeric benzoyl cyanide, m.p. 195°.]

With cyanate or thiocyanate salts. [\bar{C} with K cyanate (407), KSCN (408), or NH₄SCN (409) gives benzonitrile [Beil. IX-275, IX₁-(121)], \bar{B} .p. 191.3° at 760 mm., but \bar{C} with Pb(SCN)₂ at 160° (410), at 120° (413), or refluxed in C₆H₆ (411) (412) gives benzoyl isothiocyanate [Beil. IX-222, IX₁-107], b.p. 119° at 10 mm. (412), $D_4^{18.3} = 1.2142$ (412), $n_B^{18.5} = 1.6382$ (412).]

BEHAVIOR OF C WITH ORGANIC NITROGEN COMPOUNDS

Č reacts with primary and secondary amines to replace one of the amino hydrogen atoms by the benzoyl radical. The molecule of HCl thus split out will, of course, convert a second molecule of amine to its hydrochloride. In order to avoid this waste of amine, the benzoylation may be effected in the presence of aqueous alkali (Schotten-Baumann reaction) or of pyridine (Einhorn reaction). Since the number of amino compounds which undergoes benzoylation is legion, the present text will be restricted to a relatively few important cases.

With aliphatic primary amines. [C with aq. CH₃NH₂ (414) in pres. of alk. (415) gives N-methylbenzamide [Beil. IX-201, IX₁-(97)], cryst. from alc. (416), aq. (417), or $\lg r./C_6H_6$ (418), m.p. 82° (416), 80-81° (418) (419), 79.8° (417), 79° (414), 78° (415), b.p. 291° at 765 mm. (419), 167° at 11 mm. (420). — \bar{C} with aq. $C_2H_5NH_2$ (414) gives N-ethylbenzamide [Beil. IX-202, IX₁-(97)], ndls. from aq., m.p. 71° (419), 70° (421), 69° (417), 68-69° (414), 67° (420), b.p. 285° at 745 mm. (419). — \bar{C} with $n-C_3H_7NH_2$ presumably yields $N-(n-C_3H_7NH_2)$ propyl)benzamide [Beil. IX-203, IX₁-(97)], cryst. from alc. or C₆H₆, m.p. 84.5° (419), 83° (422), b.p. 294-295° sl. dec. (422), but this product has been reported only by other methods (419) (422). — \bar{C} with $n-C_4H_9NH_2$ presumably gives N-(n-buty) benzamide but this product has been characterized only as an oil cf. (423). — C with isobutylamine + aq. NaOH (416) cf. (424) gives N-(isobutyl) benzamide [Beil. IX-203, IX₁-(97)], ndls. from C_6H_6 , CHCl₃, alc., or lgr.), m.p. 57-58° (416), 57° (419), 55° (424), 54° (422), b.p. 295-296° sl. dec. at 760 mm. (419), 173-178° at 13 mm. (416). — C with sec-C₄H₉NH₂ should give N-(secbutyl)benzamide but the d,l-form of this product is unreported; note that its dextrorotatory form has been reported as m.p. 92° (425) or 86-88° (426); the levorotatory form as m.p. 88-89° (425). — \bar{C} with $ter-C_4H_9NH_2$ in other (427) (428) gives N-(ter-butyl) benzamide [Beil. IX₁-(97)], ndls. from ether/ C_6H_6 , m.p. 136.5° (428), 135.5° (427), 134-135° (429), 134° (430). Note that dibenzoylation does not occur and that N-methyldibenzamide [Beil. IX₁-(104), m.p. 94-95° (435), and N-ethyldibenzamide [Beil. IX-214], m.p. 101-102° (436), have been prepared only by indirect means.

With aliphatic secondary amines. [\bar{C} with $(CH_3)_2NH$ in ether (431), in aq. (414), or in aq. NaOH (405) gives N,N-dimethylbenzamide [Beil. IX-201, IX₁-(97)], cryst. from CS₂/pet. ether (405), m.p. 43° (405), 41-42° (431), 41° (414), b.p. 272-273° (420), 265-266° (432), 132-133° at 15 mm. (432). — \bar{C} with $(C_2H_5)_2NH$ in ether (431) gives N,N-diethylbenzamide [Beil. IX-202], liquid, b.p. 280-282° cor. (431), 278-282° (433), 173-175° at 35 mm. (434). — Note that the analogous N,N-dialkylbenzamides to be expected from reaction of \bar{C} with di-n-propylamine, di-isopropylamine, di-n-butylamine, di-isobutylamine, di-sec-butylamine, and di-n-butylamine have not been characterized.]

With aromatic primary amines. See below under @'s.

With aromatic secondary amines. \bar{C} with aromatic secondary amines gives the corresponding N-benzoyl derivatives but note that these same products are frequently also obtained by reaction of \bar{C} with the appropriate tertiary amines.

[Č with N-methylaniline (437), or Č with N,N-dimethylaniline at 190° (438), gives N-benzoyl-N-methylaniline (N-methylbenzanilide) [Beil. XII-269], scales from lgr., m.p. 63° (438), 59° (437), b.p. 331-332° (439). — Č with N-ethylaniline (not actually reported) or Č with N,N-diethylaniline at 200° (438) gives N-benzoyl-N-ethylaniline (N-ethylbenzanilide) [Beil. XII-270], cryst. from ether + lgr., m.p. 54° (440), 52° (441), 60° (438).]

[\bar{C} with N-methyl-o-toluidine should yield N-benzoyl-N-methyl-o-toluidine (N-methyl-benzo-o-toluidide) [Beil. XII-796], pr. from ether/lgr., m.p. 65-66°, and \bar{C} with N-ethyl-o-toluidine should yield N-benzoyl-N-ethyl-o-toluidine (N-ethyl-benzo-o-toluidide) [Beil. XII-796], pr. from ether/lgr., m.p. 71-72°, but both these products have been reported only by indirect means (442). — The analogous products to be expected from \bar{C} with N-methyl (or N-ethyl)-m-toluidine, or \bar{C} with N-methyl (or N-ethyl)-p-toluidine, have not been characterized in the literature.]

[$\bar{\mathbf{C}}$ with N-methyl-α-naphthylamine should yield N-benzoyl-N-methyl-α-naphthylamine [Beil. XII-1234], cryst. from $\mathbf{C_6H_6/lgr.}$, m.p. 121°, but this prod. has actually been reported only from $\bar{\mathbf{C}}$ with N,N-dimethyl-α-naphthylamine at 170–190° (438). — Similarly, $\bar{\mathbf{C}}$ with N-methyl-β-naphthylamine + aq. alk. yields (443) N-benzoyl-N-methyl-β-naphthylamine [Beil. XII-1287, XII₁-(539)], ndls. from pet. eth., m.p. 84° (443); this prod. is also claimed (438) from N,N-dimethyl-β-naphthylamine at 170–180° but the m.p. of 169° is not in accord with the later work under mild conditions and presumably represents an isomeric material. — The analogous benzoyl derivatives of N-ethyl-α-naphthylamine and of N-ethyl-β-naphthylamine are unreported.]

[C with diphenylamine on warming (444) in ether soln. (445) gives N-benzoyldiphenylamine (N,N-diphenylbenzamide) [Beil. XII-270, XII₁-(201)], cryst. from alc., m.p. 180° (435), 179-180° (446), 177° (447).]

 $\bar{\mathbf{C}}$ with heterocyclic secondary amines. $\bar{\mathbf{C}}$ with piperidine [Beil. XX-6, XX₁-(5)] directly (536) or better in aq. NaOH (537) (538) (539) gives (87-91% yield (537)) N-benzoyl-piperidine [Beil. XX-46, XX₁-(15)], m.p. 49° (540), 48° (538), 44° (537); b.p. 320-321° (541), 240-244° at 130 mm. (537), 195° at 25 mm. (541), 180-184° at 20 mm. (537), 172-174° at 12 mm. (537); not volatile with steam (538). [Note that this prod. with PBr₅ (542) (543) (544) (545) (546), with PBr₃ + Br₂ (547), or with PCl₃ + Br₂ (548) comprises an important method of preparation of pentamethylene dibromide (1,5-dibromopentane).]

Č with morpholine [Beil. XXVII-5] in ether gives (549) N-benzoylmorpholine, eas. sol. aq., pr. from dry ether, m.p. 74-75° (549).

Č with aromatic diamines. [Č with o-phenylenediamine [Beil. XIII-6, XIII₁-(5)] in aq. NaOH (448), or Č with o-phenylenediamine hydrochloride in aq. soln. (449), gives N,N'-dibenzoyl-o-phenylenediamine [Beil. XIII-21, XIII₁-(8)], ndls. from AcOH, m.p. 301° (450), about 300° dec. (451). — Note that this prod. on htg. above m.p. (450), or on htg. with conc. HCl in s.t. at 200° (449), gives 2-phenylbenzimidazole [Beil. XXIII-230, XXIII₁-(61)], m.p. variously reported around 290°, which latter, although stable toward Č at 260° (452), yet with Č + aq. NaOH in cold (450) reverts to N,N'-dibenzoyl-o-phenylenediamine (above). — Note that N-benzoyl-o-phenylenediamine [Beil. XIII-20, XIII₁-(8)], m.p. 140° (453), has been reported only by indirect means (453) (454); on htg. 2 hrs. at 140° followed by a few minutes at 280° (455) it gives 2-phenylbenzimidazole (see above). — Note finally that 1-benzoylbenzimidazole [Beil. XXIII-133, XXIII₁-(35)], m.p. 93-94° (456), 91-92° (450), on htg. with Č (457), or benzimidazole itself with Č + aq. NaOH (450), both give N,N'-dibenzoyl-o-phenylenediamine (above).]

[C with hydrochloride of m-phenylenediamine [Beil. XIII-33, XIII₁-(10)] on htg. gives

(458) N, N'-dibenzoyl-m-phenylenediamine [Beil. XIII-46], ndls. from AcOH, m.p. 240° (458) (460); for behavior of this prod. with PCl₅ see (459). — Note that N-benzoyl-m-phenylenediamine (benz-m-aminoanilide) [Beil. XIII-46], m.p. 125°, has been reported only by indirect means (461) (462) (464).]

[Č with p-phenylenediamine [Beil. XIII-61, XIII₁-(18)] + aq. NaOH (448) cf. (463) gives N,N'-dibenzoyl-p-phenylenediamine [Beil. XIII-98], m.p. above 300° (448) cf. (460); for behavior of this prod. with PCl₅ see (459). — Note that N-benzoyl-p-phenylenediamine (benz-p-aminoanilide) [Beil. XIII-98, XIII₁-(31)], m.p. 128° (452) (464), has been reported only by indirect means (452) (464).]

Č with aminophenols. Č with o-aminophenol [Beil. XIII-354, XIII₁-(108)] gives according to circumstances one of the two possible monobenzoyl derivatives, viz., o-(benzoylamino)phenol [Beil. XIII-372, XIII₁-(115)] (or its ring-closure product, 2-phenylbenzoxazole-1,3 [Beil. XXVII-72, XXVII₁-(235)]), or the dibenzoyl derivative, viz., o-benzoylaminophenyl benzoate [Beil. XIII-373], as more fully described below. Note, however, that the other monobenzoyl derivative of o-aminophenol, viz., O-benzoyl-o-aminophenol or o-aminophenyl benzoate, known only as its hydrochloride, m.p. 149° (465), has been prepared only by indirect means (465) viz., from O,N-(dibenzoyl)-o-aminophenol, and on heating, or even on recrystn., loses HCl giving (465) 2-phenylbenzoxazole-1,3.

[$\bar{\mathbb{C}}$ (1 mole) with o-aminophenol (2 moles) in dry ether (466) gives o-(benzoylamino)-phenol (N-benzoyl-o-aminophenol), tbls. from MeOH (465), lfts. from $\mathbb{C}_6\mathbb{H}_6$, m.p. 169–171° u.c. (465), 169° (467), 167° (468) (corresp. acetate, m.p. abt. 140° (469) cf. (470); corresp. benzoate, m.p. 182° (470) (also below); corresp. benzenesulfonate, m.p. 90.5–91.0 (471)). — Note that this prod. on htg. above m.p. loses $\mathbb{H}_2\mathbb{O}$ with ring closure yielding (468) 2-phenyl-benzoxazole-1,3, m.p. 103° (see below). — Note also that o-(benzoylamino)phenyl benzoate (above) with $\bar{\mathbb{C}}$ in nitrobenzene refluxed 12 hrs. gives (479) o-(dibenzoylamino)phenyl benzoate, m.p. 170.5–171.5° (479).]

[C with o-aminophenol on warming, followed by distn. of reaction product (472), or C with o-aminophenol hydrochloride (468) (473) gives 2-phenylbenzoxazole-1,3, ndls. from dil. alc., lfts. from dil. HCl or dil. H₂SO₄, m.p. 103° (468) (472) (473) (474), volatile with steam, b.p. 314-317° (472) (corresp. B.PkOH, m.p. 104° (477), corresp. MeI quaternary salt, m.p. 196° dec. (478)).

[$\ddot{\mathbf{C}}$ (2 pts.) with o-aminophenol in aq. NaOH (448) or in pyridine + CHCl₃ (465), or $\ddot{\mathbf{C}}$ with o-aminophenol hydrochloride in $\mathbf{C}_6\mathbf{H}_6$ at 100° (468), or $\ddot{\mathbf{C}}$ + aq. NaOH with o-formylaminophenol (480), o-(acetylamino)phenol (481), or o-(benzoylamino)phenol (467), gives O,N-dibenzoyl-o-aminophenol (o-benzoylaminophenyl benzoate), ndls. from alc. (480) or EtOAc (465), m.p. 185° (467), 183–184.5° (480), 182–183° (482), 181–182° (476), 180° (481), 179° u.c. (465). — Note that this prod. on boilg. with aq. BaCO₃ (468) or for 2 days with alc. HCl (483) hydrolyzes at the ester leakage giving o-(benzoylamino)phenol, m.p. 169° (above).]

[Č with m-aminophenol [Beil. XIII-401, XIII₁-(128)] in pyridine + ether (484) cf. (485) gives m-(benzoylamino)phenol [Beil. XIII-416], ndls. from toluene, m.p. 174° (485) (486), 173° (484). — Note that the isomeric G-benzoyl-m-aminophenol (m-aminophenyl benzoate) is unreported. — Č with m-aminophenol in aq. NaOH gives (486) O,N-dibenzoyl-m-aminophenol (m-(benzoylamino)phenyl benzoate) [Beil. XIII-416], pr. from C₀H₆ or scales from abs. alc., m.p. 153° (486); this product with boilg. alc. KOH splits at the ester linkage giving (486) m-(benzoylamino)phenol (above), m.p. 174°.]

[C with p-aminophenol [Beil. XIII-427, XIII₁-(143)] in aq. NaOH (487), in pyridine (488), in alc. (489), or in ether + aq. NaOH (490) gives p-(benzoylamino)phenol (N-benzoyl-p-aminophenol) [Beil. XIII-469, XIII₁-(165)], cryst. from AcOH, m.p. 216-217° (487), 214-215° (489) (for review of earlier confusion see (487)). — Note that the isomeric O-

benzoyl-p-aminophenol (p-aminophenyl benzoate) [Beil. XIII-440], m.p. 153-154° (491) (492), 148° (465), has been reported only by indirect means. — Č with p-aminophenol on htg. (472), or in aq. NaOH (448) (487) (488) or in pyridine (488), or Č with p-aminophenol hydrochloride (489) gives O,N-dibenzoyl-p-aminophenol (p-(benzoylamino)phenyl benzoate) [Beil. XIII-470, XIII₁-(165)], cryst. from MeOH, EtOH, AcOH, or xylene, m.p. 235° (487) (467), 233-234° (489), 231° (472).]

The acylation of aminophenols (especially of the ortho series) and the relationships of the various multiple and mixed acyl derivatives have been extensively studied by Raiford ((493)-(511), incl.), Nelson ((512)-(517), incl.), and Bell (518) (519); the cited papers are arranged in chronological sequence for each worker.

Č with tertiary amines. Č with certain tertiary amines especially in dry ether solution (520) forms addition products; these are presumably quaternary ammonium salts but have been very inadequately studied cf. (524).

[\bar{C} with Me₂N in ether at 0° or in C₆H₆ at 80° fails to react (525). — \bar{C} with Et₂N in dry ether gives an immediate ppt. which increases on stdg. but appears to be a mixture of the expected addn. prod., \bar{C} . Et₂N, with triethylamine hydrochloride (520). — \bar{C} with triamylamine in dry ether after stdg. 2 months yields (520) long needles, m.p. 117°, whose analysis is in accord with "nearly pure" addn. prod., \bar{C} . (C₅H₁₁)₂N.]

[\bar{C} with N,N-dimethylaniline in dry ether in sunlight gives gradually hygroscopic crystals probably comprising the expected addn. prod., $\bar{C}.C_8H_{11}N$, (520). — \bar{C} with N,N-diethylaniline in dry ether gives (520) a crystn. prod. containing 71% of the expected $\bar{C}.C_{10}H_{16}N$.]

[\bar{C} with pyridine in dry ether gives (520) a ppt. apparently contg. only 31% of the expected addn. prod., $\bar{C}.C_5H_5N.-\bar{C}$ with pyridine in C_6H_6 gives (521) pyridine hydrochloride, m.p. 144°. — For study of \bar{C} with pyridine in pres. of Zn dust giving the free radical N-benzoylpyridinium see (522); for study of \bar{C} with pyridine + N,N-dimethylaniline + Cu powder at 100° for 5 hrs. giving 4-(p-dimethylaminophenyl)pyridine see (523).]

Note that \bar{C} with pyridine in pres. of various inorganic salts gives benzoic anhydride; for further details see text above under behavior of \bar{C} with miscellaneous inorganic salts.

 $\bar{\mathbf{C}}$ with arylhydrazines. $\bar{\mathbf{C}}$ (1 mole) with phenylhydrazine (2 moles) [Beil. XV-67, XV₁-(23)] in dry ether gives (526) N'-benzoyl-N-phenylhydrazine (also known as sym.-benzoyl-phenylhydrazine or β-benzoylphenylhydrazine) [Beil. XV-255, XV₁-(67)], pr. from alc., m.p. 168° (526) (527). [Note that the isomeric N-benzoyl-N-phenylhydrazine (also known as asym.-benzoyl-phenylhydrazine or α-benzoyl-phenylhydrazine) [Beil. XV-250, XV₁-(65)], m.p. 70°, has been obtained only by indirect means, e.g., from $\bar{\mathbf{C}}$ with sodio-phenylhydrazine (528) or from N-chlorobenzanilide with NaNH₂ (529). However, $\bar{\mathbf{C}}$ with phenylhydrazine hydrochloride in boilg. C_6H_6 (530) (531), or $\bar{\mathbf{C}}$ with dry K phenylhydrazine-β-sulfonate on htg. (526), or $\bar{\mathbf{C}}$ with α-benzoyl-phenylhydrazine in ether (532), or $\bar{\mathbf{C}}$ with β-benzoyl-phenylhydrazine on htg. (526), gives N,N'-dibenzoyl-N-phenylhydrazine (also called α,β-dibenzoyl-phenylhydrazine) [Beil. XV-261, XV₁-(68)], pr. from alc., m.p. 177–178° (526) (530); note that this prod. on hydrolysis with alc. NaOH gives (533) β-benzoyl-phenylhydrazine (above).]

 \tilde{C} with p-nitrophenylhydrazine [Beil. XV-468, XV₁-(130)] presumably gives N'-benzoyl-N-(p-nitrophenyl)-hydrazine [Beil. XV-479, XV₁-(140)], ndls. from alc., m.p. 193° (534), although this prod. is actually reported (534) only from benzoic anhydride (1:0595) with p-nitro-phenylhydrazine.

Č with 2,4-dinitrophenylhydrazine [Beil. XV-489, XV₁-(146)] in alc. suspension on warming gives (535) N'-benzoyl-N-(2,4-dinitrophenyl)-hydrazine [Beil. XV-492], or.-red lfts. from alc., m.p. 206-207° (535).

 \tilde{C} with diazomethane. [\tilde{C} added slowly to excess CH₂N₂ in ether at 0° gives (550) (551) (552) (553) ω -diazoacetophenone [Beil. VII-362, XXIV-142]; this product may be caused

to undergo the Wolff rearrangement giving (554) phenylacetoacetic acid derivs. (e.g., amide or anilide (554)), or may be caused to react with HCl to give phenacyl chloride (3:1212): for comprehensive survey and review of the behavior of acyl halides with diazomethane see (555).]

Č with miscellaneous nitrogen compounds. [For studies on the behavior of Č with indigo see (556) (557) (558) (559) (560) (561) (562) (563).]

BEHAVIOR OF C WITH ORGANOMETALLIC COMPOUNDS

Behavior of Č with Grignard reagents. Č with excess RMgX compounds in ether reacts in general to give the corresponding tertiary alcohols. Although extensive discussion of this reaction is manifestly infeasible here, the following examples are cited.

[C̄ with excess MeMgI gives (564) dimethyl-phenyl-carbinol [Beil. VI-506, VI₂-(477)]. — C̄ with EtMgI gives (93% yield (565)) diethyl-phenyl-carbinol [Beil. VI-548, VI₁-(269), VI₂-(506)]. — C̄ with n-PrMgBr gives (81% yield (565)) di-n-propyl-phenyl-carbinol [Beil. VI₁-(273), VI₂-(513)]. — C̄ with C₆H₅MgBr as directed gives (91.5% yield (565)) triphenylcarbinol [Beil. VI-713, VI₁-(349), VI₂-(686)] (1:5985) accompanied by (7% yield (565)) biphenyl (1:7175); for study of limiting reaction of C̄ with C₆H₅MgBr to formation of diphenyl ketone (benzophenone) (1:5150) see (566); note also that C̄ with C₆H₅MgBr in presence of CoCl₂ takes a different course yielding (567) benzoic acid, ethyl benzoate, biphenyl, benzophenone, phenylbenzoin, tetraphenylethylene oxide, and stilbene dibenzoate.]

[For interference of C with the Gilman color test for RMgX compounds see (568).]

[For study of relative reactivity of \bar{C} as compared with various other organic compounds in competition for C_6H_5MgBr see (569).]

Behavior of \tilde{C} with other miscellaneous organometallic compounds. This topic cannot be treated extensively, but the following examples, mainly from the recent literature, will serve as lead references.

- [$\bar{\mathbf{C}}$ with $\mathbf{C_6H_5Li}$ gives (570) no benzophenone and only 42% yield triphenylcarbinol (1:5985). $\bar{\mathbf{C}}$ with Na phenylacetylene (571) (572) or Ag phenylacetylene (572) gives (74% yield (571)) phenyl phenylethynyl ketone (benzoyl-phenylacetylene) [Beil. VII_498, VII_1-(275)].]
- $[\bar{C} + \text{EtCu} (573)]$ in ether gives (22% yield (573)) ethyl phenyl ketone (propiophenone) (1:5525). \bar{C} with C_6H_5Cu (573) in ether gives (55% yield (573)) benzophenone (1:5150).]
- $[\bar{C} + Et_2Hg \text{ gives (small yield (574)) propiophenone (1.5525).} --\bar{C} \text{ with (C_6H_6)_2Hg}$ in C_6H_6 gives (575) benzophenone (1:5150). -- \bar{C} with excess di-p-tolyl mercury in CCl₄ fails (576) to react.]
- [\bar{C} with Me₂Be gives (577) dimethyl-phenyl-carbinol [Bed. VI-506, VI₂-(477)]. \bar{C} with Me₂Cd gives (85% yield (578)) methyl phenyl ketone (acetophenone) (1:5515). \bar{C} with Et₂Cd gives (50% yield (578)) ethyl phenyl ketone (propiophenone) (1:5525). \bar{C} with (C₆H₅)₂Cd gives (57% yield (578)) diphenyl ketone (bezophenone) (1:5150). \bar{C} with Me₂Zn gives (579) methyl phenyl ketone (acetophenone) (1:5515). \bar{C} with Et₂Zn (580) (581) or with EtZnI (582) gives ethyl phenyl ketone (propiophenone) (1:5525).]
 - **D** Benzamide: cryst. from hot aq., m.p. 130°. [For methods of prepn. see above text under behavior of \tilde{C} with various inorganic nitrogen compounds.]
 - Benzanilide: lfts. from alc., m.p. 160°. [From C with aniline directly (583), in ether contg. dry K₂CO₃ (584), in C₆H₆ (585), in toluene (586), in pyridine (or other tertiary amines) (587), in dil. aq. HCl (588), in AcOH/aq. NaOAc (589), or aq. NaOH. For study of rate of reaction of C with aniline in aq. at various temperatures 0-60° (590),

- in C_6H_6 at 25° (591) cf. (585), in hexane at 25° (592), or in CCl₄ at 25° (592) see indic. refs. Note that \bar{C} with aniline hydrochloride in boilg. C_6H_6 gives almost quant yield (530) benzanilide.]
- Benz-o-toluidide: ndls. from AcOEt/acetone, m.p. 145-146° (594) (595), 144.3-144.6° cor. (586), 142-143° (593), 142° (587). [From C with o-toluidine (593) (594) in pres. of dil. (4%) aq. NaOH (595), or in pyridine (or other tertiary bases) (75% yield (587)), or in boilg. toluene (586).]
- Benz-m-toluidide: cryst. from dil. alc., m.p. 126° (587), 124.3-124.7° cor. (586), 125° (596). [From C with m-toluidine (596) in pyridine (or other tertiary bases) (80% yield (587)) or in boilg. toluene (586).]
- Benz-p-toluidide: ndls. from alc., m.p. 158° (597), 157.7-158.2° cor. (586), 157° (587).
 [From C with p-toluidine (598) (599) in pyridine (or other tertiary bases) (85% yield (587)) or in boilg. toluene (586).]
- Benz-α-naphthalide: ndls. from alc. or AcOH, m.p. 161-162° (600), 159-160° (601) cor. (608), 159° (587), 156° (602), 155-156° (603). [From C with α-naphthylamine (604) (602) in aq. NaOH (603), pyridine (or other tertiary bases) (80% yield (587)), or in AcOH/aq. NaOAc (589). For mol. cpd. of benz-α-naphthalide with 1,3,5-trinitrobenzene, viz., C. C₆H₃(NO₂)₃, yel. ndls. from alc. soln. of components, m.p. 131-132° (605); see indic. refs. For behavior of C with α-naphthylamine in pres. of ZnCl₂ at 175-180° yielding 1-benzoylamino-4-benzoylamphthalene, m.p. 178°, 1-benzoylamino-2,4-dibenzoylnaphthalene, m.p. 224-226°, etc., see (606) (607).]
- D Benz-β-naphthalide: ndls. from C_6H_6 or AcOH, m.p. 162–163° (609), 162° (587), 161° (612), 157° (610), 156.5–157° cor. (608). [From \bar{C} with β-naphthylamine (611) (610) in ether + K₂CO₃ (612), in pyridine (or other tertiary bases) (80% yield (587)), or in AcOH/ag. NaOAc (589).]
- Benzhydrazide: m.p. 112°. [See above text under behavior of C with various inorganic nitrogen compounds, specifically with NH₂.NH₂.]
- β-Benzoylphenylhydrazine (N-Anilinobenzhydrazide): pr. from alc., m.p. 168°.

 [See above text under behavior of C with organic nitrogen compounds, specifically with arylhydrazines.]
- —— β-Benzoyl-p-nitrophenylhydrazine (N-(p-nitroanilino)benzhydrazide): ndls. from alc., m.p. 193°. See above text under behavior of C̄ with organic nitrogen compounds, specifically with arythydrazines.
- 3:6240 (1) Herbst, Kolloidchem. Beihefte 23, 334 335 (1927). (2) Kopp, Ann. 95, 341-342 (1855) (3) Kamerling, Smyth, J. Am. Chem. Soc. 55, 463 (1933). (4) Martin, Partington, J. Chem. Soc. 1936, 1177. (5) von Rechenburg, J. prakt. Chem. (2) 101, 117 (1921). (6) Norris, Gregory, J. Am. Chem. Soc. 50, 1813-1816 (1928). (7) Perkin, J. Chem. Soc. 69, 1205 (1896) (8) Kohlrausch, Pongratz, Monatsh. 64, 379-380 (1934). (9) Koehl, Wenzke, J. Am. Chem. Soc. 59, 1418 (1937). (10) Hope, Riley, J. Chem. Soc. 121, 2511-2527 (1922). (11) Dann, Davies, Hambly, Paul, Semmens, J. Chem. Soc. 1933, 18, 20. (12) Oakwood, Weissgerber, Org. Syntheses 24, 14-16 (1944). (13) Kailan, Monatsh. 53/54, 159-164 (1929).
- (11) Dann, Davies, Hambly, Paul, Semmens, J. Chem. Soc. 1933, 18, 20. (12) Oakwood,
 Weissgerber, Org. Syntheses 24, 14-16 (1944). (13) Kailan, Monatsh. 53/54, 159-164 (1929).
 (14) Bruhl, Ann. 235, 10-11 (1886). (15) Adams, Uhlich, J. Am. Chem. Soc. 42, 604 (1920).
 (16) Herz, Kahovec, Kohlrausch, Monatsh. 74, 267-270 (1943). (17) Norris, Fasce, Staud, J. Am. Chem. Soc. 57, 1420 (1935). (18) Norris, Young, J. Am. Chem. Soc. 57, 1420-1424 (1935).
 (19) Thompson, Norris, J. Am. Chem. Soc. 58, 1955 (1936). (20) Kadesch, Weller, J. Am. Chem. Soc. 63, 1311 (1941).
- (21) Kahlbaum, Z. physik. Chem. 26, 611-612 (1898). (22) Menschutkin, J. Russ. Phys.-Chem. Soc. 42, 1311 (1910); Cent. 1911, 1481. (23) Lieben, Ann. 178, 43 (1875). (24) von Auwers, Schmidt, Ber. 46, 482 (1913). (25) Lumsden, J. Chem. Soc. 87, 94 (1905) (26) Nespital, Z. physik. Chem. B-16, 170-171 (1932). (27) Wertyporoch, Firla, Z. physik. Chem. A-162, 405-407

(1932). (28) Ulich, Z. physik. Chem., Bodenstein-Festband, 429-430 (1931). (29) Wertyporoch, Kowalski, Z. physik. Chem. A-166, 213-218 (1933). (30) Kohler, Am. Chem. J. 24, 393, 395 (1900). (31) Bösseken, Rec. trav. chim. 22, 315-317 (1903). (32) Menschutkin, J. Russ. Phys.-Chem. Soc. 43, 1794 (1911); Cent. 1912, I 806. (33) Seel, Z. anorg. allgem. Chem. 252, 24-41 (1943). (34) Meerwein, Maier-Hüser, J. prakt. Chem. (2) 134, 69 (1932). (35) Menschutkin, J. Russ. Phys.-Chem. Soc. 45, 1701 (1913); Cent. 1914, I 463. (36) Monsanto Chem. Works, Brit. 397,775, Sept. 21, 1933; Cent. 1933, II 3194; C.A. 28, 1053 (1934). (37) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-104 (1933). (38) Cahours, Ann. chim. (3) 23, 334-339 (1848); Ann. 79, 41-42 (1849). (39) Scott, Hurley, J. Am. Chem. Soc. 59, 1906, 1908 (1937). (40) Bechamp, J. prakt.

(41) Scheuble, Ger. 251,806, Oct. 8, 1912; Cent. 1912, II 1503; [C.A. 7, 401 (1913)]. (42) Heumann, Köchlin, Ber. 16, 1627 (1883). (43) Carius, Ann. 106, 300-303 (1858). (44) Montonna, J. Am. Chem. Soc. 49, 2115 (1927). (45) Kissling (to I.G.), Ger. 642,519, March 10, 1937; Cent. 1937, I 3874; C.A. 31, 5816 (1937). (46) Friedel, Compt. rend. 68, 1559 (1869); Ber. 2, 80 (1869). (47) Beketow, Ann. 109, 256 (1859). (48) B.A.S.F., Ger. 146,690, Dec. 1,1903; Cent. 1904, I 65. (49) Heumann, Köchlin, Ber. 15, 1116 (1882). (50) Uvarov, Stepanov, Russ. 56,693,

Mar. 31, 1940; C.A. 36, 2869 (1942).

Chem. (1) 68, 492 (1856); Compt. rend. 42, 227 (1856).

(51) Soc. Chem. Ind. Basel, French 732,078, Sept. 13, 1932; Cent. 1934, I 287; C.A. 27, 734] (1933): Brit. 401,643, Dec. 14, 1933; Cent. 1934, II 2133; not in C.A. (52) Ullmann, Nadai, Ber. 41, 1871 (1908). (53) Crompton, Vanderstichele, J. Chem. Soc. 117, 692 (1920). (54) Gerhardt, Ann. chim. (3) 37, 291-294 (1853); Ann. 87, 63-66 (1853). (55) Heintz, Ann. Physik (1) 98, 473 (1856). (56) M.L.B., Ger. 210,805, June 16, 1909; Cent. 1909, I 79. (57) Chem. Fabrik von Heyden, A.G., Ger. 123,052, July 29, 1901; Cent. 1901, II 518. (58) Meyer, Ann. 156, 271, Note (1870). (59) Kharasch, Brown, J. Am. Chem. Soc. 64, 332 (1942). (60) Reynhart, Rec. trav. chim. 46, 63-64 (1927).

(61) Reynhart, Rec. trav: chim. 46, 72-74 (1927). (62) Gelissen, Hermans, Ber. 58, 479-481 (1925). (63) Titherly, Holden, J. Chem. Soc. 101, 1878, 1881 (1912). (64) Autenrieth, Muhlinghaus, Ber. 40, 751 (1907). (65) Michael, Am. Chem. J. 9, 213 (1887). (66) Soc. des Usines Chim. Rhone-Poulenc, Ger. 527,874, June 22, 1931; Cent. 1931, II 1350; [C.A. 25, 5175 (1931)]: Brit. 329,721, June 19, 1930; Cent. 1930, II 1611; C.A. 24, 5767 (1930): Brit. 330,511, July 10, 1930; Cent. 1930, II 2184; C.A. 24, 5767 (1930). (67) Clemmensen, Miller (to Monsanto Chem. Co.), U.S. 1,974,845, Sept. 25, 1934; Cent. 1935, I 960; [C.A. 28, 7265 (1934)]. (68) Stellmann, French 785,075, Aug. 1, 1935; Cent. 1935, II 3301; C.A. 30, 490 (1936). (69) Durrans J. Chem. Soc. 121, 45-46 (1922). (70) Bockes, Compt. rend. 196, 1674-1675 (1933).

(71) Lee, Lynn, J. Am. Pharm. Assoc. 21, 125-128 (1932); Cent. 1932, I 3403; [C.A. 26, 5064 (1932)]. (72) Goldschmidt, Endres, Dirsch, Ber. 58, 576 (1925). (73) Musante, Fusco, Gazz. Chim. ital. 66, 640, 648 (1936). (74) B.A.S.F., Ger. 331,696, Jan. 10, 1921; Cent. 1921, II 558. (75) Abkin, Medvedev, J. Chem. Ind. (Moscow) 1934, No. 1, 30-34; Cent. 1935, I 2801; C.A. 28, 3051 (1934); Russ. 34,551, Feb. 28, 1934; C.A. 29, 2973 (1935). (76) Davies, Dick, J. Chem. Soc. 1932, 2808-2809. (77) George (to Mathieson Alkali Works), U.S. 1,557,154, Oct. 13, 1925; Cent. 1926, I 1716-1717. (78) British Dyestuff Corp. and Bunberg and Shepherdson, Brit. 293,924, Aug. 9, 1928; Cent. 1929, I 1614; [C.A. 23, 1650 (1929)]. (79) Hopff (to I.G.), Ger. 524,715, May 11, 1931; Cent. 1931, II 497; [C.A. 25, 4284 (1931)]. (80) Blankshtein, Anilino-krasochnaya Prom. 4, 195-200 (1934); Cent. 1934, II 3112; C.A. 28, 5425 (1934).

(81) Verein fur Chem. Metal. Produktion, Ger. 472,422, Feb. 28, 1929; Cent. 1929, I 2823; [C.A. 23, 2448 (1929)]. (82) Kyrides, J. Am. Chem. Soc. 59, 207-208 (1937). (83) Kyrides (to Monsanto Chem. Co.), U.S. 1,963,748 and 1,963,749, June 19, 1934; Cent. 1934, II 2900; [C.A. 28, 5079 (1934)]. (84) Mills (to Dow Chem. Co.), U.S. 1,921,767, Aug. 8, 1933; Cent. 1933, II 2595; C.A. 27, 5085 (1933). (85) Mills (to Dow Chem. Co.), U.S. 1,965,556, July 3, 1934; Cent. 1934, II 2899; C.A. 28, 5474 (1934). (86) Raboewicz-Zubkowski, Roczniki Chem. 9, 523-551 (1929); Cent. 1929, II 2766; C.A. 24, 61 (1930). (87) Nesmeyanov, Kahn. Ber. 57, 372 (1934). (88) Kränzlein, Hopff (to I.G.), Ger. 574,836, April 20, 1933; Cent. 1933, II 1430; [C.A. 27, 4543 (1933)]: Brit. 384,722, Jan. 5, 1933; Cent. 1933, II 1430; C.A. 27, 4251 (1933): French 739,290, Jan. 9, 1933, Cent. 1933, I 2173; [C.A. 27, 1894 (1933)]. (89) Müller, Ehrmann, Ber. 69, 2209 (1936). (90) Korczynski, Reinholz, Schmidt, Roczniki Chem. 9, 731-740 (1929); Cent. 1936, I 2075; [C.A. 24, 1858 (1930)].

(91) Bennett, Dodd, Sprent and Imperial Chem. Ind., Ltd., Brit. 310,910, May 29, 1929;
 Cent. 1929, II 1217; [C.A. 24, 631 (1930)].
 (92) Henderson, Percival and Imperial Chem. Ind.,
 Ltd., Brit. 310,909, May 29, 1929; Cent. 1929, II 1217; C.A. 24, 631 (1930).
 (93) Staudinger,
 Slegwart, Helv. Chim. Acta 3, 832 (1920).
 (94) Perrot, Compt. rend. 199, 586-587 (1934).
 (95) Perrot, Compt. rend. 206, 1577 (1938).
 (96) Zetsche, Hubacher, Helv. Chim. Acta 9, 292-293 (1926).
 (97) Chapman, J. Chem. Soc. 127, 2818-2819 (1925).
 (98) van Peski, Rec. trav. chim.

41. 689, 695-697 (1921). (99) Conover (to Monsanto Chem. Co.), U.S. 2,006,335, July 2, 1935; Cent. 1935, II 2446; C.A. 29, 5460 (1935). (100) Norris, Fuller, U.S. 1,542,264, June 16, 1925; Cent. 1925, II 1802-1803; [C.A. 19, 2345 (1925)]: Ind. Eng. Chem. 14, 406-409 (1922).

(101) Friedel, Crafts, Ador, Ber. 10, 1857-1858 (1877); Ann. chim. (6) 1, 520-521 (1884). (102) Staudinger, Ber. 41, 3566 (1908). (103) Barger, J. Chem. Soc. 93, 567 (1908). Seelig, J. prakt. Chem. (2) 39, 168 (1889). (105) Wohler, Liebig, Ann. 3, 262-268 (1832). (106) Gauthier, Ann. chim. (6) 14, 362-363 (1888). (107) Loth, Michaelis, Ber. 27, 2548 (1894). (108) Erlenmeyer, Leo, Helv. Chim. Acta 16, 903 (1933). (109) Mailhe, Compt. rend. 180, 1111-1113 (1925); Cent. 1925, I 2554; C.A. 19, 2033 (1925). (110) Mailhe, de Godon, Bull. soc. chim. (4) **19,** 449-452 (1916).

(111) Weygand, Meusel, Ber. 76, 503-504 (1943). (112) Rosenmund, Ber. 51, 590-591 (1918). (113) Froschl, Danoff, J. prakt. Chem. (2) 144, 222-223 (1936). (114) Saytzeff, J. prakt. Chem. (2) 6, 130-132 (1872). (115) Zetsche, Arnd, Helv. Chim. Acta 9, 173-177 (1926). (116) Zetsche, Enderlin, Flutsch, Menzi, Helv. Chim. Acta 9, 177-181 (1926). (117) Chiozza, Compt. rend. 63, 632 (1852); Ann. 85, 232-233 (1853). (118) Neunhoeffer, Nerdel, J. prakt. Chem. (2) 144, 63-66 (1936). (119) Graf, J. prakt. Chem. (2) 146, 199 (1936). (120) Hadaghian, Levaillant, Compt. rend. 194, 2059-2061 (1932).

(121) Lippmann, Bull. soc. chim. (2) 4, 249-250 (1865); Ann. 137, 252-254 (1866). (122) Brigel, Ann. 135, 172–175 (1865). (123) Klinger, Ber. 16, 994–997 (1883). (124) Klinger, Standke, Ber. 24, 1264–1266 (1891). (125) Klinger, Schmitz, Ber. 24, 1276–1277 (1891). (126) N. V. de Bataafsche Petroleum Maatschappij, Brit. 540,370, Oct. 15, 1941; C.A. 36, 4226 (1942). (127) Gauthier, Ann. chim. (6) 14, 363-368 (1888). (128) Hope, Riley, J. Chem. Soc. 123, 2470-2480 (1923). (129) Bornwater, Holleman, Rec. trav. chim. 31, 239-242 (1912). (130) van den Linden, Rec. trav. chim. 52, 703-714 (1934).

(131) Engelhardt, Z. Chem. 1864, 43. (132) Oppenheim, Ber. 3, 735-738 (1870). (133) Kammerer, Carius, Ann. 131, 156 (1864). (134) Kammerer, Ber. 4, 219-220 (1871). (135)Moore, Thomas, J. Am. Chem. Soc. 44, 368 (1922). (136) Elliott, Kleist, Wilkins, Webb, J. Chem. Soc. 1926, 1220-1221. (137) I.G., Swiss 214,609, Aug. 1, 1941; Cent. 1942, I 1055; not in C.A. (138) Daudt, Youker (to Kinetic Chemicals, Inc.), U.S. 2,005,710, June 18, 1935; Cent. 1936, I 1501; [C.A. 29, 5123 (1935)]: U. S. 2,062,743, Dec. 1, 1936; Cent. 1937, I 4557; [C.A. 31, 700 (1937)]. (139) Fredenhagen, Cadenbach, Z. physik. Chem. A-164, 206 (1933). (140) Tseng, Mai, J. Chinese Chem. Soc. 4, 22-26 (1936); Cent. 1936, II 3297; C.A. 30, 2943 (1936).

(141) Enternanu, Johnson, J. Am. Chem. Soc. 55, 2902 (1933). (142) Borodine, Compt. rend. 55, 555 (1862); Ann. 126, 60-62 (1863). (143) Meslans, Girardet, Bull. soc. chim. (3) 15, 878-879 (1896). (144) Guénez, Bull. soc. chim. (3) 5, 886-887 (1891). (145) Voznesenskii, J. Gen. Chem. (U.S.S.R) 9, 2148-2152 (1939); CA. 34, 4053-4054 (1940). (146) Traube, Krahmer, Ber. 52, 1296 (1919). (147) Nesmeyanov, Kahn, Ber. 67, 372-373 (1934); J. Gen. Chem. (U.S.S.R.) 4, 1243-1246 (1936); Cent. 1936, I 4288. (148) Staudinger, Anthes, Ber. 46, 1421-1424 (1913). (149) Claisen, Ber. 14, 2474 (1881). (150) Martin, Partington, J. Chem. Soc. 1936, 1177.

(151) Kishner, J. Russ. Phys.-Chem. Soc. 41, 654 (1909); Cent. 1909, II 1132. (152) Thiele, Haakh, Ann. 369, 146-147 (1909). (153) Pearl, Evans, Dehn., J. Am. Chem. Soc. 60, 2479 (1938). (154) Kharasch, Nudenberg, Archer, J. Am. Chem. Soc. 65, 495-496 (1943). (155) Hartel, Trans. Faraday Soc. 30, 189 (1934). (156) Varvoglis, Ber. 70, 2391-2395 (1937). (157) B. T. Brooks, W. B. Brooks, J. Am. Chem. Soc. 55, 4309-4311 (1933). (158) Bergel, Widmann, Ann. 467, 86 (1928). (159) Bergmann, Witte, Ger. 409,779, Feb. 11, 1925; Cent. 1925, I 1911; not in C.A. (160) Braun, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 431-434 (1941).

(161) Pummerer, Reindel, Ber. 66, 336-337 (1933). (162) Swern, Findley, Scanlan. J. Am. Chem. Soc. 66, 1926 (1944). (163) Lewin, J. prakt. Chem. (2) 127, 81-82 (1930). (164) Prilezhaev, J. Russ. Phys.-Chem. Soc. 42, 1395 (1910); Cent. 1911, I 1279; not in C.A. (165) Nencki, Zaleski, Z. physiol. Chem. 27, 493 (1899). (166) Gambarjan, Ber. 42, 4008 (1909). (167) von Pechmann, Vanino, Ber. 27, 1511 (1894). (168) Kroeber, Ger. 441,808, March 14, 1927; Cent. 1927, II 505; not in C.A. (169) Brodie, Ann. 108, 80-81 (1858). (170) Sonnenschein, Monatsh. 7, 522, Note 3 (1886).

(171) Orndorff, White, Z. physik. Chem. 12, 64 (1893). (172) Baeyer, Villiger, Ber. 33, 1581 (1900). (173) Vanino, Herzer, Arch. Pharm. 263, 426-440 (1915). (174) Minunni, Caberti, Gazz. chim. ital. 20, 655-656 (1890). (175) Francesconi, Cialdea, Gazz. chim. ital. 34, I 444-446 (1904). (176) Ferrario, Gazz. chim. ital. 40, II 99-100 (1910). (177) Diels, Okada, Ber. 44, 3335 (1911). (178) Lachowicz, Ber. 17, 1282-1283 (1884). (179) Lachowicz, Ber. 18, 2992 (1885). (180) Gray, Murray (to Eastman Kodak Co.), U.S. 2,087,030, July 13, 1937; Cent. 1937, II 2261; C.A. 31, 6260 (1937).

(181) Gazopulos, Praktika Akad. Athenon, 6, 154-162 (1931); Cent. 1931, II 1700; C.A. 26, 4318 (1932). (182) Deninger, J. prakt. Chem. (2) 50, 479-480 (1894). (183) Binz, Marx, Ber. 40. 3857-3859 (1907). (184) Gal, Compt. rend. 56, 361 (1863); Ann. 128, 127 (1863). (185) Barrett, Porter, J. Am. Chem. Soc. 63, 3434-3435 (1941). (186) Stollé, Ber. 55, 1292, Note (1922). (187) Wieland, Z. angew Chem. 39, 900 (1926). (188) Bergel, Z. angew. Chem. 49, 974 (1927). (189) Powell, J. Am. Chem. Soc. 51, 2436-2439 (1929). (190) Nelles, Ber. 65, 1345-1347 (1932).

(191) Labruto, Landi, Gazz. chrm. ital. 67, 213-216 (1937); Cent. 1937, II 2523; C.A. 31, 8517 (1937). (192) Naegell, Grüntuch, Lendorff, Helv. Chrm. Acta 12, 256-260 (1929). (193) Porter, Young, J. Am. Chem. Soc. 69, 1497-1500 (1938). (194) Schroeter, Ber. 42, 3359 (1909). (195) Straus, Hüssy, Ber. 42, 2169, 2171 (1909). (196) Olivier, Berger, Rec. trav. chim. 46, 618 (1927). (197) Karvé, Dolé, J. Indian Chem. Soc. 12, 733-739 (1935). (198) Dunstan, Mussell, J. Chem. Soc. 99, 570-571 (1911). (199) Menschutkin, J. Russ. Phys.-Chem. Soc. 47, 1870 (1915); Cent. 1916, II 315. (200) Olivier, Berger, Rec. trav. chrm. 46, 861 (1927).

(201) Usanovich, Yatsimirskii, J. Gen. Chem. (U.S.S.R.) 11, 954-956 (1941); C.A. 39, 4540 (1945). (202) Usanovich, Yatsimirskii, J. Gen. Chem. (U.S.S.R.) 11, 957-958 (1941); C.A. 36, 6444 (1942). (203) Sunner, Nilson, Svensk Kem. Tul. 54, 163-167 (1942); Cent. 1943, I 829; C.A. 38, 3249 (1944). (204) Lewis, J. Chem. Soc. 1940, 831-832. (205) Kym, Ber. 32, 3533, Note (1899). (206) Kitamura, J. Pharm. Soc. Japan 57, 2937 (1937), Cent. 1937, II 374; [C.A. 31, 3871 (1937)]. (207) Engelhardt, Latschinow, Malyschew, Zeit. fur Cheme. 1868, 354. (208) Mingois, Gazz. Chrm. vtal. 55, 717-718 (1925). (209) Moness, Lott, Christiansen, J. Am. Assoc. 25, 397-402 (1936); Cent. 1937, I 851; C.A. 30, 5198 (1936). (210) Shelton, Rider, J. Am.

Chem. Soc. 58, 1282-1284 (1936).

(211) Rider, Shelton (to W. S. Merrell Co.), U.S. 2,028,246, Jan. 21, 1936; Cent. 1936, I 3217; C.A. 30, 1811 (1936). (212) Braker (to E. R. Squibb and Sons), U.S. 2,154,488, April 18, 1939; Cent. 1939, II 229; [C.A. 33, 5415 (1939)]. (213) Szperl, Wasilewska, Rocznki Chem. 16, 207-212 (1936); Cent. 1936, II 2342-2343; [C.A. 30, 8189 (1936)]. (214) Cook, Bambach, J. Am. Pharm. Assoc. 27, 758-760 (1938); Cent. 1939, I 744, C.A. 32, 9060 (1938). (215) Lehmann, Z. physiol. Chem. 17, 406 (1893). (216) Govaert, Natuurw. Tydschr. 15, 149-153 (1933); Cent. 1934, I 1471; C.A. 28, 740 (1934). (217) Gerhardt, Chiozza, Compt. rend. 37, 88 (1853), Ann. chrm. (3) 46, 135 (1856). (218) Baumert, Landolt, Ann. 111, 5-8 (1859). (219) Jaffé, Ber. 25, 3120-3121 (1892). (220) Mailhe, Bull. soc. chim. (4) 23, 380-381 (1918); Ann. chim. (9) 13, 211 (1920).

(221) Jones, Hurd, J. Am. Chem. Soc. 43, 2446-2447 (1921). (222) Lossen, Ann. 161, 347-362 (1872). (223) Hauser, Renfrow, Org. Syntheses, Coll. Vol. 2 (1st ed.), 67-68 (1943), 19, 15-17 (1939). (224) Davidson, J. Chem. Education, 17, 81-84 (1940). (225) Curtius, Struve, J. prakt. Chem. (2) 50, 295-296 (1894). (226) Frey, Gilbert, J. Am. Chem. Soc. 59, 1345 (1937). (227) Stollé, J. prakt. Chem. (2) 69, 154 (1904). (228) Hatt, Org. Syntheses, Coll. Vol. 2 (1st ed.), 208-209 (1943); 16, 18-21 (1936). (229) Anderson, Gilbert, J. Am. Chem. Soc. 64, 2369 (1942).

(230) Pucher, Day, J. Am. Chem. Soc. 48, 672-676 (1926).

(231) Nenitzescu, Ionescu, Ann. 491, 199-202, 209-210 (1931). (232) Allen, Cressmann, Bell, Can. J. Research 8, 440-446 (1933). (233) Norris, Couch, J. Am. Chem. Soc. 42, 2329-2332 (1920). (234) Wieland, Bettag, Ber. 55, 2252-2255 (1922). (235) Christ, Fuson, J. Am. Chem. Soc. 59, 895 (1937). (236) Nelles, Bayer (to I.G.), Ger. 642,147, Feb. 25, 1937; Cent. 1937, II 2597; C.A. 31, 3501 (1937): Brit. 461,080, March 11, 1937; Cent. 1937, II 2597; C.A. 31, 4676 (1937). (237) Wertyporoch, Ber. 66, 1237-1238 (1933). (238) Gangloff, Henderson, J. Am. Chem. Soc. 39, 1425-1427 (1917). (239) Marvel, Sperry, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 95-98 (1941); (1st ed.), 89-92 (1932); 8, 26-29 (1928). (240) Friedel, Crafts, Ann. chm. (6) 1, 510 (1884).

(241) Böeseken, Rec. trav. chim. 19, 20-21 (1900). (242) Norris, Thomas, Brown, Ber. 43, 2959 (1910). (243) Rubidge, Qua, J. Am. Chem. Soc. 36, 735-736 (1914). (244) Olivier, Rec. trav. chim. 37, 205-215 (1918). (245) Ulich, Heyne, Z. Elektrochem. 41, 509-514 (1935); Cent. 1935, II 2652; C.A. 29, 7768 (1935). (246) Hencki, Stoeber, Ber. 30, 1768 (1897). (247) Böeseken, Rec. trav. chim. 22, 315-317 (1903). (248) Nencki, Ber. 32, 2414-2416 (1899). (249) Riddell, Noller, J. Am. Chem. Soc. 52, 4365-4369 (1930). (250) Ulich, Die Chemie 55, 37-38 (1942); Cent. 1942, I 2233; C.A. 37, 2521 (1943).

(251) Kashtanov, J. Gen. Chem. (U.S.S.R.) 2, 515-523 (1932); Cent. 1933, I 600; C.A. 27, 975 (1933). (252) Kashtanov, J. Gen. Chem. (U.S.S.R.) 3, 229-233 (1933); Cent. 1933, II 2512; C.A. 28, 1687 (1934). (253) Krishnamurti, J. Madras Univ. 1928, 5 pp. (reprint); Cent. 1929, I 2156; C.A. 28, 2164 (1929). (254) Chakrabarty, Dutt, J. Indian Chem. Soc. 5, 513-517 (1928). (255) Comstock, Am. Chem. J. 18, 550-551 (1896). (256) Menschutkin, J. Russ. Phys.-Chem. Soc. 45, 1710-1739 (1913); Cent. 1914, I 463; C.A. 8, 910 (1914); J. chim. phys. 12, 193-205 (1914). (257) Menschutkin, J. Russ. Phys.-Chem. Soc. 46, 259-283 (1913); Cent. 1914, I 2161-2162; C.A. 8, 2551 (1914). (258) Simons, Hart, J. Am. Chem. Soc. 66, 1310 (1944). (259) Lecher, Ber. 46, 2667-2668 (1913). (260) Lecher, Ger. 281,802, Jan. 27, 1914; Cent. 1915, I 281; C.A. 9, 2292 (1915).

(261) Clemo, McQuillen, J. Chem. Soc. 1936, 808-809. (262) Elbs, J. prakt. Chem. (2) 35,

466-472 (1887). (263) Steele, J. Chem. Soc. 83, 1470-1490 (1903). (264) Blakey, Scarborough, J. Chem. Soc. 1928, 2492. (265) Martin, Pizzolato, McWaters, J. Am. Chem. Soc. 57, 2584-2589 (1935). (266) Sdilscher, Ber. 15, 1682 (1882). (267) AGFA, Ger. 267,271, Nov. 12, 1913; Cent. 1913, II 2015; [C.A. 8, 791 (1914)]. (268) Norris, Blake, J. Am. Chem. Soc. 50, 1811 (1928). (269) Smith, Ber. 24, 4029 (1891). (270) Long, Henze, J. Am. Chem. Soc. 63, 1939-1940 (1941).

(271) Hsu, Ingold, Wilson, J. Chem. Soc. 1935, 1784–1785. (272) Wolf, Ber. 14, 2031 (1881). (273) Perrier, Compt. rend. 116, 1299 (1893). (274) Montagne, Rec. trav. chim. 27, 357–358 (1908). (275) Staudinger, Kon, Ann. 384, 97 (1911). (276) Cohen, Rec. trav. chim. 38, 121 (1919). (277) Bachmann, Barton, J. Org. Chem. 3, 300–311 (1938). (278) Koller, Monatsh. 12, 502 (1891). (279) Cannoni de Degiori, Anales asoc. quim. argentina 21, 135–141 (1933); Cent. 1934, II 603; C.A. 28, 2704–2705 (1934). (280) Bradsher, J. Am. Chem. Soc. 66, 45–46 (1944).

(281) Olifson, J. Gen. Chem. (U.S.S.R.) 9, 36-40 (1939); Cent. 1939, II 4473; C.A. 33, 6291 (1939). (282) Garcia-Banus, Monche, Anales soc. españ. Is. quím. 33, 655-679 (1935); Cent. 1936, II 2131; [C.A. 30, 457 (1936)]. (283) Perrier, Caille, Compt. rend. 146, 749 (1908); Bull. soc. chim. (4) 3, 654-656 (1908). (284) Montagne, Rec. trav. chim. 26, 281-283 (1907). (285) Elbs, J. prakt. Chem. (2) 35, 502-504 (1887). (286) Roux, Ann. chim. (6) 12, 338-341 (1887). (287) Ross, Percy, Brandt, Gebhart, Mitchell, Yolles, Ind. Eng. Chem. 34, 924-926 (1942). (288) Grucarevic, Merz, Ber. 6, 1238, 1240 (1873). (289) de Fazi, Gazz. chim. ital. 49, I 247 (1919). (290) Lippmann, Pollak, Ber. 34, 2766 (1901).

(291) Lippmann, Keppich, Ber. 33, 3087-3089 (1900). (292) Lippmann, Fleissner, Ber. 32, 2249-2251 (1899). (293) Perrier, Ber. 33, 816 (1900). (294) Krollpfeiffer, Ber. 36, 2364 (1923). (295) Nenitzescu, Isacescu, Ionescu, Ann. 491, 218 (1931). (296) Cook, J. Chem. Soc. 1926, 1284-1285. (297) Willgerodt, Albert, J. prakt. Chem. (2) 84, 392-393 (1911). (298) Bachmann, J. Am. Chem. Soc. 57, 555-559 (1935); 56, 1363 (1936). (299) Marquis, Compt. rend. 129, 111 (1899); Bull. soc. chim. (3) 23, 32-34 (1900); Ann. chim. (8) 4, 275-277 (1905). (300) Asahina, Muravama. Arch. Pharm. 252, 448 (1914).

(301) Gol'dfarb, Smorgonskii, J. Gen. Chem. (U.S.S.R.) 8, 1523-1526 (1938); Cent. 1939, II 424; C.A. 33, 4593 (1939). (302) Minnis, Org. Syntheses, Coll. Vol. 2 (1st ed.), 520-521 (1943); 12, 62-63 (1932). (303) Stadnikoff, Rakowsky. Ber. 61, 269 (1928). (304) Gol'dfarb, J. Russ. Phys.-Chem. Soc. 62, 1073-1082 (1930); C.A. 25, 2719 (1931). (305) Steinkopf, Ann. 413, 349 (1917). (306) Steinkopf, Bauermeister, Ann. 403, 70 (1914). (307) Volhard, Ann. 267, 179-180 (1892). (308) Steinkopf, Killingstad, Ann. 532, 291 (1937). (309) Lossen, Ann. 161, 347-362 (1872); 265, 129-178 (1891). (310) Menalda, Rec. trav. chim. 49, 967-995 (1930).

(311) Henstock, J. Chem. Soc. 1933, 216. (312) Lipscomb, Baker, J. Am. Chem. Soc. 64, 179–180 (1942). (313) Autenrieth, Thomae, Ber. 57, 1002–1008 (1924). (314) Norris, Haines, J. Am. Chem. Soc. 57, 1425 (1935). (315) Davies, Hambly, Semmens, J. Chem. Soc. 1933, 1313–1314. (316) Zaki, J. Chem. Soc. 1928, 988–989. (317) Norris, Green, Am. Chem. J. 26, 312 (1901). (318) Spassow, Ber. 70, 1929 (1937). (319) Kenyon, Phillips, Pittman, J. Chem. Soc. 1935, 1080. (320) Cohen, J. Am. Chem. Soc. 66, 1396 (1944).

(321) Cohen, Schneider, J. Am. Chem. Soc. 63, 3386 (1941). (322) Norris, Rigby, J. Am. Chem. Soc. 54, 2098 (1932). (323) Vavon, Barbier, Thiebaut, Bull. soc. chim. (5) 1, 812 (1934). (324) Blaise, Picard, Ann. chim. (8) 25, 261 (1912). (325) Magnani, McElvain, J. Am. Chem. Soc. 69, 817 (1938). (326) Huntress, Mulliken, "Tables of Data of Selected Compounds of Order I," John Wiley & Sons, Inc. (1941). (327) Blatt, Chem. Revs. 27, 413-436 (1940). (328) Blatt, Org. Reactions, 1, 342-369 (1942). (329) Bernouilli, St. Goar, Helv. Chim. Acta 9, 730-765 (1926). (330) Michael, Weiner, J. Org. Chem. 3, 374, 382 (1938).

(331) Michael, Ross, J. Am. Chem. Soc. 53, 2401-2402, 2410 (1931). (332) Shriner, Schmidt, J. Am. Chem. Soc. 51, 3636-3638 (1929). (333) Isbell, Wojcik, Adkins, J. Am. Chem. Soc. 54, 3685 (1932). (334) Shriner, Schmidt, Roll, Org. Syntheses, Coll. Vol. 2 (1st ed.), 266-267 (1943); 18, 33-35 (1938). (335) Michael, Carlson, J. Am. Chem. Soc. 57, 167, 172 (1935). (336) von Pechmann, Ber. 25, 1046 (1892). (337) Claisen, Ann. 391, 65-70 (1896). (338) Michael, Hibbert, Ber. 40, 4384-4385 (1907). (339) Spassow, Ber. 76, 2385 (1937). (340) McElvain, Weber, Org. Syntheses 23, 35-37 (1943).

(341) Michael, Carlson, J. Am. Chem. Soc. 58, 353-364 (1936). (342) Nef, Ann. 277, 68-70 (1893). (343) Claisen, Ann. 277, 200-203 (1893). (344) Claisen, Ann. 291, 106-111 (1896). (345) Fischer, Bulow, Ber. 18, 2133 (1885). (346) Claisen, Ann. 277, 188-200 (1893). (347) Claisen, Ann. 291, 56-59, 62-63 (1896). (348) Michael, Ann. 390, 54 (1912). (349) Claisen, Ann. 291, 100 (1896). (350) Weygand, Forkel, Bischoff, Ber. 61, 688 (1928).

(351) Claisen, Ann. 291, 92-93, 102-105 (1896). (352) Abell, J. Chem. Scc. 101, 998 (1912). (353) Perkin, J. Chem. Soc. 47, 252-253 (1885). (354) Descudé, Compt. rend. 133, 1129-1131 (1901). (355) Lydén, Finska Kemistamfindets Medd. 35, 19-36; Cent. 1927, I 1813; C.A. 23, 3880 (1928): ibid. 37, 53-75 (1928); Cent. 1928, II 2133; C.A. 23, 1868 (1929): ibid. 38, 19-46;

Cent. 1930, I 2379; C.A. 24, 335 (1930): ibid. 38, 72-84 (1929); Cent. 1930, I 3171; C.A. 24, 1628 (1930). (356) Kishner, J. Russ. Phys.-Chem. Soc. 41, 651-659 (1909); Cent. 1909, II 1132; C.A. 5, 883 (1911). (357) Underwood, Wakeman, J. Am. Chem. Soc. 52, 387-391 (1930). (358) Meerwein, Maier-Hüser, J. prakt. Chem. (2) 134, 51-53, 77-80 (1932). (359) Kyrides, J. Am. Chem. Soc. 55, 1209-1212 (1933). (360) Kaufmann, Fuchs, Arch. Pharm. 262, 122-125 (1924).

(361) Wedekind, Haeussermann, Ber. 34, 2081–2082 (1901). (362) Kozlov, Bogdanovskaya, Sologub, J. Gen. Chem. (U.S.S.R.) 6, 315-317 (1936); Cent. 1936, II 1896; C.A. 30, 4813 (1936). (363) Underwood, Baril, Toone, J. Am. Chem. Soc. 52, 4087-4092 (1930). (364) Underwood, Toone, J. Am. Chem. Soc. **52**, 391-394 (1930). (365) Hell, Stockmayer, Ber. **37**, 225-226 (1904). (366) Gattermann, Ehrhardt, Maisch, Ber. **23**, 1204-1206, 1209 (1890). (367) Peterson, Am. Chem. J. 46, 335-336 (1911). (368) Gattermann, Ber. 22, 1129-1130 (1889). (369) Jones, J. Chem. Soc. 1936, 1860-1861. (370) van Alphen, Rec. trav. chim. 49, 384 (1930).

(371) Ullmann, Goldberg, Ber. 35, 2814 (1902). (372) Bachmann, Ferguson, J. Am. Chem. Soc. 56, 2082 (1934). (373) Montagne, Rec. trav. chim. 39, 344 (1920). (374) Torres y Gonzales, Bull. soc. chim. (4) 37, 1593-1594 (1925): Anales soc. españ. fís. quím. 24, 82-90 (1926); Cent. 1926, I 21; C.A. 20, 2159 (1926). (375) Kipper, Ber. 38, 2492 (1905). (376) Dilthey, Bach, Grutering, Hausdörfer, J. prakt. Chem. (2) 117, 353 (1927). (377) Schroeder, Brewster, J. Am. Chem. Soc. 60, 751-753 (1938). (378) Fierz-David, Jaccard, Helv. Chim. Acta 11, 1042-1047 (1928). (379) Fieser, Bradsher, J. Am. Chem. Soc. 61, 420-421 (1939). (380) Ray, Moomaw,

J. Am. Chem. Soc. 55, 3835 (1933).

(381) Fieser, J. Am. Chem. Soc. 53, 3558 (1931). (382) Seer, Scholl, Ann. 398, 85 (1913). (383) Popov, J. Gen. Chem. (U.S.S.R.) 5, 986-992 (1935); Cent. 1936, I 2933; C.A. 30, 1049 (1936). (384) Gerhardt, Ann. chim. (3) 37, 321 (1853); Ann. 87, 157-158 (1853). (385) Béhal, Compt. rend. 148, 649 (1909). (386) Knöll and Co., Ger. 117, 267, Jan. 24, 1901; Cent. 1901, I 347. (387) Béhal, Compt. rend. 129, 683 (1899); Bull. soc. chim. (3) 23, 73-75 (1900); Ann. chim. (7) 19, 277-279 (1900). (388) Loir, Bull. soc. chim. (2) 32, 168-169 (1879). (389) Tschitchibabin, J. Russ. Phys.-Chem. Soc. 33, 404-410 (1901); Cent. 1901, II 543. (390) Hurd, Dull, J. Am. Chem. Soc. 54, 3429-3430 (1932).

(391) Williams, Dickert, Krynitsky, J. Am. Chem. Soc. 63, 2511 (1941). (392) Anschutz, Ann. 226, 5 (1884). (393) Minunni, Gazz. chim. ital. 22, II 214-215 (1892). (394) Wedekind, Ber. 34, 2072 (1901). (395) Gerbardt, Ann. chim. (3) 37, 299-203 (1853); Ann. 87, 73-76 (1853). (396) Clarke, Rahrs, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 91-94 (1941); (1st ed.), 85-87 (1932); 3, 21-24 (1932). (397) Dvornikoff (to Monsanto Chem. Co.), U.S. 1,948,342, Feb. 20, 1934; C.A. 28, 2730 (1934). (398) Claisen, Ber. 31, 1024 (1898). (399) Jander, Scholz, Z. physik. Chem. 192, 199-201 (1943); C.A. 38, 2549 (1944). (400) Wöhler, Liebig, Ann. 3, 267-268 (1832).

(401) Guinchant, Ann. chim. (9) 9, 86 (1918). (402) Nef, Ann. 287, 303-307 (1895). (403) Claisen, Ber. 10, 430 (1877). (404) Kolbe, Strecker, Ann. 90, 62-63 (1854). (405) Staudinger, Kon, Ann. 384, 114, 116 (1911). (406) Diels, Pillow, Ber. 41, 1896 (1908). (407) Schiff, Ann. 101, 93 (1857). (408) Limpricht, Ann. 99, 117 (1856). (409) Benson, Hillyer, Am. Chem. J. 26, 373-377 (1901). (410) Miguel, Ann. chim. (5) 11, 300-302 (1877).

(411) Dixon, J. Chem. Soc. 75, 379 (1899). (412) Dixon, Taylor, J. Chem. Soc. 93, 692 (1908). (413) Johnson, Chernoff, J. Am. Chem. Soc. 34, 167 (1912). (414) van Romburgh, Rec. trav. chim. 4, 384, 388 (1885). (415) Beckmann, Ann. 365, 208 (1909). (416) Wheeler, Am. Chem. J. 23, 139, 142 (1900). (417) Reid, Am. Chem. J. 45, 43 (1911). (418) Bodendorf, J. prakt. Chem. (2) 126, 239 (1930). (419) Titherly, J. Chem. Soc. 79, 403-406 (1901). (420) von Braun, Ber. 37, 2814-2815 (1904).

(421) Oliveri-Mandala, Gazz. chim. ital. 44, I 669 (1914). (422) Descudé, Compt. rend. 135, 973-974 (1902). (423) Coleman, Howells, J. Am. Chem. Soc. 45, 3088 (1923). (424) Mitter, Ray, J. Indian. Chem. Soc. 14, 424 (1937). (425) Kenyon, Phillips. Pittman, J. Chem. Soc. 1935, (426) Levene, Rothen, Kuna, J. Biol. Chem. 120, 767, 769 (1937). (427) Schroeter, Ber.
 1205 (1911). (428) Brander, Rec. trav. chim. 37, 77 (1918). (429) K. N. Campbell, A. H. Sommers, B. K. Campbell. J. Am. Chem. Soc. 68, 140 (1946). (430) Brown, Jones, J. Chem. Soc. 1936, 782.

(431) Hallmann, Ber. 9, 846 (1876). (432) von Braun, Ber. 36, 3525 (1903). (433) French, Adams, J. Am. Chem. Soc. 43, 657 (1921). (434) Ulich, Adams, J. Am. Chem. Soc. 43, 665 (1921), (435) Mumm, Hesse, Volquartz, Ber. 48, 387-388 (1915). (436) Wheeler, Walden, Metcalf, Am. Chem. J. 20, 73 (1898). (437) Hepp, Ber. 10, 329 (1877). (438) Hess, Ber. 18, 685-688 (1885). (439) von Braun, Ber. 37, 2681 (1904). (440) Mills, Harris, Lambourne, J. Chem. Soc. 119, 1298 (1921)

(441) Abrahart, J. Chem. Soc. 1936, 1274. (442) Lander, J. Chem. Soc. 83, 408 (1903). Morgan, Evens, J. Chem. Soc. 115, 1144 (1919). (444) Hofmann, Ann. 132, 166 (1864). Bernthsen, Ann. 224, 12, Note (1884). (446) Herzog, Hancu, Ber. 41, 636 (1908). (447) Johnson, Levy, Am. Chem. J. 38, 460 (1907). (448) Hinsberg, Adranszky, Ann. 254, 254-256 (1889). (449) Walther, von Pulawski, J. prakt. Chem. (2) 59, 250-252 (1899). (450) Bamberger. Berlé. Ann. 273, 343-347, 360-361 (1893).

(451) Bistrzycki, Ulffers, Ber. 23, 1876-1878 (1890). (452) Hübner, Ann. 208, 295, 307 (1881). (453) Mixter, Am. Chem. J. 6, 27 (1884/85). (454) Witt, Ber. 45, 2381-2382 (1912). Galimberti, Gazz. chim. ital. 63, 98 (1933). (456) Gerngross, Ber. 46, 1912 (1913). (457) Oddo, Raffa, Gazz. chim. stal. 67, 541-542 (1937); Cent. 1938, I 1581; C.A. 32, 1697 (1938). (458) Ruhemann, Ber. 14, 2652 (1881). (459) Rao, Wheeler, J. Chem. Soc. 1937, 1644. (460) Major, J. Am. Chem. Soc. 53, 4375 (1931).

(461) Bell, Ber. 7, 498 (1874). (462) Sachs, Goldmann, Ber. 35, 3342 (1902). (463) Dreyfus, Brit. 363,986, 364,040, Jan. 28, 1932; Cent. 1932, II 1723; [C.A. 27, 1639 (1933)]: French 719,596, Feb. 8, 1932; Cent. 1932, II 1723; [C.A. 26, 3920 (1932)]. (464) Rivier, Zeltner, Helv. Chim. Acta 20, 699 (1937). (465) Bergmann, Ulpts, Camacho, Ber. 55, 2801–2807 (1922). (466) Ransom, Ber. 31, 1062 (1898); Am. Chem. J. 23, 17 (1900). (467) Ciamician, Silber, Ber. 38, 1181 (1905); Gazz. chim. ital. 36, II 193, 198 (1906). (468) Hubner, Ann. 210, 385-388 (1881). (469) Bell, J. Chem. Soc. 1931, 2966. (470) Raiford, J. Am. Chem. Soc. 41, 2078-2080 (1919).

 (471) Pollard, Amundsen, J. Am. Chem. Soc. 57 358 (1935).
 (472) Ladenburg, Ber. 9, 1526, 1529 (1876).
 (473) Hubner, Morse, Ber. 7, 1319 (1874).
 (474) Wheeler, Am. Chem. J. 17, 399 (1895). (475) Nelson, Matchett, Tindall, J. Am. Chem. Soc. 50, 922 (1928). (476) Knowles, Watt, J. Org. Chem. 7, 56 (1942). (477) Fischer, J. prakt. Chem. (2) 73, 438 (1906). (478) Clark, J. Chem. Soc. 1926, 235. (479) Amundsen, Pollard, J. Am. Chem. Soc. 57, 1536 (1935).

(480) Bamberger, Ber. 36, 2051 (1903).

(481) Tingle, Williams, Am. Chem. J. 37, 58-59 (1907). (482) Skraup, Ann. 419, 68 (1919). (483) Einhorn, Ann. 311, 41 (1900). (484) Fierz-David, Meister, Helv. Chim. Acta 22, 580 (1939). (485) Meyer, Sundmacher, Ber. 32, 2124 (1899). (486) Ikuta, Am. Chem. J. 15, 43 (1893). (487) Hewitt, Ratcliffe, J. Chem. Soc. 101, 1769 (1912). (488) von Auwers, Sonnenstuhl, Ber. 37, 3940, 3941 (1904). (489) Reverdin, Dresel, Ber. 37, 4453 (1904); Bull. soc. chim. (3) 31, 1269 (1904). (490) Smith, Ber. 24, 4042 (1891).

(491) Hubner, Ann. 210, 379 (1881). (492) Reddelien, Danilot, Ber. 54, 3140 (1921). (493) Raiford, J. Am. Chem. Soc. 41, 2068-2080 (1919). (494) Raiford, Couture, J. Am. Chem. Soc. 44, 1792-1798 (1922). (495) Raiford, Iddles, J. Am. Chem. Soc. 45, 469-475 (1923). (496) Raiford, Clark, J. Am. Chem. Soc. 45, 1738-1743 (19.3). (497) Raiford, Greider, J. Am. Chem. Soc. 46, 430-437 (1924). (498) Raiford, Taft, Lankelma, J. Am. Chem. Soc. 46, 2051-2057 (1924). (499) Raiford, Woolfolk, J. Am. Chem. Soc. 46, 2246-2255 (1924). (500) Raiford, Couture, J. Am. Chem. Soc. 46, 2305-2318 (1924).

(501) Raiford, Lankelma, J. Am. Chem. Soc. 47, 1111-1123 (1925). (502) Raiford, Colbert, J. Am. Chem. Soc. 47, 1454-1458 (1925). (503) Raiford, Clark, J. Am. Chem. Soc. 48, 483-489 (1926). (504) Raiford, Talbot, J. Am. Chem. Soc. 49, 559-561 (1927). (505) Raiford, Mortenson, J. Am. Chem. Soc. 50, 1201-1204 (1928). (506) Raiford, Grosz, J. Am. Chem. Soc. 53, 3420-3426 (1931). (507) Raiford, Inman, J. Am. Chem Soc. 56, 1586-1590 (1934). (508) Raiford, Shelton, J. Org. Chem. 4, 207-219 (1939). (509) Raiford, Alexander, J. Org. Chem. 5, 300-312 (1940). (510) Bacher, Raiford, Proc. Iowa Acad. Sci. 50, 247-251 (1943). C.A. 38, 2327 (1944).

(511) Raiford, Crounse, J. Am. Chem. Soc. 66, 1240-1241 (1944). (512) Ransom, Wilson, J. Am. Chem. Soc. 36, 390-393 (1914). (513) Nelson, Davis, J. Am. Chem. Soc. 48, 1677-1679 (1926). (514) Nelson, Aitkenhead, J. Am. Chem. Soc. 48, 1680-1683 (1926). (515) Nelson, Shock, Sowers, J. Am. Chem. Soc. 49, 3129-3131 (1927). (516) Nelson, Matchett, Tindall, J. Am. Chem. Soc. 50, 919-923 (1928). (517) Nelson, Rothrock, J. Am. Chem. Soc. 51, 2761-2764 (1929). (518) Bell, J. Chem. Soc. 1930, 1981-1987. (519) Bell, J. Chem. Soc. 1931, 2962-2967. (520) Dehn, Ball, J. Am. Chem. Soc. 36, 2100-2101 (1914).

(521) Prey, Ber. 75, 543 (1942). (522) Weitz, Roth, Nelken, Ann. 425, 161-186 (1921). Koenigs, Ruppelt, Ann. 509, 142-158 (1934). (524) Lewis, J. Chem. Soc. 1940, 831. (525) Jones, Whalen, J. Am. Chem. Soc. 47, 1344 (1925). (526) Fischer, Ann. 190, 125-129 (1877). (527) Autenrieth, Thomae, Ber. 57, 436 (1924). (528) Michaelis, Schmidt, Ann. 252, 310-317 (1889). (529) Short, J. Chem. Soc. 119, 1447 (1921). (530) Franzen, Ber. 42, 2466-2467 (1909).
(531) Pellizzari, Gazz. chim. ital. 42, II 38 (1911). (532) Michaelis, Schmidt, Ber. 29, 46-47.

1713 (1887). (533) von Auwers, Mauss, J. prakt. Chem. (2) 117, 314 (1927). (534) Hyde, Ber. 32, 1811 (1899). (535) Curtius, Mayer, J. prakt. Chem. (2) 76, 381 (1907). (536) Cahours, Ann. chim. (3) 38, 87-88 (1853). (537) Marvel, Lazier, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 99-101 (1941); (1st ed.), 93-95 (1932); 9, 16-19 (1929). (538) Schotten, Ber. 21, 2238 (1888). (539) Schotten, Ber. 17, 2545 (1884). (540) Autenrieth, Thomae, Ber. 57, 1006 (1924).

(541) von Braun, Ber. 36, 3524, Note (1903). (542) von Braun, Ber. 37, 3210-3213 (1904). (543) von Braun, Steindorff, Ber. 38, 2338-2339 (1905). (544) Merck, Ger. 164,365, Oct. 28, 1905; Cent. 1905, II 1563. (545) Lespieau, Bull. soc. chim. (4) 37, 422 (1925). (546) Johnson, J. Chem. Soc. 1933, 1531. (547) von Braun, Org. Syntheses, Coll. Vol. I (2nd ed.), 428-430 (1941); (1st ed.), 419-420 (1932); 9, 70-71 (1929). (548) von Braun, Irmisch, Ber. 65, 882 (1932). (549) Knorr, Ann. 301, 7 (1898). (550) Arndt, Amende, Ber. 61, 1122-1124 (1928).

(551) Arndt, Eistert, Amende, Ber. 61, 1949-1952 (1928). (552) Bradley, Robinson, J. Chem. Soc. 1928, 1310-1318. (553) Bradley, Schwarzenbach, J. Chem. Soc. 1928, 2904-2912. (554) Arndt, Eistert, Ber. 68, 206 (1935). (555) Bachmann, Struve, Org. Reactions 1, 38-62 (1942). (556) Posner, Ber. 59, 1804-1805, 1815-1817 (1926). (557) de Diesbach, Lempen, Helv. Chim. Acta 16, 148-154 (1933). (558) de Diesbach, de Bie, Rubli, Helv. Chim. Acta 17, 113-128 (1934). (559) de Diesbach, Dobbelman, Helv. Chim. Acta 19, 1213-1222 (1936). (560) de Diesbach, Moser, Helv. Chim. Acta 20, 132-141 (1937).

(561) de Diesbach, Jacobi, Taddei, Helv. Chim. Acta 23, 469-484 (1940). (562) de Diesbach, Klement, Helv. Chim. Acta 24, 158-173 (1941). (563) de Diesbach, Rey-Bellet, Kiang, Helv. Chim. Acta 26, 1869-1885 (1943). (564) Tissier, Grignard, Compt. rend. 132, 684 (1901). (565) Gilman, Fothergill, Parker, Rec. trav. chim., 48, 748-751 (1929). (566) Gilman, Mayhue, Rec. trav. chim. 51, 47-50 (1932). (567) Kharasch, Nudenberg, Archer, J. Am. Chem. Soc. 65, 495-498 (1943). (568) Gilman, Heck, J. Am. Chem. Soc. 52, 4949-4954 (1930). (569) Entemann, Johnson, J. Am. Chem. Soc. 55, 2900-2903 (1933). (570) Gilman, Van Ess, J. Am. Chem. Soc. 55, 1260 (1933).

(571) Hurd, Cohen, J. Am. Chem. Soc. 53, 1071 (1931).
(572) Nef, Ann. 308, 275-276 (1899).
(573) Gilman, Straley, Rec. trav. chem. 55, 823, 825 (1936).
(574) Mel'nikov, Rokitskaya, J. Gen. Chem. (U.S.S.R.)
(7, 464-466 (1937); Cent. 1937, II 1557; C.A. 31, 4266 (1937).
(575) Calvery, J. Am. Chem. Soc. 48, 1011-1012 (1926).
(576) Whitmore, Thurman, J. Am. Chem. Soc. 51, 1496-1497 (1929).
(577) Gilman, Schulze, J. Chem. Soc. 1927, 2668.
(578) Gilman, Nelson, Rec. trav. chim. 55, 518-530 (1936).
(579) Popoff, Ber. 4, 720 (1871).
(580) Freund, Ann. 118, 20-21 (1861).

(581) Kalle, Ann. 119, 165-168 (1861). (582) Michael, Am. Chem. J. 25, 423 (1901). (583) Gerhardt, Ann. chim. (3) 14, 124-125 (1845); Ann. 60, 311-312 (1846). (584) Claisen, Ber. 27, 3182-3183 (1894). (585) Ott, Ber. 55, 2122 (1922). (586) Lukashevich, Amlinokrasochnaya Prom. 5, 193-196 (1935); Cent. 1936, I 1858; [C.A. 30, 7108 (1936)]. (587) Shah, Deshpande, J. Univ. Bombay 2, Pt. 2, 125-127 (1933); Cent. 1934, II 3109; C.A. 28, 6127 (1934). (588) Biehringer, Busch, Ber. 36, 137 (1903). (589) Jacobs, Heidelberger, J. Am. Chem. Soc. 39, 1446 (1917). (590) Vles, Rec. trav. chim. 53, 962 (1934).

(591) Williams, Hinshelwood, J. Chem. Soc. 1934, 1079-1084. (592) Grant, Hinshelwood, J. Chem. Soc. 1933, 1351-1357. (593) Bruckner, Ann. 205, 127-130 (1880). (594) Jacobsen, Huber, Ber. 41, 663 (1908). (595) von Auwers, Ber. 52, 1335 (1919). (596) Just, Ber. 19, 983 (1886). (597) Wallach, Ann. 214, 217 (1882). (598) Jailland, Compt. rend. 60, 1097 (1865). (599) Hübner, Kelbe, Meyer, Ann. 208, 310-311 (1881). (600) Kuhn, Ber. 18, 1477 (1885).

(601) Hofmann, Ber. 20, 1798 (1887). (602) Hubner, Ebell, Ann. 208, 334 (1881). (603) Berlingozzi, Barni, Gazz. chim. ital. 50, I 219 (1920). (604) Church, Chem. News 5, 324 (1862). (605) Hibbert, Sudborough, J. Chem. Soc. 83, 1340-1341 (1903). (606) Dziewonski, Sternbach, Bull. intern. acad. polon. sci. Classe sci. math. nat. 1933-A, 416-431, [Cent. 1934, II 1621]; C.A. 28, 2717 (1934); Roceniki Chem. 13, 704-719 (1933); Cent. 1934, I 2590-2592; not in C.A. (607) Dziewonski, Sternbach, Bull. intern. acad. polon. sci. Classe sci. math. nat. 1935-A, 327-332, Cent. 1936, I 2093; C.A. 30, 2971 (1936). (608) Loovenich, Loeser, Ber. 60, 322-323 (1927). (609) Young, Clark, J. Chem. Soc. 71, 1203 (1897). (610) Klopsch, Ber. 18, 1585 (1885). (611) Cosiner, Ber. 14, 59 (1881). (612) Ley, Ber. 34, 2629-2630 (1901).

B.P. M.P. $D_{20}^{20} = 1.2535 (6)$ (2) (3) 200° at 770 mm. (1) 4-5° (6) 199° at 761 mm. (2) 198-200° at 760 mm. (3) 197.7-198.1° at 760 mm. (4) 196-198° at 756 mm. (5) 194° at 745 mm. (6) 82.5-82.8° at 15 mm. (4)

[For prepn. of \bar{C} from 5-chloro-2-aminotoluene [Beil. XII-835] via diazotization and use of Cu_2Cl_2 reaction (yield: 87.6% (1), 70% (3) (7)) (4) (6) (2) see indic. refs.; from K (1) or Na (5) salt of 2,5-dichlorotoluenesulfonic acid-6 by hydrolysis in conc. H_2SO_4 with superheated steam see (1) (5); for formn. of \bar{C} (together with other isomers) from toluene with Cl_2 in pres. of FeCl₃ or MoCl₅ see (8), from o-chlorotoluene (3:8245) or m-chlorotoluene (3:8275) with Cl_2 in pres. of Al/Hg see (9).]

[\ddot{C} with Cl₂ in pres. of Al/Hg yields (10) both 2,3,6-trichlorotoluene (3:0625) and 2,4,5-trichlorotoluene (3:2100).]

 \bar{C} on mononitration in cold with mixt. of $1\frac{1}{2}$ pts. conc. HNO₃ (D=1.4) and 3 pts. conc. H₂SO₄ yields (3) (11) 2,5-dichloro-4-nitrotoluene [Beil. V-332], ndls. from alc. + ether, m.p. 50-51° (3); \bar{C} on dinitration with mixt. of 7 pts. fumg. HNO₃ (D=1.5) and $3\frac{1}{2}$ pts. conc. H₂SO₄ at 100° yields (3) (11) 2,5-dichloro-4,6-dinitrotoluene [Beil. V-345], cryst. from AcOH, m.p. 100-101° (3).

C on oxidn. with dil. HNO₃ in s.t. at 120-150° gives (yield: 82% (7), 60% (2)) (3) (5) (6) 2,5-dichlorobenzoic acid (3:4340), m.p. 154°.

 \bar{C} on sulfonation with fumg. H₂SO₄ yields (1) (3) (12) 2,5-dichlorotoluenesulfonic acid-4 (corresp. sulfonyl chloride, m.p. 43° (1) (12), corresp. sulfonamide, m.p. 191-192° (1) (3) (12)).

[For behavior of C with NaOMe see (2).]

3:6245 (1) Wynne, J. Chem. Soc. 61, 1049-1053 (1892). (2) de Crauw, Rec. trav. chim. 50, 773, 783, 788 (1931). (3) Cohen, Dakin, J. Chem. Soc. 79, 1130-1131 (1901). (4) Kohlrausch, Stockmair, Ypsilanti, Monatsh. 67, 90 (1935). (5) Turner, Wynne, J. Chem. Soc. 1936, 712. (6) Lellmann, Klotz, Ann. 231, 318-319 (1885). (7) Feldman, Kopeliowitsch, Arch. Pharm. 273, 491 (1935). (8) Wynne, Proc. Chem. Soc. 17, 116 (1901). (9) Ref. 3, pp. 1117-1118. (10) Cohen, Dakin, J. Chem. Soc. 81, 1342 (1902).

(11) Cohen, Dakin, J. Chem. Soc. 81, 1347 (1902). (12) Silvester, Wynne, J. Chem. Soc. 1936, 692.

3:6255 o-CHLOROANISOLE
$$C_7H_7OCl$$
 Beil. VI - 184 VI_{1} (o-Chlorophenyl methyl cther) OCH_3 VI_{2} (171)

B.P.
$$198.5-199.5^{\circ}$$
 (1) $D_{4}^{25} = 1.1865$ (18) $n_{D}^{25} = 1.5433$ (18) $195-196^{\circ}$ (2) $D_{4}^{12.6} = 1.1978$ (6) $n_{He}^{12.6} = 1.54786$ (6) $194-200^{\circ}$ u.c. at 751 mm. (3) $192-100^{\circ}$ at 20 mm. (18) 100° at 16 mm. (4) 100° at 13 mm. (5) 100° at 10 mm. (1)

Oil with odor like acetophenone (7). — Volatile with steam.

[For prepn. of \bar{C} from o-chlorophenol (3:5980) by methylation with Me₂SO₄ + KOH (3) or with MeI + KOH in MeOH in s.t. at 130° (8) see (3) (8); from o-aminoanisole via diazo and Sandemeyer reactns. see (9) (2); from guaiacol (1:1405) with PCl₅ see (8); from o-nitroanisole with SOCl₂ at 180-200° see (10).]

 \bar{C} on mononitration with fumg. HNO₃ (8) (11) (12) or with HNO₃ (D=1.5) in Ac₂O (5) yields a mixt. of all 4 possible mononitro products from which the 3-nitro- and 5-nitro isomers are removed by refluxing with 5% NaOH for 1 hr. (5); the unaffected residue extracted by ether consists of 2-chloro-4-nitro-anisole, m.p. 94° (5), and 2-chloro-6-nitro-anisole, m.p. 53° (5); for f.p./compn. data on this system see (5). [2-Chloro-4,6-dinitro-anisole [Beil. VI-260] has m.p. 36° (16), 37° (17).]

[For a study of the reactn. kinetics of the splitting of C in acid soln. see (15).]

3-Chloro-4-methoxybenzenesulfonamide: cryst. from dil. alc., m.p. 130-131° u.c. (13), 130° cor. (14). [From Č + chlorosulfonic acid followed by conversion of the resultant sulfonyl chloride, m.p. 77-80° (14), to sulfonamide with (NH₄)₂CO₃; 85% yield (13).] [A by-product, 3,3'-dichloro-4,4'-dimethoxydiphenyl sulfone, m.p. 165-166° cor. (14) (but unlike the sulfonamide insol. in alk.), has also been observed (14).]

3:8255 (1) Reitz, Ypsilanti, Monatsh. 66, 304 (1935). (2) Gattermann, J. prakt. Chem. (2) 59, 583 (1899). (3) Kohn, Sussmann, Monatsh. 48, 196-197 (1927). (4) Hayashi, J. prakt. Chem. (2) 123, 293 (1929). (5) Ingold, Smith, J. Chem. Soc. 1927, 1690-1695. (6) von Auwers, Z. physik. Chem. A-158, 418 (1932). (7) Holleman, Rec. trav. chim. 37, 104 (1918). (8) Fischli, Ber. 11, 1463 (1878). (9) Wallach, Heusler, Ann. 243, 237-238 (1888). (10) Meyer, Monatsh. 36, 726 (1915).

(11) Reverdin, Ber. 29, 2598 (1896). (12) Reverdin, Eckhard, Ber. 32, 2622 (1899). (13) Huntress, Carten, J. Am. Chem. Soc. 62, 603-604 (1940). (14) Child, J. Chem. Soc. 1932, 718. (15) Ghaswalla, Donnan, J. Chem. Soc. 1936, 1341-1346. (16) Schouten, Rec trav. chim. 56, 550 (1937). (17) van de Vliet, Rec. trav. chim. 43, 623-624 (1924). (18) Anzillotti, Curran, J. Am. Chem. Soc. 65, 609 (1943).

$$d$$
, l -2,2,3-TRICHLOROBUTANOL-1 H Cl C₄H₇OCl₃ Beil. I - 369
CH₃--C --- CH₂OH I_1 --- I_2 -(398)

B.P. 199-200°

M.P. 62°

See 3:1336. Division A: Solids.

3:6270 2,6-DICHLOROTOLUENE

B.P. 199-200° at 760 mm. (13) (1)
$$D_4^{20} = 1.2686$$
 (5) $n_D^{20} = 1.5510$ (5) 198-200° (2) 198° at 760 mm. (3) 197-199° at 757 mm. (4) 54-56° at 8 mm. (5)

[For prepn. of \bar{C} from 6-chloro-2-aminotoluene [Beil. XII-836, XII₁-(389)] via diazotization and use of Cu₂Cl₂ reactn. (70% yield (2)) (1) (3) see indic. refs.; from 2,6-dichlorotoluenesulfonic acid-4 (itself obtd. by chlorination of p-toluenesulfonyl chloride and subsequent hydrolysis) by hydrolysis in conc. H₂SO₄ with superheated steam (yield 42-50% (5)) (4) (6) together with 2,3,6-trichlorotoluene (3:0625) as by-product (5) (6) see indic. refs.; for formn. of \bar{C} (together with other isomers) from toluene with Cl₂ in pres. of MoCl₅ (7) (8) (9), from o-chlorotoluene (3:8245) with Cl₂ in pres. of Fe (9) or Al/Hg (10), or from 2,6-dichlorobenzaldehyde hydrazone by Wolff-Kishner reduction (32-80% yield (19)) see indic. refs.]

\[C\] with Cl₂ in pres. of Al/Hg yields (11) 2,3,6-trichlorotoluene (3:0625); C\] at its b.p. in u.v. light treated with Cl₂ yields (5) 2,6-dichlorobenzyl chloride (3:0410) cryst. from lgr. or ether, m.p. 39-40° (5).]

[C with Br₂ at 170° in sunlight (2) yields (2) (12) 2,6-dichlorobenzyl bromide which on oxidn. with alk. KMnO₄ yields (2) (12) 2,6-dichlorobenzoic acid (3:4200), m.p. 143-144°.]

 $\bar{\mathbb{C}}$ on mononitration in cold with 2 pts. fumg. HNO₃ (11) or with mixt. of 2 pts. conc. HNO₃ (D=1.4) + 3 pts. conc. H₂SO₄ at 100° (3) yields 2,6-dichloro-3-nitrotoluene [Beil. V-332], ndls. from alc. + AcOH, m.p. 53° (3), 52-53° (11), 50° (13); note that the other possible isomer, viz., 2,6-dichloro-4-nitrotoluene, m.p. 65° (14), 63-64° (15), has been obtd. only by other means. — $\bar{\mathbb{C}}$ on dinitration with mixt. of 7 pts. fumg. HNO₃ (D=1.5) and 3½ pts. conc. H₂SO₄ at 100° yields (3) 2,6-dichloro-3,5-dinitrotoluene [Beil. V-345], ndls. from alc., m.p. 121-122° (3), 121° (4) (14); note that the isomeric 2,6-dichloro-3,4-dinitrotoluene, m.p. 130-131° (14), 129-130° (16), has been obtd. only by other means.

Č is extremely resistant to oxidn. either with dil. HNO₃ (9) (1) (3), aq. alk. KMnO₄ (4) (12), acid KMnO₄ (12), KMnO₄ in acetone (4), CrO₃ in H₂SO₄ or AcOH (12), or K₂Cr₂O₇ in H₂SO₄ (12); by conversion of Č with Br₂ to 2,6-dichlorobenzyl bromide (see above) and oxidn. of this with alk. KMnO₄ (2) (12) 2,6-dichlorobenzoic acid (3:4200), m.p. 143-144°, is obtd. in 57% yield (12).

Č on sulfonation with fumg. H₂SO₄ (3) yields 2,6-dichlorotoluenesulfonic acid-3 (corresp. sulfonyl chloride, m.p. 60° (3) (13), corresp. sulfonamide, m.p. 204° (3) (13), 199-201° u.c. (17)); Č on treatment with chlorosulfonic acid in CHCl₃ as directed (17) cf. (18) yields 2,6-dichlorotoluenesulfonyl chloride-3, m.p. 54-56° u.c. (17), 60° (3) (13) (18).

3:6270 (1) Wynne, Greeves, Proc. Chem. Soc. 11, 151-152 (1895). (2) Lehmstedt, Schrader, Ber. 70, 1530 (1937). (3) Cohen, Dakin, J. Chem. Soc. 79, 1131-1133 (1901). (4) Davies, J. Chem. Soc. 119, 873 (1921). (5) Austin, Johnson, J. Am. Chem. Soc. 54, 657-659 (1932). (6) Geigy and Co., Ger. 210,856, June 16, 1909; Cent. 1909, II 79-80. (7) Aronheim, Dietrich, Ber. 8, 1402 (1875). (8) Schultz, Ann. 187, 263 (1877). (9) Claus, Stavenhagen, Ann. 269, 231 (1892). (10) Ref. 3, p. 1117.

Cohen, Dakin, J. Chem. Soc. 81, 1343, 1346 (1902).
 Norris, Bearse, J. Am. Chem. Soc. 62, 956 (1940).
 Silvester, Wynne, J. Chem. Soc. 1936, 692, 695.
 Davies, J. Chem. Soc. 121, 812, 814 (1922).
 Ley, Stephen, J. Chem. Soc. 1931, 78-79.
 Davies, Leeper, J. Chem. Soc. 1926, 1416.
 Huntress, Carten, J. Am. Chem. Soc. 62, 512-513 (1940).
 I.G., Brit. 281,290, Jan. 25, 1928; French 644,319, Oct. 5, 1928; Cent. 1929, II 352.
 Lock, Stach, Ber. 76, 1252-1256 (1943).

3:6280 1,1,2,3,3-PENTACHLOROPROPANE H
$$C_2H_3Cl_6$$
 I— $(sym.-Pentachloropropane)$ $Cl_2CH-C-CHCl_2$ Beil. I_1 -(34) I_2 —

B.P.
$$198-200^{\circ}$$
 (1) $D_{4}^{34} = 1.6086$ (1) $n_{D}^{16.5} = 1.5131$ (1) 126° at 90 mm. (1) $98-100^{\circ}$ at 20 mm. (2)

Colorless liq. — Dissolves sulfur and vulcanized rubber.

[For prepn. (yields: 70-75% (3), 63% (2), 46% at 17° for 22 hrs. (3)) from CHCl₃ (3:5050) + sym-dichloroethylene (3:5030) + AlCl₃ by stirring with sand for 20 hrs. at 30° see (2) (3) (4).]

Č with alc. KOH (1 mole) gives (70% yield (2)) 1,2,3,3-tetrachloropropene-1 (3:5920), b.p. 165-167° (2).

3:6280 (1) Prins, J. prakt. Chem. (2) 89, 421 (1914). (2) Heilbron, Heslop, Irving, J. Chem. Soc. 1936, 782-783. (3) Porns, Engelhard, Rec. trav. chim. 54, 307-312 (1935). (4) Prins, Ger. 261,689, July 2, 1913; Cent. 1913, II 394; [C.A. 7, 3641 (1913)].

3:6290 2,4-DICHLOROTOLUENE CH₃
$$C_7H_6Cl_2$$
 Beil. V - 295 $V_{1^-}(152)$ $V_{2^-}(230)$

B.P. F.P. 199.9-200.5° cor. at 760 mm. (1) -13.5° (1)
$$D_{20}^{20} = 1.2498$$
 (1) 198-200° (2) 1.24597 (6) 1.24597 (6) 196.4-198.2° (3) 196-197.5° (4) $n_{\rm D}^{22} = 1.5480$ (1) 196-197.0° (5) 194° u.c. at 745 mm. (6) 82.0-82.9° at 15 mm. (3)

For f.p./compn. diagram of system: $\bar{C} + 3,4$ -dichlorotoluene (3:6355) see (1); the eutectic conts. 48% \bar{C} and freezes about -38° (1).

[For prepn. of \bar{C} from 2-chloro-4-aminotoluene [Bcil. XII-988, XII₁-(435)] via diazotization and use of Cu₂Cl₂ reaction (yield: 72% (5), 30% (6)) see indic. refs.; similarly from 4-chloro-2-aminotoluene [Beil. XII-835, XII₁-(389)] see (2); from 2,4-diaminotoluene [Beil. XIII-124, XIII₁-(40)] via tetrazotization and use of CuCl₂ reaction (yield: 75% (7), 57% (16), 45% (4)) (3) see indic. refs.; from toluene + AlCl₃ + SO₂Cl₂ at 70° (68% yield) see (10).]

[For formn. of \bar{C} (58% together with 42% 3,4-dichlorotoluene (3.6355) from p-chlorotoluene (3.8287) with Cl_2 in pres. of Fe see (1); for formn. of \bar{C} (together with other isomers) from toluene with Cl_2 in pres. of FeCl₃ or MoCl₅ (8) or by electrolysis in conc. HCl/AcOH soln. (9) see indic. refs.; from p-chlorotoluene (3.8245) or p-chlorotoluene (3.8287) with Cl_2 in pres. of FeCl₃ or MoCl₅ (8) or Al/Hg (11) see indic. refs.; from potassium salt of 2,4-dichlorotoluenesulfonic acid-5 (12), sodium salt of 2,4-dichlorotoluenesulfonic acid-6 (12), or the sodium salt or amide of 2,4-dichlorotoluenesulfonic acid-3 (12) by hydrolysis in H_3PO_4 with steam at 240° see indic. refs.]

[C with Cl₂ in pres. of Fe (13) or of Al/Hg (14) yields 2,4,5-trichlorotoluene (3.2100) together with other isomers; C with Br₂ at 180-200° yields (15) 2,4-dichlorobenzal dibromide which upon hydrolysis with conc. H₂SO₄ as directed gives 92% overall yield 2,4-dichlorobenzaldehyde (3:1800), m.p. 74.5° (15) (for similar reaction with Cl₂ see (5)).]

[C with AlCl₃ + phthalic anhydride gives (60% yield (16)) (17) o-(2,4-dichloro-5-methyl)benzoyl-benzoic acid, cryst. from hot toluene, m.p. 140° (16); this prod. htd. 2 hrs. at 100° with 20 pts. conc. H₂SO₄ + 0.2 pt. H₃BO₃ ring-closes yielding 2,4-dichloro-1-methylanthraquinone, yel. cryst. from CHCl₃, m.p. 155° (16).]

 \bar{C} on mononitration, e.g., with cold mixt. of 2 pts. conc. HNO₃ (D=1.42) + 3 pts. conc. H₂SO₄ (2), yields (2) (8) 2,4-dichloro-5-nitrotoluene [Beil. V-332, V₁-(163)], long hard ndls. from alc., m.p. 54-55° (2), 55° (18), 53° (8), 49-50° (19); \bar{C} on dinitration, e.g., with 7 pts. fumg. HNO₃ (D=1.5) + 3½ pts. conc. H₂SO₄ (2), yields (2) (8) (10) 2,4-dichloro-3,5-dinitrotoluene [Beil. V-345, V₁-(169)], ndls. from MeOH, m.p. 104° (2) (18) (10)

 \tilde{C} on oxidn. with dil. HNO₃ in s.t. at 130-150° (2) (6) (12), with alk. KMnO₄ (70% yield (25)), with Na₂Cr₂O₇ + H₂SO₄ (60% yield (20)), or on electrolytic oxidn. (6.5% yield (21)) gives 2,4-dichlorobenzoic acid (3:4560), m.p. 164°.

 \ddot{C} on sulfonation with fumg. H₂SO₄ yields (2) (22) 2,4-dichlorotoluenesulfonic acid-5 (corresp. sulfonyl chloride, m.p. 72° (22), 71° (2) (24), corresp. sulfonamide, m.p. 176° (2) (22); 175–176° u.c. (23)); \ddot{C} on treatment with chlorosulfonic acid in CHCl₃ as directed (23) cf. (24) yields 2,4-dichlorotoluenesulfonyl chloride, m.p. 71–72° u.c. (23), 71° (24).

3:6290 (1) Wahl, Compt. rend. 202, 2161-2163 (1936); Bull. soc. chim. (5) 4, 344-349 (1937). (2) Cohen, Dakin, J. Chem. Soc. 79, 1129-1130 (1901). (3) Kohlrausch, Stockmair, Ypsilanti, Monatsh. 67, 89 (1935). (4) Erdmann, Ber. 24, 2769-2770 (1891). (5) van de Lande, Rec. trav. chim. 51, 103, 109 (1932). (6) Lellmann, Klotz, Ann. 231, 314-316 (1885). (7) Hodgson, Walker, J. Chem. Soc. 1935, 530. (8) Seelig, Ann. 237, 157, 163, 166, 167 (1887). (9) Fichter, Glantzstein, Ber. 49, 2481-2487 (1916). (10) Silberrad, J. Chem. Soc. 127, 2680-2681 (1925). (11) Ref. 2, pp. 1116-1117. (12) Wynne, J. Chem. Soc. 1936, 703, 705. (13) Feldman,

Ref. 2, pp. 1116-1117. (12) Wynne, J. Chem. Soc. 1936, 703, 705. (13) Feldman,
 Kopeliowitsch, Arch. Pharm. 273, 493-495 (1935). (14) Cohen. Dakin, J. Chem. Soc. 81, 1340-1341 (1902). (15) Lock, Bock, Ber. 70, 923 (1937). (16) Stouder, Adams, J. Am. Chem. Soc. 49, 2044-2045 (1927). (17) Adams (to Newport Co.), U.S. 1,711,165, Apr. 30, 1929; Cent. 1929, II 796; C.A. 23, 2989 (1929). (18) Blanksma, Rec. trav. chim. 29, 415 (1910). (19) Dadswell,
 Kenner, J. Chem. Soc. 1927, 585. (20) Magidsson, Grigorowski, Russ. 47,689, July 31, 1936; Cent. 1937, I 430-431.

(21) Fichter, Adler, Helv. Chim Acta 9, 286 (1926). (22) Silvester, Wynne, J. Chem. Soc. 1936, 692. (23) Huntress, Carten, J. Am. Chem. Soc. 62, 512-513 (1940). (24) I.G., Brit. 281, 290, Jan 25, 1928; French 644, 319, Oct. 5, 1928, Cent. 1929, II 352. (25) Bornwater, Holleman, Rec. trav. chim. 31, 226-230 (1912).

B.P.			B.P. Cont.			
200°	(1) (2)	(13)	193-197°	u.c.	(7)	$D_4^{128} = 1.1851 (11)$
198-200°		(3)	94-96°	at 25 mm.	(8)	
197.5°	at 760 mm.	(20)	88°	at 18 mm.	(9)	
197.7°	at 759 mm.	(4)	79.5°	at 12 mm.	(10)	$n_{\rm He}^{12.8} = 1.54015 (11)$
196.6-197	at 759 mm.	(5)	74.8-75.4	° at 10 mm.	(5)	
194-198° u	.c.	(6)				

Insol. aq.; eas. sol. alc., ether, CHCl₃. — Does not freeze at -18° (3).

[For prepn. from p-chlorophenol (3:0475) by methylation with $Me_2SO_4 + alk$. (7) (6) (1) (60% yield (10)) or with MeI + KOH in s.t. at 120-140° (3) see indic. refs.; from anisole (1:7445) + PCl_5 (2) (100% yield (12)) or SO_2Cl_2 (4) see indic. refs.; from p-chloro-aniline by diazotization and htg. with MeOH see (13).]

Č on mononitration as directed (7) (14) (6) gives (93% yield (6)) 4-chloro-2-nitroanisole [Beil. VI-240], pale yel. lfts. from pet. eth, ndls. or pr. from alc, m.p. 98.5° (15), 98° (14), 96-97.5° (6), 96° (7). [The principal dinitration product, 4-chloro-2,6-dinitroanisole [Beil. VI-260] (best prepd. (16) by further nitration of the 2-nitro prod.), has m.p. 66° (16), 65° (17), 64° (18).]

 \bar{C} on htg. with conc. HCl in s.t. (12) or with NaOMe in MeOH in s.t. at 176° (21) gives MeCl (3:7005) + p-chlorophenol (3:0475). [For study of rate of splitting by acids see (19).]

5-Chloro-2-methoxybenzenesulfonamide: m.p. 154° (22), 150-151° (23). [From C + chlorosulfonic acid followed by conversion of the resultant sulfonyl chloride, m.p. 104° (22), to sulfonamide with (NH₄)₂CO₃; 82% yield (23).]

3:6300 (1) von Auwers, Baum, Lorenz, J. prakt. Chem. (2) 115, 89 (1927). (2) Henry, Ber. 2, 710 (1869). (3) Beilstein, Kurbatow, Ann. 176, 30 (1875). (4) Peratoner, Ortoleva, Gazz. Chim. ital. 28, I 226 (1898). (5) Reitz, Ypsilanti, Monatsh. 66, 305 (1935). (6) Ingold, Smith, Vass, J. Chem. Soc. 1927, 1248. (7) Kohn, Kramer, Monatsh. 49, 151 (1928). (8) Hayashi, J. prakt. Chem. (2) 123, 297 (1929). (9) Jones, J. Chem. Soc. 1942, 419. (10) Bergmann, Engel, Z. physik. Chem. B-15, 95-96 (1931).

(11) von Auwers, Z. physik. Chem. A-158, 418 (1932). (12) Autenrieth, Arch. Pharm. 233, 31-32 (1895). (13) Cameron, Am. Chem. J. 20, 241 (1898). (14) Reverdin, Eckhard, Ber. 32, 2623 (1899). (15) Reverdin, Ber. 29, 2599 (1896). (16) Schouten, Rec. trav. chim. 56, 555 (1937).

(17) van de Vliet, Rec. trav. chim. 43, 622 (1924). (18) Ref. 7, pp. 154-155. (19) Ghaswalla, Donnan, J. Chem. Soc. 1936, 1341-1346. (20) Paulsen, Monatch. 72, 257 (1939).

(21) de Lange, Rec. trav. chim. 38, 103 (1918). (22) Gauntlett, Smiles, J. Chem. Soc. 127, 2745 (1925). (23) Huntress, Carten, J. Am. Chem. Soc. 62, 603-604 (1940).

B.P. M.P. 201-202° cor. at 760 mm. (1) 26-27° (10)
$$n_{\rm D}^{20} = 1.5438$$
 (12) 200° at 750 mm. (2) 26° (2) (3) (5) (6) (7) 195° at 729 mm. (3) 24.8-25.0° (4) 78-79° at 9 mm. (12) 24.5° (12) Sublimes at ord. temp. (3).

[For prepn. of Č from 3,5-dichloro-2-aminotoluene [Beil. XII-837] via diazotization and reactn. with alc. (yield: 80-85% (2), 57% (5)) (1) see indic. refs.; similarly from 3,5-dichloro-4-aminotoluene [Beil. XII-990] see (3) (4); for formn. of Č from 3,5-dibromo-2-aminotoluene [Beil. XII-840, XII₁-(390)] or from 3,5-dibromo-4-aminotoluene [Beil. XII-993, XII₁-(437)] by diazotization followed by treatment with HCl gas in alc. see (6); for prepn. from 3,5-dichloro-2-acetaminotoluene by hydrolysis with EtOH/HCl followed by HNO₂ (34% yield) see (12).]

[Č with Cl₂ in pres. of Al/Hg gives (7) exclusively 2,3,5-trichlorotoluene (3:0610), m.p. 43-45° (7); Č with Cl₂ at 180-190° for 10-12 hrs. gives (2) 3,5-dichlorobenzal dichloride (3:0370).]

[\overline{C} with Br₂ in pres. of Fe gives in cold (70% yield (8)) 2-bromo-3,5-dichlorotoluene, ndls. from alc., m.p. 33.5° (8).]

 \bar{C} on mononitration by soln. in ice-cold fumg. HNO₃ (D=1.52) (9) yields 3,5-dichloro-2-nitrotoluene [Beil. V-331], ndls. from alc. + AcOH, m.p. 61-62° (5) (crude prod. m.p. 57° (9)); \bar{C} on dinitration with mixt. of 4 pts. HNO₃ (D=1.5) + 4 pts. conc. H₂SO₄ (5) or the above mononitro deriv. on further nitration with HNO₃ (D=1.52) at 65° (9) yields 3,5-dichloro-2,6-dinitrotoluene, ndls. from alc., m.p. 99-100° (5); note that the crude dinitration prod. often melts about 90° (9), probably because of contamination with 3,5-dichloro-2,4-dinitrotoluene, m.p. 127° (9).

C on oxidn. with dil. HNO₃ (5) (10) in s.t. at 170° (3) yields 3,5-dichlorobenzoic acid (3:4840), m.p. 188°.

 \bar{C} on sulfonation with fumg. H₂SO₄ yields (5) (11) 3,5-dichlorotoluenesulfonic acid-2, (corresp. sulfonyl chloride, m.p. 44-45° (5) (11), corresp. sulfonamide, m.p. 168-169° (5) (11)).

3:6310 (1) Wynne, Greeves, Proc. Chem. Soc. 11, 151-152 (1895).
 (2) Asinger, Lock, Monatsh.
 62, 345 (1933).
 (3) Lellmann, Klotz, Ann. 231, 322-324 (1885).
 (4) Maryott, Hobbs, Gross, J. Am. Chem. Soc. 62, 2321 (1940).
 (5) Cohen, Dakin, J. Chem. Soc. 79, 1133-1134 (1901).
 (6) Hantssch, Ber. 30, 2344-2346 (1897).
 (7) Cohen, Dakin, J. Chem. Soc. 81, 1343-1344 (1902).
 (8) Asinger, J. prakt. Chem. (2) 139, 299 (1934).
 (9) Borsche, Trautner, Ann. 447, 13 (1926).
 (10) Cohen, Miller, J. Chem. Soc. 85, 174-179 (1904).

(11) Silvester, Wynne, J. Chem. Soc. 1936, 692. (12) Marvel, Overberger, Allen, Johnston, Saunders, Young, J. Am. Chem. Soc. 68, 864 (1946).

3:6312 HEXACHLOROPROPANONE-2
$$Cl_3C$$
— CCl_3 C_3OCl_6 Beil. I - 657 (Hexachloroacetone) I_1 — I_2 — I_3 — I_4 — I_5

B.P. F.P. 202-204° (1) (7)
$$-2$$
° (1) $D_{12}^{12} = 1.744$ (1) (7) 110° at 40 mm. (2) -3 to -4 ° (2)

[See also pentachloropropanone-2 (3:6205).]

Colorless limpid liq. with odor which although faint at low temp. becomes sharp and lachrymatory at higher temps. — \tilde{C} is spar. sol. aq. but with it forms a cryst. monohydrate, m.p. + 15°, alm. insol. aq.

[For prepn. of \tilde{C} from acetone (1:5400) in 90% AcOH + a little HCl with Cl₂ for 12 hrs. at room temp., followed (after addn. of NaOAc) by 40 hrs. further chlorination at b.p. (2), or with Cl₂ in sunlight (1) (some pentachloroacetone (3:6205) is formed by either method): for prepn. of \tilde{C} from chloracetone (3:5425) with Cl₂ at 50–100° in light (3) (4) or under press. (5) see indic. refs.; for formn. of \tilde{C} from citric acid (1:0455) in conc. aq. soln. with Cl₂ in sunlight (1) (6) (7), or from glycerol (1:6540) with Cl₂ in pres. of I₂ (7), see indic. refs.]

C on stdg. with aq. at 30° (2) or with aq. in s.t. at 120° (1) readily undergoes hydrolytic cleavage yielding chloroform (3:5050) and trichloroacetic acid (3:1150).

 \bar{C} with conc. aq. NH₄OH readily splits yielding (1) chloroform (3:5050) and trichloroacetamide, spar. sol. aq., m.p. 141°; similarly \bar{C} with aniline yields (1) chloroform (3:5050) and trichloroacetanilide, m.p. 95-97°.

3:6312 (1) Cloëz, Ann. chim. (6) 9, 199-205 (1886). (2) Edwards, Evans, Wilson, J. Chem. Soc. 1937, 1944-1945. (3) Heisel, Hendschel (to I.G.), U.S. 2,199,934, May 7, 1940; C.A. 34, 5855 (1940). (4) I.G., French 816,956, Aug. 21, 1937, Cent. 1938, I 2216. (5) I.G., French 837,741, Feb. 20, 1939; Cent. 1939, II 228. (6) Stadeler, Ann. 111, 299-300 (1859). (7) Cloës, Ann. 122, 119-122 (1862). (8) Zaharia, Cent. 1896, I 100.

— DI-(TRICHLOROMETHYL) CARBONATE OCCl₃
$$C_3O_3Cl_6$$
 Beil. III - 17 $III_{1^-}(8)$ $III_{2^-}(16)$

B.P. 203° at 760 mm.

M.P. 78-79°

See 3:1915. Division A: Solids.

3:6315 n-BUTYL TRICHLOROACETATE $C_6H_9O_2Cl_3$ Beil. S.N. 160 $n-C_4H_9O.CO.CCl_3$

B.P. 203-205° (1)
$$D_4^{25} = 1.266$$
 (3) $n_D^{25} = 1.4495$ (3) 111° at 40 mm. (2) 100-101° at 24 mm. (3) $D_4^{20} = 1.2778$ (4) $n_D^{20} = 1.4525$ (4)

[For prepn. (82-89% yield (3), 98% yield (2)) from *n*-butyl alc. (1:6180) + trichloro-acetic ac. (3:1150) see (2) (3).]

3:6315 (1) Cheng, Z. physik. Chem. B-24, 308 (1934). (2) Liston, Dehn, J. Am. Chem. Soc. 66, 1264-1265 (1938). (3) Waddle, Adkins, J. Am. Chem. Soc. 61, 3361-3364 (1939). (4) Schjanberg, Z. physik. Chem. A-172, 229 (1935).

3:6317 TRICHLOROACETALDEHYDE DIETHYLACETAL $C_8H_{11}O_2Cl_3$ Beil. I - 621 $(\beta,\beta,\beta$ -Trichloroacetal) Cl_3C — $CH(OC_2H_5)_2$ I₁— (Chloral diethylacetal) I₂—

Colorless oil, spar. sol. aq. (abt. 5 g. C per liter aq. (2)), but misc. with alc., ether, or giveerol.

[For prepn. of \tilde{C} from ethyl α,β,β,β -tetrachloroethyl ether [Beil. I-623, I_2 -(681)] (itself prepd. (25–33% yield (3)) cf. (7) from chloral ethylalcoholate (3:0860) with PCl₅) by protracted boilg. (4) (5) (1) with abs. alc. (70% yield (3)) see indic. refs.; for formn. of \tilde{C} from chloral ethylalcoholate (3:0860) with Cl₂ at 80° (2), or from 75% ethyl alc. with Cl₂ (2), see indic. refs.]

 \ddot{C} above 200° or on distn. with conc. H_2SO_4 yields (2) anhydrous chloral (3:5210).

Č is stable toward alkalies (2) and is unattacked by HCl gas even at 150° (6).

[$\bar{\mathbf{C}}$ with K ter-butylate in ter-butyl alc. splits out HCl giving (76% yield (3)) dichloroketene diethylacetal, b.p. 177° at 732-740 mm., $D_{25}^{25} = 1.1672$, $n_{25}^{25} = 1.4350$ (3).]

3:6317 (1) Paterno, Pisati, Gazz. chim. ital. 2, 333-338 (1872). (2) Byasson, Compt. rend. 87, 26 (1878); Bull. soc. chim. (2) 32, 304-305 (1879). (3) Magnani, McElvain, J. Am. Chem. Soc. 60, 2211-2212 (1938). (4) Wurtz, Frapolh, Jahresber. 1872, 438. (5) Wurtz, Vogt, Zeit. fur Chemie, 1871, 680. (6) Jacobsen, Neumeister. Ber. 15, 602 (1882). (7) Post. J. Org. Chem. 6, 833 (1941).

3:6318
$$\beta,\beta'$$
-DICHLORO-ISOPROPYL ACETATE $C_6H_8O_2Cl_2$ Beil. II - 130 (Glycerol α,α' -dichlorohydrin CH_2Cl II₁-(59) β -acetate, β -aceto- α,γ -dichlorohydrin) H_C —O.CO.CH₃ H_C —O.CO.CH₃

B.P. 205° (1) at 760 mm.	(2)	$D_4^{25} = 1.267$	(6)	$n_{\rm D}^{25} = 1.4513 \ (6)$
202-208°	(3)			_ ,,
204 °	(13)	$D_{20}^{20}=1.281$	(9)	$n_{\rm D}^{20} = 1.4555 \ (7)$
202-203° at 740 mm.	(4)			1.4542 (9)
194–195° u.c.	(11)			• •
193-195°	(9)			
115-120° at 40 mm.	(5)			
108-110° at 40 mm.	(6)			
87-89° at 12 mm.	(7)			
86° at 12 mm.	(8)			
84.5° at 8 mm.	(10)			

[See also β, γ -dichloro-n-propyl acetate (3:6220).]

[For prepn. of \bar{C} from 1,3-dichloropropanol-2 (" α -dichlorohydrin") (3:5985) with AcCl (3:7065) under reflux (11) (9) (15) (3) or with Ac₂O (1:1015) (12) (13) in pres. of a trace of H₂SO₄ (8) see indic. refs.]

[For prepn. of C from 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358) with AcCl (3:7065) (73% yield (7)) in s.t. at 100° for 2 hrs. (10) or 30 hrs. (4) or with Ac₂O (1:1015) in s.t. at 180° for 4 hrs. (4) or in pres. of anhydrous FeCl₃ at ord. temp. for 24 hrs. (90% yield (14)) see indic. refs.]

[For formn. of C from glycerol (1:6540) with AcCl (3:7065) (1) or with AcOH (1:1010) + HCl gas at 100° (1) or from glyceryl triacetate (triacetin) with HCl gas (5) see indic. refs.]

[\bar{C} with MeOH contg. 1% HCl at 60° for 6 hrs. gives (85% yield (7)) 1,3-dichloropropanol-2 (" α -dichlorohydrin") (3:5985); for study of rate of hydrolysis of \bar{C} with N/10 HCl see (15).]

 \bar{C} with K phthalimide at 150-170° for ½ hr., then extracted with AcOH, gives (3) β,β' -bis-(phthalimido)isopropyl acetate, m.p. 194° (3).

3:6318 (1) Berthelot, de Luca, Ann. chim. (3) 52, 459-460 (1858). (2) Gibson, J. Soc. Chem. Ind. 50, 950 (1931) (3) Fairbourne, Cowdrey, J. Chem. Soc. 1929, 133-134. (4) Truchot, Compt. rend. 61, 1171 (1865), Ann. 138, 297-299 (1866), 140, 244-246 (1866). (5) De La Acena, Compt. rend. 139, 868 (1904). (6) Gibson, J. Soc. Chem. Ind. 50, 973 (1931). (7) Sjöberg, Svensk Kem. Tud. 53, 454-457 (1941), Cent. 1942, II25; C.A. 37, 4363 (1943). (8) Wegscheider, Zmerslikar, Monatsh. 34, 1075 (1913). (9) Humnicki, Bull. soc. chim. (4) 45, 280 (1929). (10) Abderhalden, Weil, Fermentforschung 4, 84 (1920); Cent. 1920, III 643.

(11) Henry, Ber 4, 704 (1871). (12) Seelig, Ber. 24, 3470 (1891). (13) Bigot, Ann. chim. (6) 22, 492-493 (1891). (14) Knoevenagel, Ann. 402, 134-138 (1914). (15) Bancroft, J. Am. Chem. Soc. 41, 425, 429 (1919).

3:6323 m-CHLOROPHENETOLE
$$C_8H_9OCl$$
 Beil. VI - 185 VI_1 — VI_2 —

B.P. $204-205^\circ$ cor. at 717 mm. (1) $D_4^{20}=1.1712$ (1) $204-205^\circ$ (2)

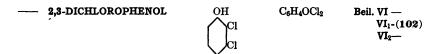
Colorless oil with agreeable odor. - Eas. sol. alc., ether, AcOH, C6H6.

[For prepn. of \tilde{C} from *m*-chlorophenol (3:0255) with EtI + KOH on alc. in s.t. at 100° for 3 hrs. see (1).]

[Č with HCN + C₆H₆ + AlCl₃ at room temp. for 2 hrs. followed by hydrolysis gives (80% yield (2)) 2-chloro-4-cthoxybenzaldehyde [Beil. VIII-81], m.p. 66.5° (2).]

The direct nitration of \tilde{C} has not been reported. [Note, however, that all 4 possible mononitration products are known: viz., 3-chloro-2-nitrophenetole, m.p. 52° (3); 3-chloro-4-nitrophenetole, m.p. 39-40° (3); 3-chloro-5-nitrophenetole, m.p. 47° (4); and 3-chloro-6-nitrophenetole, m.p. 63° (3) (5), 62-63° (6). — The only known dinitro-derivative of \tilde{C} is 3-chloro-4,6-dinitrophenetole [Beil. V1-259], m.p. 112° (7) (8). — The only known trinitro-derivative of \tilde{C} is 3-chloro-2,4,6-trinitrophenetole [Beil. VI-292], m.p. 51° (5). — All 6 of these nitro products were obtained indirectly.]

3:6323 (1) Wohlleben, Ber. 42, 4372 (1909). (2) Gattermann, Ann. 357, 349-350 (1907). (3) Hodgson, Clay, J. Chem. Soc. 1930, 966. (4) van Erp, J. prakt. Chem. (2) 129, 335 (1931). (5) Blanksma, Rec. trav. chim. 21, 322, 325 (1904). (6) Beilstein, Kurbatow, Ann. 182, 110 (1876). (7) Robert, Rec. trav. chim. 56, 939 (1937). (8) Blanksma, Rec. trav. chim. 23, 123 (1904).



B.P. 206°

M.P. 58°

See 3:1175. Division A: Solids.

3:6327 BENZAL (DI)CHLORIDE CHCl₂
$$C_7H_6Cl_2$$
 Beil. V - 297 (Benzylidene (di)chloride, α,α -dichlorotoluene; α,ω -dichlorotoluene) V_2 -(232)

B.P. [207° cor. (1)]
$$-16.0^{\circ}$$
 to -16.2° cor. (9) $D_4^{14} = 1.2557$ (1) -16.1° cor. (10) $n_D^{20} = 1.5503$ (8) 205.2° at 760 mm. (2) -16.4° (11) 1.5502 (13) 205.15° at 760 mm. (3) -17.0° (12) 205° (37) -17.4° (2) $D_4^{0} = 1.2699$ (4) $n_D^{19.4} = 1.5515$ (14) 203.5° (5) See Note 2. See Note 3. (5) See Note 2. See Note 3. (6) 118° at 60 mm. (7) Note 1. The b.p. of 214° given by (15) appears without 104–105° at 30 mm. (8) See Note 1. (9) $D_4^{135.5} = 1.2122$ (4); $D_4^{79.2} = 1.1877$ (4); $D_4^{135.5} = 1.2127$ (4).

Note 3. The value of n_{20}^{20} for mixtures of \bar{C} with benzyl chloride (3:8535) ($n_{20}^{20} = 1.5391$ (13)) is a linear function of their composition (13).

[See also benzyl chloride (3:8535) and benzotrichloride (3:6540).]

Ordinary comml. \bar{C} , usually obtd. by chlorination of toluene, frequently conts. benzyl chloride (3:8535) and benzotrichloride (3:6540), which are difficult (if not impossible) to remove by distillation methods. For purification of \bar{C} by repeated fractional freezing see (5); for patent on purification of \bar{C} from inorganic contaminants see (16). The best approach to pure \bar{C} is from benzaldehyde by action of PCl₅ (see below).

 \overline{C} is insol. aq.; sol. alc., ether, or below -20° in equal vol. of pet. ether (17).

[For a method for quant. detn. of $\bar{\mathbf{C}}$ in mixtures with benzyl chloride (3:8535) and benzotrichloride (3:6540) see (18); for a rapid combustion method for detn. of chlorine in $\bar{\mathbf{C}}$ see (19).]

PREPARATION OF C

From benzaldehyde. [For prepn. of \bar{C} from benzaldehyde (1:0195) with PCl₅ (yield: 80-85% (20)) (21) in CHCl₃ (9), with POCl₃ in C₆H₆ (22), with SOCl₂ (23) (24), with COCl₂ (3:5000) in s.t. at 120-130° (25), with oxalyl (di)chloride (3:5060) in s.t. at 130-140° for 2 hrs. (26), or with succinyl (di)chloride (3:6200) in s.t. at 100° (27) see indic. refs.]

From toluene. [For prepn. of \overline{C} from toluene (1.:7405) with SO₂Cl₂ (2 moles) in presence of a trace of dibenzoyl peroxide refluxed for 6 hours (90% yield (8)), with SOCl₂ in s.t. at 230-250° (28), with PCl₅ in s.t. at 190-195° for 2 hours (29), or with NOCl at 350° (30) see indic. refs.]

[For studies of formn. of C from toluene (1:7405) with Cl₂, especially in light, see the scientific papers (13) (31) (32) (33) and patents (34) (35) (36).]

From other sources. [For formn. of \tilde{C} from benzyl chloride (3:8535) with Cl_2 (37) (38), with NOCl at 150° (39), or with PbCl₄.2NH₄Cl (40) see indic. refs.; from various benzyl ethers by cleavage with PCl₅ see (41); from α -chlorobenzyl chloroformate [Beil. VII-211] by loss of CO_2 on distn. see (42); or from benzaldazine with NOCl see (43).]

CHEMICAL BEHAVIOR OF C

Pyrolysis. [Č passed over red-hot Pt wire gives (44) HCl and both cis (3:1380) and trans (3:4210) tolane dichlorides $(\alpha, \alpha'$ -dichloro- α, α' -diphenylethylenes).]

Reduction. [\bar{C} with H_2 in pres. of Pd/CaCO₃ (45) or Ni (46) in alc. KOH loses all its halogen as HCl (use in quant. detn.) but the corresp. org. reduction prod. has not been characterized. — \bar{C} with H_2 in pres. of colloidal Pd in dil. alc. gives (47) toluene (1:7405), benzyl chloride (3:8535), and α -stilbene dichloride (3:4854). — \bar{C} in MeOH/KOH with hydrazine hydrate in pres. of Pd gives (19% yield (48)) α -stilbene dichloride (3:4854).]

Hydrolysis. C upon hydrolysis yields benzaldehyde (1:0195) and HCl; frequently the reaction is so executed that the benzaldehyde reacts further according to the nature of the environment; examples of both types of reaction are cited below.

[\bar{C} with aq. in s.t. at 140–160° (1), with aq. in pres. of ferric salts (49) or metallic Fe (50) below 100°, with 50% aq. acetone at 72° (59), with conc. H_2SO_4 (2 moles) at 50° subsequently poured into aq. (51), with H_3BO_3 (1 mole) at 130–160° (52) (note that benzyl chloride (3:8535) is unaffected while benzotrichloride (3:6540) gives benzote acid (1:0715)), with boilg. aq. K_2CO_3 (53), with moist NiCO₃ at 120° or moist CoCO₃ at 60° for 3 hrs. (60), with aq. Na₂SO₃ at 110° (54), with ZnO in C_6H_6 followed by aq. (55), with anhydrous formic acid (56) (57), or with anhydrous oxalic acid at 130° (58) gives (yields: 85% (52), 82% (58), 79% (51), 76% (60), 75% (59), 70% (54), 30% (55)) benzaldehyde (1:0195).]

[For study of kinetics of hydrolysis of \bar{C} at 30° and 60° in aq. acetone either directly or in pres. of H_2SO_4 or KOH see (61), with aq. or KOH in 95% alc. see (62): for study of influence of substituents on hydrolysis of \bar{C} see (61) (63) (64).]

[\bar{C} with AcOH + ZnCl₂ gives (65) benzaldehyde (1:0195) + acetyl chloride (3:7065) + HCl. — \bar{C} with anhydrous alkali acetate at 180–200° for 10–20 hrs. gives (66) cinnamic acid (1:0735). — \bar{C} with AgOAc (32) (1) (67) or with PbO in AcOH (68) gives benzal diacetate [Beil. VII-210, VII₁-(119)], m.p. 45–46°.]

Alcoholysis. [C̄ with EtOH + ZnCl₂ gives (65) benzaldehyde (1:0195) + ethyl chloride (3:7015) + HCl; an analogous reaction occurs with C̄ + ZnCl₂ + aromatic alcohols (69). — C̄ with sodium alcoholates under ord. press. gives the corresp. benzaldehyde acetals: e.g., C̄ with MeOH/NaOMe at 100° for 15 hrs. gives (15% yield (70)) (67) benzaldehyde dimethylacetal [Beil. VII-209], b.p. 194-196°; C̄ with EtOH/NaOEt at 100° for 24 hrs. gives (33% yield (70)) (67) benzaldehyde diethylacetal [Beil. VII-209, VII₁-(119)], b.p. 222°. — However, C̄ with sodium alcoholates under press. in s.t. gives (70) benzaldehyde (1:0195) together with the corresp. alkyl chlorides.]

Substitution. Chlorination. [C with Cl₂ in pres. of I₂ gives (32) p-chlorobenzal (di)chloride (3:6700). — Note, however, that C with excess liquid Cl₂ in s.t. in sunlight gives (71) an addn. prod., viz., benzal (di)chloride hexachloride, m.p. 153° (71); also that C with NOCl at 150° substitutes in the side chain giving (39) benzotrichloride (3:6540). — Note further that C with SO₂Cl₂ + dibenzoyl peroxide does not react even when refluxed for 20 hrs. (8); cf. prepn. of C from toluene by this method (above).]

Bromination. [C with Br₂ in pres. of metallic beryllium gives (72) p-bromobenzal (di)-bromide, b.p. 170-171° at 19 mm. (72). — C with Br₂ at 120-140° gives (57) benzodichloride bromide, C₆H₅CCl₂Br, b.p. 88-94° at 1 mm., and benzochloride dibromide, C₆H₅OClBr₂, b.p. 98-103° at 1 mm.]

Sulfonation. [\tilde{C} with SO₃ does not sulfonate but instead undergoes hydrolysis: e.g., \tilde{C} with sulfuric acid monohydrate at 35° gives (73) a mixt. of benzaldehyde-sulfonic acids in the ratio 10% o-+30% m-+60% p-, although these products cannot be isolated as such.] Nitration. [All three isomeric mononitro derivatives of \tilde{C} are known, viz., o-nitrobenzal

(di)chloride [Beil. V-332, V_{1} -(163)], m.p. 27.5° (63), 26–26.5° (61), 25.7° (11); *m*-nitrobenzal (di)chloride [Beil. V-332, V_{1} -(163), V_{2} -(254)], m.p. 64.5–65° (61), 64.5° (11); *p*-nitrobenzal

(di)chloride [Beil. V-332, V₁-(163), V₂-(255)], m.p. 43.0–43.5° (61), 43° (63), 42.8° (11); however, they are best prepared by reaction of the corresp. nitrobenzaldehydes with PCl₅ (74) (75). — For thermal anal. of mixtures of the three nitrobenzal (di)chlorides see (11). — For study of the mononitration of \bar{C} with anhydrous HNO₃ in Ac₂O at 20° giving about 23% o-+34% m-+43% p- see (11) cf. (76). — Note that neither dinitro nor trinitro derivatives of \bar{C} have been reported.]

Behavior with other inorganic reactants. \bar{C} with metals. $[\bar{C}$ with Na on htg. gives {1} stilbene (1:7250). For behavior of \bar{C} with Na in liq. NH₃ giving dibenzyl, benzylamine, and other products see (80). — \bar{C} with equal wt. of Cu powder at 100° for 12 hrs. couples with loss of 2 Cl giving (77) α -stilbene dichloride (3:4854). — \bar{C} on boiling with Cu in aq. Na₂CO₃ for 24 hrs. gives (78) benzaldehyde-copper, 2C₆H₅ CHO Cu, green cryst., decg. about 220° without melting. — \bar{C} with Cu in pyridine reacts vigorously (79), but the products have not been characterized.]

C with inorganic salts [C with AlCl₃ in pet. eth. or CS₂ evolves HCl and resinifies (37); C with yery small amt. AlCl₃ at -15° gives (small yield (81)) phenyl-m-dichloromethyl-phenylchloromethane, b.p. 285° at 750 mm.]

[Č with SbF₃ on htg. gives (82) (83) benzal (di)fluoride [Beil. V-290, V₁-(149), V₂-(224)], b.p. 139.95° (83), $D_{-}^{20} = 1.13572$ (84), $n_{D}^{20} = 1.45775$ (84)]

[C with alc. Na₂S under N₂ gives (85) cf. (86) monomeric thiobenzaldehyde, but this cannot be isolated since it immediately undergoes polymerization to β-trithiobenzaldehyde and/or other reactions. — C with alc. NaSH refluxed 3-4 hrs. gives (86) dibenzyl disulfide [Beil VI-465, VI₁-(229), VI₂-(437)], m.p. 69-70° (86).]

[\bar{C} with conc. aq. NH₄OH on stdg 4 months at ord temp. (87), or \bar{C} with alc. NH₄OH in s.t. at 100° (88), or \bar{C} with alc. NH₄OH + trace of Zn dust at room temp. (88), gives hydrobenzamide [Beil. VII-215, VII₁-(120)], m p. 110°, doubtless through intermediate hydrolysis to benzaldehyde since this can sometimes (88) be isolated.]

Behavior with organic reactants. \bar{C} with hydrocarbons [\bar{C} with C_6H_6 in pres. of AlCl₃ (37) (89), Cr (90), BeCl₂ at 130–140° for 20 hrs. (91), or Zn dust (92) undergoes Friedel-Crafts reaction giving (yields: 28 7% (91), 19.5% (90), 13 4% (37)) triphenylmethane (1:7220) frequently accompanied (37) (89) by other products such as diphenylmethane (1:7120) and triphenylchloromethane (3:3410). — \bar{C} with $C_6H_6+Al+H_6Cl_2$ at 50–55° gives (93) cf. (89) 9, 10-diphenyl-9, 10-dihydroanthracene [Beil. V-745, V₂-(681)], m.p. 164° (89), 159° (93).]

[\bar{C} with toluene in pres. of BeCl₂ refluxed 3 hrs. gives (73% yield (91)) phenyl-di-p-tolylmethane (4,4'-dimethyl-triphenylmethane) [Beil V-712, V₁-(352), V₂-(623)], accompanied by other products. — \bar{C} with toluene + Al + HgCl₂ at 60-70° for 2 hrs. gives (93) a hydrocarbon C₂₈H₂₄, m.p. 185°, possibly having the structure 9,10-di-p-tolyl-9,10-dihydroanthracene.]

[\bar{C} with o-xylene (1:7430) + AlCl₃ in acetylene tetrachloride (3:5750) as solvent gives (very small yield (94)) 2,3,6,7-tetramethyl-9,10-diphenylanthracene, m.p. 312°; note that this product has composition $C_{30}H_{26}$ and is not a dihydroanthracene deriv.]

[For use of \tilde{C} + conc. H_2SO_4 as a color test for various aromatic hydrocarbons see (95) (96).]

 \bar{C} with phenols. [\bar{C} with phenol at 120° for 10 hrs. condenses with loss of HCl giving (87% yield (70)) 4,4'-dihydroxy-triphenylmethane (leucobenzaurin) [Beil. VI-1042, VI₁-(1010)], ndls. from aq. alc. or from CHCl₃, m.p. 160-161° (corresp diacetate, m.p. 115° (97)): this prod. is also obtd. from benzaldehyde (1:0195) by condensation with phenol (1:1420) in pres. of H₂SO₄ (yields: 25% (98), 22% (99)) or H₃PO₄ (100): note that the isomeric benzaldehyde diphenylacetal is unreported. For formn. of resin from \bar{C} with phenol see (101).]

[\tilde{C} with 2 moles β -naphthol (1:1540) on htg. condenses with loss of HCl + H₂O giving (97% yield (102)) (103) 9-phenyl-1,2,7,8-dibenzoxanthene [Beil. XVII-98], pr. or tbls. from AcOH, m.p. 190-191° (103), 190° (102); this prod. is also obtd. from benzaldehyde (1:0195) by condensation with β -naphthol in AcOH in s.t. at 200° for 2 days (104) or in pres. of H₂SO₄ (104) at 100°; see also under benzaldehyde (1:0195) for use as test for latter.]

 \bar{C} with amines. [\bar{C} with aniline (2 moles) in pres. of Zn dust (92) or BeCl₂ at 120–125° for 2 hrs. (91) condenses giving (54% yield (91)) 4,4'-diamino-triphenylmethane [Beil. XIII-274, XIII₁-(89)], cryst. from C₆H₆ with 1 mole solvent, m.p. 106° (106), 104–105° (92), cryst. from dry ether without solvent, m.p. 139–140° (106), 139° (107) (corresp. diacetyl deriv., m.p. 233–234° (108) (109)); this compound is also obtd from benzaldehyde (1:0195) by condensation with 2 moles aniline in various ways, e.g., see (108) (106) (107).]

[Č with N,N-dimethylaniline (2 moles) in pres. of ZnCl₂ at 100° (110) condenses giving 4,4'-bis-(dimethylamino)-triphenylmethane (leuco-Malachite Green) [Beil. XIII-275, XIII₁-(89)], cryst. from C_6H_6 or alc. in 3 forms, mp. 102° (111) (112), m.p. 93–94° (111), 92–93° (112), and 77° (112) cf. (111); thus prod is also obtd from benzaldehyde (1:0195) by condensation with 2 moles N,N-dimethylaniline in various ways, e.g., with ZnCl₂ at 100° (113) (112), or with POCl₃ (alm. 100% yield (114))

[For study of reactivity of C toward pyridine or piperidine see (115).]

 \bar{C} with other nutrogenous reactants. [\bar{C} (excess) with thiourea at not above 150° gives (116) (117) a salt, $C_9H_9N_3S_2$ HCl, m.p. 236° (117), regarded as 4,6-di-imino-2-phenyl-1,3,5-dithiazane (117). — For analogous behavior of \bar{C} with N-phenylthiourea and with N-(p-tolyl)-thiourea see (117) [

[C with Zn salt of o-aminophenyl mercaptan in AcOH/NaOAc refluxed 30 min. in current of H₂S gives (low yield (118)) 2-phenylbenzothiazole, m.p. 114° cor]

 \bar{C} with organometalic reactants. [\bar{C} with MeMgI gives (22% yield (119)) α -stilbene dichloride (3:4854) + ethane but no isopropylbenzene (cumene) or sym.-dimethyldiphenylethane; however, \bar{C} with MeMgCl gives (120) no α -stilbene dichloride but instead a mixture of four other compds., viz., isopropylbenzene (cumene) (1:7440), 1-chloro-1,2-diphenylpropane, and two forms of 2,4-diphenylbutane.]

[\bar{C} with C_6H_6MgBr gives (119) cf. (121) triphenylmethane (1:7220) + α -stilbene dichloride (3:4854) + biphenyl (1:7175) |

[C with Me₂Zn gives (122) isopropylbenzene (cumene) (1:7440).]

[C does not react with Hg di-p-tolyl even on refluxing in toluene for 300 hrs. (123).]

- ₱ Hydrolysis to benzaldehyde: C on boilg. with 10% K₂CO₃ soln. gives benzaldehyde (1:0195); after acidification with HCl the benzaldehyde may be detected with fuchsin aldehyde reagent. (Dif. from pure benzyl chloride (3:8535) or pure benzotrichloride (3:6540).)
- **©** Benzaldehyde phenylhydrazone: m.p. 156° u.c. (From \bar{C} with 3 moles phenylhydrazine refluxed in alc. for 2 hrs. (55% yield {124}); note that from the mother liquor small amounts of an isomeric (γ) benzaldehyde phenylhydrazone, m.p. 154–155°, are obtd. (124).]
- Benzaldehyde semicarbazone: m.p. 219-220° u.c. (124). [From Č (3.2 g.) with semicarbazide hydrochloride (4.4 g.) + Na₂CO₃ (2.1 g.) refluxed a few hrs. in alc. and the ppt. recrystd. from hot aq. (124); note that the m.p. of this prod. varies somewhat with rate of htg. cf. (1:0195).]

3:6327 (1) Limpricht, Ann. 139, 317-321 (1866). (2) Timmermans, Bull. soc. chim. Belg. 25, 334-343 (1913); Cent. 1914, I 618. (3) Locat, Ann. soc. sci. Bruxelles B-47, 68 (1927); Cent. 1927, II 905; C.A. 22, 4296 (1928). (4) Schiff, Ber. 18, 563 (1886). (5) Olivier, Weber, Rec. trav. chim. 53, 880 (1934). (6) Lock, Asinger, Monatsh. 59, 157 (1932). (7) Lauer, J. prakt. Chem. (2) 142, 257 (1935). (8) Kharasch, Brown, J. Am. Chem. Soc. 61, 2146 (1939). (9) Sutton,

Proc. Roy. Soc. (London) A-133, 672-673 (1931). (10) von Schneider, Z. physik. Chem. 22, 234

(11) Holleman, Vermeulen, DeMooy, Rec. trav. chim. 33, 17-25 (1914). (12) Altschul, von Schneider, Z. physik. Chem. 16, 24 (1895). (13) King, Beasley, Proc. Nova Scotian Acad. Sci., 18, 204-212 (1932-33); Cent. 1934, I 3201; C.A. 28, 2686 (1934). (14) Cotton, Mouton, Ann. chim. (8) 28, 214 (1913). (15) "International Critical Tables," Vol. 1, p. 208 (1926). (16) Britton (to Dow Chem. Co.), U.S. 1,804,458, May 12, 1931; Cent. 1931, II 497; C.A. 25, 3668 (1931). (17) Prins, Rec. trav. chim. 42, 26 (1923). (18) Lubs, Clark, J. Am. Chem. Soc. 49, 1449-1453 (1918). (19) Van Winkle, Smith, J. Am. Chem. Soc. 42, 333-347 (1920). (20) Asinger, Lock, Monatsh. 62, 331-333 (1933).

(21) Cahours, Ann. 70, 39-40 (1849). (22) Backes, Compt. rend. 196, 1674-1675 (1933). (23) Loth, Michaelis, Ber. 27, 2548 (1894). (24) Hoering, Baum, Ber. 41, 1918 (1908). (25) Kempf, J. prakt. Chem. (2) 1, 412-413 (1870). (26) Staudinger, Ber. 42, 3976 (1909). (27), Rembold, Ann. 188, 189-190 (1866). (28) Meyer, Monatsh. 36, 729 (1915). (29) Colson, Gautier, Ann. chim. (6) 11, 21-22 (1887). (30) Moyer (to Solvay Process Co.), U.S. 2,152,357, March 28, 1939;

Cent. 1939, II 1775, [C.A. 33, 5001 (1939)].

(31) Mason, Smale, Thompson, Wheeler, J. Chem. Soc. 1931, 3150-3157. (32) Beilstein, Kuhlberg, Neuhof, Ann. 146, 332-323, 327 (1868). (33) Beilstein, Ann. 116, 336-341 (1860). (34) Conklin (to Solvay Process Co.), U.S. 1,828,858 + 1,828,859, Nov. 27, 1931; Cent. 1932, I 1575; [C.A. 26, 632 (1932)]. (35) Imperial Chemical Industries, Ltd., and Wheeler, Brit. 378,866, Sept. 15, 1932; Cent. 1933, II 936; [C.A. 27, 3947 (1933)]. (36) The Selden Co., Swiss 87,961, Jan. 17, 1921; Cent. 1921, IV 354; not in C.A. (37) Böeseken, Rec. trav. chum. 22, 311-312 (1903). (38) Zelinsky, Schering-Kahlbaum, A.G., Ger. 478,084, June 20, 1929; Cent. 1929, II 1216; C.A. 23, 4228 (1929). (39) Perrot, Compt. rend. 198, 1424-1426 (1934). (40) Seyewetz, Trawitz, Compt. rend. 136, 241 (1903).

(41) Whitmore, Langlois, J. Am. Chem. Soc. 55, 1518-1520 (1933). (42) F. Bayer and Co., Ger. 121,223, June 3, 1901; Cent. 1901, II 69. (43) Franzen, Zimmermann, Ber. 40, 2011-2012 (1907). (44) Lob, Ber. 36, 3060 (1903). (45) Busch, Stöve, Ber. 49, 1068 (1916). (46) Kelber, Ber. 50, 309 (1917). (47) Borsche, Heimburger, Ber. 48, 457-458 (1915). (48) Busch, Weber, J. prakt. Chem. (2) 146, 49-50 (1936). (49) Schultze, Ger. 82,927, July 22, 1895; Friedlander 4,

143 (1899). (50) Schultze, Ger. 85,493, Jan. 13, 1896; Friedländer 4, 145 (1899).

(51) Oppenheim, Ber. 2, 212-214 (1869).
(52) Makaroff-Semliansky, Prokin, J. prakt. Chem.
(2) 147, 317-320 (1936/37).
(53) Meunier, Bull. soc. chim. (2) 38, 160 (1882).
(54) Ger, Russian 40,349, Dec. 31, 1934; Cent. 1935, II 3704; [C.A. 30, 3838 (1936)].
(55) Davies, Dick, J. Chem. Soc. 1932, 2808.
(56) Gavankar, Heble, Wheeler, J. Univ. Bombay 6, Pt. II, 112-113 (1937); Cent. 1938, I 4610; [C.A. 32, 3757 (1938)].
(57) Heble, Nadkarni, Wheeler, J. Chem. Soc. 1938, 1322-1323.
(58) Anschütz, Ann. 226, 18 (1884).
(59) Asinger, Lock, Monatsh. 62, 323, 330 (1933).
(60) Vanin, Chernovarova, J. Russ. Phys.-Chem. Soc. 59, 891-894 (1927); Cent. 1928, I 2941; [C.A. 22, 3107 (1928)].

(61) Olivier, Weber, Rec. trav. chim. 53, 869-890 (1934). (62) Petrenko-Kritschenko, Opotzky, Ber. 59, 2136 (1926). (63) Asinger, Lock, Monatsh. 62, 323-348 (1933). (64) Lock, Asinger, Monatsh. 59, 152-160 (1932). (65) Jacobsen, Ger. 11,494, Dec. 7, 1879; Friedländer 1, 24 (1888). (66) B.A.S.F., Ger. 17,467, Aug. 14, 1880, Friedländer 1, 26 (1888); B.A.S.F., Ger. 18,232, Feb. 16, 1881, Friedländer 1, 28 (1888). (67) Wicke, Ann. 102, 363-368 (1857). (68) Bodroux, Bull. soc. chim. (3) 21, 331-333 (1899). (69) Jacobsen, Ger. 13,127, May 25, 1880;

Friedländer 1, 26 (1888). (70) Mackenzie, J. Chem. Soc. 79, 1212-1220 (1901).

(71) van der Linden, Rec. trav. chrm. 57, 1080-1083 (1938).
(72) Pajeau, Compt. rend. 204, 1203 (1937).
(73) Lauer, J. prakt. Chem. (2) 142, 252-257 (1935); (2) 143, 127-138 (1935).
(74) Kliegl, Ber. 40, 4939 (1907); 42, 2583 (1909).
(75) Zimmermann, Müller, Ber. 18, 997 (1885).
(76) Flürscheim, Holmes, J. Chem. Soc. 1928, 1607-1616.
(77) Onufrowicz, Ber. 17, 835-836 (1884).
(78) Bernoulli, Schaaf, Helv. Chim. Acta 5, 726-728 (1922).
(79) Karrer, Wehrli, Biedermann, dalla Vedova, Helv. Chim. Acta 11, 233 (1928).
(80) Dean, Berchet, J. Am. Chem. Soc. 52, 2825 (1930).

(81) Wertyporoch, Farnik, Ann. 491, 265-271 (1931).
(82) van Hove, Bull. acad. roy. Belg.
1913, 1074-1093; Cent. 1914, I 1565; not in C.A.
(83) Swarts, J. chim. phys. 17, 31 (1919).
(84) Swarts, J. chim. phys. 20, 65 (1923).
(85) Wood, Bost, J. Am. Chem. Soc. 59, 1011-1012 (1937).
(86) Fromm, Schmoldt, Ber. 40, 2869-2870 (1907).
(87) Engelhardt, Ann. 110, 77-78 (1859).
(88) Böttinger, Ber. 11, 841 (1878).
(89) Linebarger, Am. Chem. J. 13, 556-559 (1891).
(90) Chakrabarty, Dutt, J. Indian Chem. Soc. 5, 513-518 (1928); Cent. 1929, I 501; [C.A. 23, 822] (1929)].

(91) Bredereck, Lehmann, Schönfeld, Fritzsche, Ber. 72, 1415-1416, 1423 (1939). (92) Böttinger, Ber. 12, 976 (1879). (93) Ray, J. Chem. Soc. 117, 1336, 1338 (1920). (94) Barnett,

J. Chem. Soc. 1939, 348. (95) Levy, Campbell, J. Chem. Soc. 1939, 1442, 1445. (96) Lippmann, Pollak, Monatsh. 23, 670-671 (1902). (97) Meyer, Gerloff, Ber. 56, 103 (1923). (98) Zincke, Wollenberg, Ann. 363, 268 (1908). (99) Russanow, Ber. 22, 1944-1945 (1889). (100) Tanasescu, Simonescu, J. prakt. Chem. (2) 141, 318 (1934).

(101) Baekeland, Bender, Ind. Eng. Chem. 17, 236 (1925). (102) Dilthey, Quint, Heinen, J. prakt. Chem. (2) 152, 66 (1939). (103) Mackensie, Joseph, J. Chem. Soc. 85, 793 (1904). (104) Claisen, Ann. 237, 265-270 (1887). (105) Böttinger, Ber. 11, 276-277 (1878). (106) Fischer, Ann. 206, 147-155 (1880). (107) Weil, Sapper, Krämer, Klöter, Selberg, Ber. 61, 1299 (1928). (108) Baeyer, Villiger, Ber. 37, 2860 (1904). (109) Shoesmith, Sosson, Hetherington, J. Chem. Soc. 1927, 2227. (110) Fischer, Ann. 206, 136-137 (1880).

(111) E. Fischer, O. Fischer, O. Lehmann, Ber. 12, 798 (1879). (112) Heertjes, Bakker, van Kerkhof, Rec. trav. chim. 62, 738-739 (1942). (113) Fischer, Ann. 266, 122-129 (1880). (114) Nencki, Monatsh. 9, 1148-1149 (1888). (115) Tronov, J. Russ. Phys.-Chem. Soc. 58, 1278-1301 (1926); Cent. 1927, II 1145-1146; C.A. 22, 2737 (1928). (116) Abel, Am. Chem. J. 13, 118-119 (1891). (117) Underwood, Dains, J. Am. Chem. Soc. 57, 1769-1770 (1935). (118) Bogert, Stull, J. Am. Chem. Soc. 47, 3081 (1925). (119) Fuson, Ross, J. Am. Chem. Soc. 55, 720-722 (1933). (120) Ellingboe, Fuson, J. Am. Chem. Soc. 55, 2960-2964 (1933).

(121) Reychler, Bull. soc. chim. (3) 35, 739-740 (1906). (122) Liebmann, Ber. 13, 45-46 (1880). (123) Whitmore, Thurman, J. Am. Chem. Soc. 51, 1493, 1497 (1929). (124) Bodforss,

Ber. 59, 666-670 (1926).

3:6335 1,2,3-TRICHLORO-2(CHLOROMETHYL)
$$C_4H_6Cl_4$$
 Beil. I — PROPANE CH_2Cl I_1 — I_2 —(89) I_2 — I_2 —(89) I_1 — I_2 —(89) I_2 — I_3 — I_4 — I_4 — I_5 — I_5 — I_5 — I_5 — I_5 — I_6

Colorless odorless oil (2).

87° at 9 mm. (2)

[For formn. of \bar{C} (together with other products) from ter-butyl chloride (3:7045) + Cl_2 see (1); from 3-chloro-2-(chloromethyl)propene-1 (3:5633) in CHCl₃ by shaking with Cl_2/aq , see (2).]

3:6335 (1) Rogers, Nelson, J. Am. Chem. Soc. 58, 1028 (1936). (2) Kleinfeller, Ber. 62, 1595 (1929).

B.P. 208° M.P. 63°

61-62° at 3 mm. (8)

See 3:1400. Division A: Solids.

[For prepn. of \tilde{C} from 2-chloro-3-aminotoluene [Beil. XII-870, XII₁-(404)] via diazotization and use of Cu_2Cl_2 reaction (alm. quant. yield (2), 64% (8)) see indic. refs.; for formn. of \tilde{C} (together with other dichlorotoluenes) from toluene or o-chlorotoluene (3:8245) with Cl_2 in pres. of FeCl₃ or $MoCl_5$ see (3) (4), from o-chlorotoluene + Cl_2 + Al/Hg see (4).]

[$\bar{\mathbf{C}}$ with Cl₂ in pres. of Al/Hg gives (70% yield (5)) 2,3,4-trichlorotoluene (3:0425), m.p. 41°.] [$\bar{\mathbf{C}}$ with Br₂ at 180–200° gives (8) 2,3-dichlorobenzal (di)bromide (not isolated) which on hydrolysis with conc. H₂SO₄ gives (71% yield (8)) 2,3-dichlorobenzaldehyde (3:1480).]

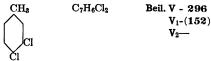
 \bar{C} on mononitration with conc. HNO₃ (6) or cold mixt. of 2 pts. conc. HNO₃ + 3 pts. conc. H₂SO₄ (2) yields 2,3-dichloro-4-nitrotoluene [Beil. V-332], ndls. from alc. + AcOH, m.p. 50.5-51.5° (2), 51° (6); \bar{C} on dinitration with mixt. of 7 pts. fumg. HNO₃ + 3.5 pts. conc. H₂SO₄ yields (2) 2,3-dichloro-4,6-dinitrotoluene [Beil. V-345], cryst. from AcOH or alc., m.p. 71-72° (2).

C on oxidn. with alk. KMnO₄ (6) or with dil. HNO₃ for some hrs. in s.t. at 140° (2) (6) yields 2,3-dichlorobenzoic acid (3:4650), m.p. 166° (6), 163° (2).

Č on sulfonation with 2 pts. 10% oleum at 50° gives (7) mixt. of 89% 2,3-dichlorotoluene-sulfonic acid-6 (corresp. sulfonyl chloride, m.p. 51-52° (7), corresp. sulfonamide, m.p. 228° (7)) and 11% 2,3-dichlorotoluenesulfonic acid-5 (corresp. sulfonyl chloride, m.p. 87° (7), corresp. sulfonamide, m.p. 185° (7)).

3:6345 (1) Wynne, Greeves, Proc. Chem. Soc. 11, 151 (1895). (2) Cohen, Dakin, J. Chem. Soc. 79, 1128-1129 (1901). (3) Seelig, Ann. 237, 157, 166 (1887). (4) Ref. 2, pp 1114-1117. (5) Cohen, Dakin, J. Chem. Soc. 81, 1339-1340 (1902). (6) Ref. 3, pp. 162-163. (7) Silvester, Wynne, J. Chem. Soc. 1936, 692-694. (8) Marvel, Overberger, Allen, Johnston, Saunders, Young, J. Am. Chem. Soc. 68, 861-862 (1946).

3:6355 3,4-DICHLOROTOLUENE



B.P.	F.P.		
207-208.1° cor. at	770 mm. (1) -16.0° (1	$D_{20}^{20}=1.2541 (1)$	
208.3-208.8° at	745.5 mm. (2)	1.2512 (4)	
205.5-206.5°	(3)	$n_{\rm D}^{22} = 1.5490$	(1)
200.5° u.c. at	741 mm. (4)		

For f.p./compn. diagram of system: $\bar{C} + 2.4$ -dichlorotoluene (3:6290) see (1); the eutectic conts. 52% \bar{C} and freezes about -38° (1).

[For prepn. of \bar{C} from 4-chloro-3-aminotoluene [Beil. XII-871, XII₁-(404)] by diazotization and Cu₂Cl₂ reactn. (77% yield (5)) see (5) (6); similarly from 3-chloro-4-aminotoluene [Beil. XII-989, XII₁-(436)] see (4) (3) (1); from 2-chloro-4-methylphenol (3:6215) with PCl₅ see (7); from salts of 3,4-dichlorotoluenesulfonic acid-2 or 3,4-dichlorosulfonic acid-5 by hydrolysis see (8).]

[For formn. of \bar{C} (42% together with 58% 2,4-dichlorotoluene (3:6290)) from p-chlorotoluene (3:8287) with Cl_2 in pres. of Fe see (1); for formn. of \bar{C} (together with other isomers) from toluene with Cl_2 in pres. of I_2 (9) (10) or of $MoCl_5$ (11) (12) or with SO_2Cl_2 at 160° (13) see indic. refs.; for formn. of \bar{C} (together with other isomers) from m-chlorotoluene (3:8275) or p-chlorotoluene (3:8287) with Cl_2 in pres. of Al/Hg see (14).]

[Č with Cl₂ in pres. of Al/Hg yields exclusively (15) 2,4,5-trichlorotoluene (3:2100), m.p. 81-82° (15); Č at its b.p. treated with Cl₂ yields (16) (5) (17) 3,4-dichlorobenzal dichloride (3:6876), b.p. 257°.

Č on mononitration with mixt. of 2 pts. conc. HNO₃ + 4 pts. conc. H₂SO₄ yields (6) (18) 3,4-dichloro-6-nitrotoluene [Beil. V-331], ndls. from alc. + AcOH, m.p. 63-64° (6) (19), 63° (20); Č on dinitration yields (6) 3,4-dichloro-2,6-dinitrotoluene [Beil. V-345], ndls. from AcOH, m.p. 91.5-92.5° (6) (19).

C on oxidn. (2) with CrO₃ (9) (10), with KMnO₄ (21), or with dil. HNO₃ in s.t. at 130-150° (4) (6) (8) yields 3,4-dichlorobenzoic acid (3:4925), m.p. 206°.

[C on sulfonation with fumg. H₂SO₄ yields (6) 3,4-dichlorotoluenesulfonic acid-6 (corresp. sulfonyl chloride, m.p. 81° (6), 82° (22), corresp. sulfonamide, m.p. 190-191° (6), 189° (22)); note, however, that the isomeric derivs., viz., 3,4-dichlorotoluenesulfonyl chloride-2, m.p. 49° (8), and 3,4-dichlorotoluenesulfonamide, m.p. 186° (8), have been independently prepd.]

3:6355 (1) Wahl, Compt. rend. 202, 2161-2163 (1936); Bull. soc. chim. (5) 4, 344-349 (1937). (2) Kraay, Rec. trav. chim. 49, 1085, 1090 (1930). (3) Wynne, J. Chem. Soc. 61, 1059-1060 (1892). (4) Lellmann, Klotz, Ann. 231, 312-314 (1885). (5) Ruggli, Zaeslin, Lang, Hels. Chim. Acta 21, 1248 (1938). (6) Cohen, Dakin, J. Chem. Soc. 79, 1133 (1901). (7) Schall, Dralle, Ber. 17, 2535 (1884). (8) Wynne, J. Chem. Soc. 1936, 702, 705. (9) Beilstein, Kuhlberg, Ann. 146, 319 (1868); 152, 224 (1869). (10) Beilstein, Ann. 179, 283 (1875).

berg, Ann. 146, 319 (1868); 152, 224 (1869). (10) Beilstein, Ann. 179, 283 (1875). (11) Aronheim, Dietrich, Ber. 8, 1402 (1875). (12) Schultz, Ann. 187, 263 (1877). (13) Töhl, Eberhard, Ber. 26, 2942 (1893). (14) Ref. 6, pp. 1117-1118. (15) Cohen, Dakin, J. Chem. Soc. 81, 1343 (1902). (16) Beilstein, Kuhlberg, Ann. 150, 291 (1869). (17) Booth, Elsey, Burchfield, J. Am. Chem. Soc. 57, 2068 (1935). (18) Ruggli, Zaeslin, Helv. Chrm. Acta 19, 437 (1936). (19) Cohen, Dakin, J. Chem. Soc. 81, 1349 (1902). (20) Kenner, Tod, Witham, J. Chem. Soc. 127, 2348 (1925).

(21) Bornwater, Holleman, Rec. trav. chim. 31, 228-229 (1912). (22) Silvester, Wynne, J. Chem. Soc. 1936, 692.

3:6370 HEXACHLOROPROPENE Cl
$$C_3Cl_6$$
 Beil. I - 200 $I_{1^-}(83)$ $Cl_3C-C=Ccl_2$

B.P.
$$209-210^{\circ}$$
 at 760 mm. (1) (2) $D_{4}^{20}=1.7652$ (1) $n_{D}^{20}=1.5091$ (1) $122-123^{\circ}$ at 50 mm. (1) 99° at 15 mm. (2)

Oil with fragrant odor. - Insoluble aq.

[For prepn. of C from sym.-heptachloropropane (3:6860) by loss of HCl in presence of AlCl₃ in CCl₄ at 60-70° (83% yield) see (3); from asym.-heptachloropropane (3:0200) by htg. at 250-420°, especially in presence of ZnCl₂ or CuCl (4) (with latter tetrachloroethylene (3:5460), is also formed (4) (5)), or by htg. with ale KOH at 50-60° (90% yield (6)) (1); from heptachloro-n-butyraldehyde [Beil. I₁-(346)] by actn. of 2 moles NaOEt see (7).]

 \tilde{C} with AlCl₃ + 1 mole trichloroethylene (3:5170) in CH₂Cl₂ (3:5020) or CHCl₃ (3:5050) at 30-37° gives (82% yield (6)) 1,1,2,3,3,4,5,5,5-nonachloropentene-1, colorless liq. with cedar-like odor, b.p. 128° at 2-3 mm., 86° at 0.2 mm., $D_2^{20} = 1.812$, $n_2^{20} = 1.5703$ (6); with excess trichloroethylene (3:5170) prod. is mixt. consisting exclusively of two dodecachloroheptenes, $C_7H_2Cl_{12}$, one m.p. 94-96°, the other, m.p. 58-62° (6).

 \bar{C} with AlCl₃ + 1,2-dichloroethylene (3:5030) in CH₂Cl₂ soln. yields (8) a single 1,1,2,3,-3,4,5,5-octachloropentene-1, b.p. 145-147° at 11 mm., 113-113.5° at 2 mm., $D_{21}^{21} = 1.749$, $n_{21}^{21} = 1.5607$ (8). [This product with conc. H₂SO₄ gives (80% yield (8)) a mixt. of pentachlorobutenecarboxylic acids (8).]

Č forms with AlCl₃ at 80° a yel. cryst. addn.-prod. sparingly sol. in CCl₄ but regenerating Č upon treatment with aq. (8).

 \tilde{C} on cautious warming with conc. H₂SO₄ (9) (10) (2) (11) or on boilg. with an aqueous suspension of BaCO₃ (2) yields α,β,β -trichloroacrylic acid (3:1840) spar. sol. cold aq., eas. sol. hot aq., pr. from CS₂, m.p. 76° (2).

Č does not add Br₂ (10), but Č in sunlight adds Cl₂ yielding (10) octachloropropane (3:4450) q.v.

 \bar{C} with alc. NaOEt yields (1) triethyl ortho- α,β,β -trichloroacrylate, b.p. 236-237°, $D_4^{20}=1.2183$, $n_D^{20}=1.4649$ (1). [This ortho ester on htg. with 2 vols. conc. HCl yields (1) ethyl α,β,β -trichloroacrylate, b.p. 192-194°, $D_4^{20}=1.3740$, $n_D^{20}=1.4839$ (1), which can be hydrolyzed by conventional methods to α,β,β -trichloroacrylic acid (see above).]

\$:8376 (1) Fritsch, Ann. 297, 314-316 (1897).
 \$\text{B\"o}\"o}\"o\$ B\"o\$eseken, Dujardin, Rec. trav. chim. 32, 98-100 (1913).
 \$\text{Prins}\"o\$, Rec. trav. chim. 54, 251-252 (1935).
 \$\text{B\"o}\"o\$eseken, van der Scheer, de Voogt, Rec. trav. chim. 34, 78-95 (1915).
 \$\text{B\"o}\"o\$eseken, Rec. trav. chim. 45, 467-468 (1915).
 \$\text{Prins}\"o\$, Rec. trav. chim. 57, 661-662 (1938).
 \$\text{P\"o}\"o\$eseken, Schimmel, Rec. trav. chim. 32, 132 (1913).
 \$\text{P\"o}\"o\$ Prins, Rec. trav. chim. 56, 781-783 (1937).
 \$\text{P\"o}\"o\$ Prins, Ger. 261,689, July\$\(\frac{1}{2}\)2, 1913; Cent. 1913, II 394.
 \$\text{P\"o}\"o\$ Prins, J. prakt. Chem. (2) 89, 415-416 (1914).

(11) Böeseken, Carrière, Rec. trav. chim. 34, 179-186 (1915).

3:6373 DI(TRICHLOROVINYL) ETHER Cl Cl C4OCl6 Beil. I - 725 Cl₂C=C-O-C=CCl₂
$$I_1$$
- I_2 -

B.P. 210° (1)
$$D_{-}^{21} = 1.654$$
 (1)

[For prepn. of \bar{C} from decachlorodiethyl ether (3:1676) by treatment with alc. K_2S see (1).]

C with Cl₂ in sunlight adds 2 moles halogen yielding (1) decachlorodiethyl ether (3:1676), m.p. 69°.

 $\ddot{\mathbf{C}}$ with Br₂ in sunlight adds 2 moles halogen yielding (1) bis- $(\alpha,\beta$ -dibromo- α,β,β -trichloro-ethyl) ether, m.p. 96° (1).

3:6373 (1) Malaguti, Ann. chim. (3) 16, 19-28 (1846).

3:6375 ETHYL
$$\gamma$$
-CHLOROACETOACETATE $C_{\theta}H_{\theta}O_3Cl$ Beil. III - 663 (Ethyl γ -chloro- β -keto- n - CH_2 — C — CH_2 — C — C III₁-(233) butyrate) Cl O O Et

			O1	0 020	
B.P.			F.P.		
210° dec.	•	(1)	-5° (2) (9)	$D_4^{20} = 1.2157 (4)$	
205° dec.	•	(2) (9)	-8° (1)		
117-119	° at 17 mm.	(3)		$D_4^{17} = 1.2176 (4)$	$n_{\rm D}^{17} = 1.4546 (4)$
107°	at 14 mm.				1.45452 (1)
105°	at 11 mm.	(2) (9)		14	
102°	at 12 mm.	(1)		$D_4^{16} = 1.2182 (4)$	
103°	at 12 mm.				
92-93°	at 6 mm.				
80°	at 3 mm.	(19)			

[See also ethyl α -chloroacetoacetate (3:6207).]

Colorless limpid liq. which soon turns yellow (4). — Almost insol. aq. but miscible with most org. solvents. — [Note that purity of material of earlier workers (5) has been seriously questioned (2).]

[For prepn. of \bar{C} from acetylketene (ketene dimer (6) (7)) by conversion with Cl_2 to γ -chloroacetoacetyl chloride (3:9088) and reactn. of the latter with excess abs. EtOH at 0° see (3); from ethyl chloroacetate (3:5700) (2 moles) with Mg (1 mole) in dry ether contg. HgCl₂ (58% yield (1)) cf. (19) or with Mg in dry ether contg. I₂ (35% yield (4)) or with

Al/Hg in pres. of a trace of EtOH (8) see indic. refs.; from chloroacetaldehyde (3:7212) with ethyl diazoacetate see (5); from ethyl γ -chloro- β -hydroxy-n-butyrate [Beil. III-310, III₁-(116)] by careful oxidn. with $K_2Cr_2O_7 + H_2SO_4$ (poor yield) see (9).]

 \bar{C} on hydrolysis with aq. HCl for 3 hrs. undergoes ketonic splitting yielding (1) chloroscetone (3:5425) + CO₂ + EtOH (note that this does not distinguish \bar{C} from ethyl α -

chloroacetoacetate which yields same products).

[Č with alc. NaOEt at 100° undergoes bimolecular condensation with loss of 2 HCl yielding (10) diethyl succinylosuccinate [Beil. X-894, X₁-(434)], m.p. 125-126° (10); this same condensation is also effected by other alkaline agents, e.g., sodium phenolate, dil. aq. NaOH, NH₄OH, NH₃ in ether, KOAc alone or in pres. of alc. or C₆H₆, diethyl sodiomalonate or Me₂NH in C₆H₆, or K phthalimide (10).]

[Č with ethyl orthoformate (1:3241) in Ac₂O refluxed for $\frac{1}{2}$ hr. ppts. on cooling (45% yield (11)) ethyl γ -chloro- α -ethoxymethylene-acetoacetate, colorless ndls. from alc. or C₆H₆, m.p. 98° (11).]

Note that \bar{C} is capable of displaying keto-enol tautomerism as is shown by the following reactions:

 \bar{C} with FeCl₂ soln. gives red coloration (1) (4) (9) (19); \bar{C} conts. 10.9% enol, but 4% soln. of \bar{C} in ether conts. 53% enol. (19).

 $\bar{\rm C}$ forms a series of metallic salts of the enolic form; these are in general insol. in aq. but soluble in org. solvents: e.g., ${\rm Cu}({\rm C}_6{\rm H}_8{\rm O}_3{\rm Cl})_2$ (from $\bar{\rm C}$ on shaking with aq. ${\rm Cu}({\rm OAo}_2)$, green ndls. from ${\rm C}_6{\rm H}_6$, m.p. 168–169° dec. (9) (4) cf. (19), 167.5° dec. (1), 163° (8); Mg-(C₆H₈O₃Cl)₂ (from $\bar{\rm C}$ shaken with aq. MgSO₄ + NH₄Cl), m.p. 170° (1); Zn(C₆H₈O₃Cl)₂ (from $\bar{\rm C}$ on shaking with NH₄OH/ZnSO₄), m.p. 121° (1); Ni(C₆H₈O₃Cl)₂ (from $\bar{\rm C}$ on shaking with Ni(OAc)₂ + NH₄OH), m.p. 131–132° (1); other metals behave similarly (1).

 $\ddot{\mathbf{C}}$ couples with diazonium salt solns. in pres. of NaOAc yielding the corresp. α -(arylhydrazones) of ethyl γ -chloro- α , β -diketo-n-butyrate (ethyl γ -chloro- α -(arylazo)aceto-acetates (cf. dif. behavior of isomeric ethyl α -chloroacetoacetate (3:6207)): e.g., $\ddot{\mathbf{C}}$ with benzenediazonium chloride soln. in pres. of NaOAc at 0° gives (12) (13) ethyl γ -chloro- β -keto- α -phenylhydrazono-n-butyrate, sparing sol. yel. ndls. from alc., m.p. 92-93° (12) (13), 92° (14) (note that this prod. on htg. with alc. KOAc loses HCl and ring-closes to 3-carbethoxy-4-hydroxy-1-phenylpyrazole, colorless pr. from alc., m.p. 85° (14) (15)); similarly $\ddot{\mathbf{C}}$ with p-nitrobenzenediazonium chloride soln. in pres. of NaOAc at 0° gives (16) ethyl γ -chloro- α -(p-nitrobenzeneazo)acetoacetate, yel. ndls. from alc., m.p. 135° (16) (note that this prod. with hot alc. KOAc loses HCl and ring-closes to 3-carbethoxy-4-hydroxy-1-(p-nitro)phenylpyrazole, colorless ndls. from AcOH, m.p. 220° (16). — [For analogous reactions of $\ddot{\mathbf{C}}$ with numerous other diazonium salts see the papers represented by (16) (14) (17).]

 \bar{C} with thiourea on warming in alc. for 4 hrs. loses HCl and ring-closes yielding (9) ethyl (2-aminothiazolyl-4)acetate, colorless cryst. from C_6H_6 , m.p. 94° (18), 74° (9) (one of these is probably a misprint for the other).

3:6375 (1) Hamel, Bull. soc. chim. (4) 29, 390-402 (1921). (2) Lespieau, Bull. soc. chim. (4) 9, 31-33 (1911). (3) Hurd, Abernathy, J. Am. Chem. Soc. 62, 1147-1148 (1940). (4) Alexandrow, Ber. 46, 1021-1024 (1913). (5) Schlotterbeck, Ber. 42, 2570-2571 (1909). (6) Boese, Ind. Eng. Chem. 32, 16-22 (1940). (7) Hurd, Williams, J. Am. Chem. Soc. 58, 962-968 (1936). (8) Picha, Doht, Weisl, Monatsh. 27, 1245-1249 (1906). (9) Lespieau, Bull. soc. chim. (3) 33, 463-464 (1905); Compt. rend. 138, 422 (1904). (10) Sommelet, Couroux, Bull. soc. chim. (4) 29, 402-406 (1921).

(11) Benary, Ebert, Ber. 56, 1897-1898 (1923). (12) Favrel, Compt. rend. 145, 196 (1907). (13) Favrel, Prevost, Bull. soc. chim. (4) 49, 245-246 (1931). (14) Chattaway, Lye, Proc. Roy. Soc. London A-137, 492, 497, 501 (1932). (15) Wolff, Ann. 313, 15 (1900). (16) Chattaway, Ashworth, J. Chem. Soc. 1933, 1146. (17) Chattaway, Lye, Proc. Roy. Soc. London A-136,

294-295 (1932). (18) Steude, Ann. 261, 30-31 (1891). (19) Arndt, Loewe, Capuano, Rev. faculté sci. univ. Istanbul 8-A, 122-152 (1943); C.A. 39, 1626 (1945).

—
$$d_1l$$
- α,β -DICHLOROPROPIONIC ACID $C_3H_4O_2Cl_2$ Beil. II - 252 Π_1 -(111) Π_2 —

B.P. M.P. 210° sl. dec. at 762 mm. 49-50°

See 3:0855. Division A: Solids.

B.P. 211° at 744 mm.

M.P. 58°

Sec 3:1190. Division A: Solids.

 $D_{-}^{25} = 1.4723$ $n_{\rm D}^{25} = 1.1729$ B.P. 211° M.P. 45°

See 3:0560. Division A: Solids.

101.5°

at 17 mm. (3)

3:6380 ETHYL
$$\alpha,\alpha,\beta$$
-TRICHLORO- n -BUTYRATE $C_0H_0O_2Cl_3$ Beil. II - 281 II_1 — Cl_3 — Cl_4 — Cl_5 — C

[For prepn. of \bar{C} from α,α,β -trichloro-n-butyric acid (3:1280) in EtOH with 10% conc. H₂SO₄ in s.t. at 100° for 3 days see (2); note that the acid esterifies with difficulty and attempts to use the dry HCl method give only very poor yields (2).]

 \bar{C} with Zn dust in moist ether loses HCl giving (almost 100% yield (3)) ethyl α -chlorocrotonate (3:8523).

3:6380 (1) Judson, Ber. 3, 787 (1870). (2) Perkin, J. Chem. Soc. 65, 424 (1894). (3) Michael, Schulthess, J. prakt. Chem. (2) 43, 594-596 (1891).

[For prepn. of \bar{C} from o-chlorobenzyl alcohol [Beil. VI-444, VI₁-(222)] with PCl₅ (7) or with SOCl₂ + pyridine (5) see indic. refs.; from o-chlorotoluene (3:8245) with PbCl₄-2NH₄Cl (1) or with Cl₂ (8) (9) in ultra-violet light (4) see indic. refs.; from benzyl chloride (3:8535) with Cl₂ see (10).]

[For condens. of \tilde{C} with p-chlorophenol and use of prod. as anti-moth prepn. see (11); for use in prepn. of condensation prod. with sulfonated phenol see (12).]

[C with phenol in toluene yields (13) 2-(o-chlorobenzyl)phenol, b.p. 146-151° at 3 mm. (benzoate, b.p. 173-176° at 2.5 mm.), and o-chlorobenzyl phenyl ether, b.p. 140-145° at 2.5 mm.; C with 2,4-dichlorophenol (3:0560) in toluene yields 2-(o-chlorobenzyl)-4,6-dichlorophenol, m.p. 59.5-60.5° (benzoate, m.p. 81-82°), and o-chlorobenzyl 2,4-dichlorophenyl ether, m.p. 61-62°.]

[C with phenol + AlCl₃ yields (13) 4-(o-chlorobenzyl)phenol, m.p. 68-69° (benzoate, m.p. 64.5-65.5°), and 2-(o-chlorobenzyl)phenol (see above); C with 2,6-dichlorophenol (3:1595) + AlCl₃ yields (13) 4-(o-chlorobenzyl)-2,6-dichlorophenol, m.p. 86.5-87.5° (benzoate, m.p. 86-87°).]

[C with Mg in 10 moles dry ether gives (60-75% yield (4)) cf. (25) o-Cl.C₆H₄.CH₂MgCl (particularly sensitive to air oxidn.); this with CO₂ followed by acidification or with methyl chloroformate (3:5075) followed by hydrolysis yields (4) o-chlorophenylacetic acid, m.p. 94-95° (3:2640); the R.MgCl cpd. with phenyl isocyanate as directed (22) for p-isomer should yield o-chlorophenylacetanilide [Beil. XII-275], m.p. 140° cor. (23), 138.5° (24), although this method has not been specifically reported for C; the RMgCl cpd. with HgCl₂ gives (25) o-chlorobenzyl HgCl, m.p. 111°, or with HgBr₂ gives (25) o-chlorobenzyl HgBr, m.p. 128°.]

[For study of behavior of \bar{C} with NaOEt see (14) (7); for study of rate of reaction of \bar{C} with LiI, NaI, or KI (6) (5) or with Na₂SO₃ (2) see indic. refs.; for study of acid hydrolysis of \bar{C} in various solvents see (5); for reaction of \bar{C} with KCN yielding o-chlorobenzyl cyanide (which on hydrolysis gives o-chlorophenylacetic acid (3:2640)) see (15) (16); for behavior of \bar{C} with cellulose (17) or sodium cellulose (18) see indic. refs.]

Č refluxed 4 hrs. with hexamethylenetetramine (1 mole) in 60% alc. soln. yields (19) o-chlorobenzaldehyde (3:6410) q.v.; Č htd. in xylene with p-nitrophenylhydrazine yields (20) o-chlorobenzal-p-nitrophenylhydrazone, m.p. 241° (20).

Č on mononitration with 1.2 pts. fumg. HNO₃ at 30-40° gives (35% yield (21)) 2-chloro-5-nitrobenzyl chloride, pr. from alc., m.p. 66° (21).

3:6400 (1) Seyewetz, Trawitz, Compt. rend. 136, 241 (1903). (2) Sprung, J. Am. Chem. Soc. 52, 1640-1649 (1930). (3) de Bruyne, Davis, Gross, J. Am. Chem. Soc. 55, 3938 (1933). (4) Austin, Johnson, J. Am. Chem. Soc. 54, 657 (1932). (5) Bennett, Jones, J. Chem. Soc. 1935, 1818. (6) Conant, Hussey, J. Am. Chem. Soc. 47, 486 (1925). (7) Olivier, Rec. trav. chim. 41, 308-309 (1921). (8) Jones, J. Chem. Soc. 1935, 1839. (9) Zelinsky & Schering-Kahlbaum, Ger. 478,084, June 20, 1929; Cent. 1929, II 1216. (10) Olivier, Rec. trav. chim. 41, 419-421 (1921).

(11) Weiler, Berres (to I.G.), Ger. 542,069, Jan. 20, 1932; Cent. 1932, I 3014. (12) I.G., Brit. 320,056, Oct. 31, 1929; Cent. 1939, I 590; Brit. 321,190, Nov. 28, 1929; Cent. 1939, I 1259. (13) Huston, Guile, Chen, Headley, Warren, Baur, Mate, J. Am. Chem. 50c. 55, 4639-4643 (1933). (14) Franzen, Rosenberg, J. prakt. Chem. (2) 101, 333-334 (1921). (15) Cerecedo, Sherwin, J. Biol. Chem. 58, 220 (1923). (16) Mehner, J. prakt. Chem. (2) 62, 554-555 (1900). (17) Niethammer, König, Cellulosechem. 10, 201-205 (1929). (18) Ball, Hibbert, Can. J. Research 7, 481-498 (1932). (19) Mayer, English, Ann. 417, 78 (1918). (20) Busch, Lang, J. prakt. Chem. (2) 144, 312 (1936).

(21) Meisenheimer, Zimmermann, von Kummer, Ann. 446, 225-226 (1926). (22) Underwood, Gale, J. Am. Chem. Soc. 56, 2117-2119 (1934). (23) Jenkins, Richardson, J. Am. Chem. Soc. 55, 1619 (1933). (24) Mehner, J. prakt. Chem. (2) 62, 558 (1900). (25) Ware, Hixon, J. Am.

Chem. Soc. 69, 1262-1263 (1938).

3:6410 o-CHLOROBENZALDEHYDE
$$C_7H_5OCl$$
 Beil. VII - 233 VII_1 -(132)

B.P.
$$M,P.$$
 (1) 11° (4) $D_4^{20} = 1.2512$ (6) $n_D^{20} = 1.56708$ (6) (2) (14) $209.7-211.7^{\circ}$ at 760 mm. (3) 208° at 748 mm. (4) $205-206^{\circ}$ cor. at 740 mm. (5) $96.0-96.6^{\circ}$ at 16 mm. (3)

Oil, volatile with steam. — \tilde{C} often contains o-chlorobenzyl chloride (3:6400) as impurity (7). — \tilde{C} very easily oxidized in air (probable cause of variant constants). — \tilde{C} yields NaHSO₃ cpd. (15) (21).

[For prepn. of \bar{C} from o-chlorotoluene (3:8245) with MnO₂ + H₂SO₄ (8), or PbO₂ (24% yield (21)), or CrO₂Cl₂ in CCl₄ (9) or CS₂ (10), or via halogenation to o-chlorobenzal (di)chloride (3:6625) (5) (12) or o-chlorobenzal (di)bromide (11) and subsequent hydrolysis with fumg. H₂SO₄ (11) (12) (1) or anhydrous oxalic ac. (14) see indicated refs.; for prepn. from o-nitrobenzaldehyde via o-aminobenzaldehyde see (12); from o-chlorobenzyl alc. by dehydrogenation with CuO + dinitrobenzene in quinoline (86% yield) see (13); from o-chlorobenzyl chloride (3:6400) with hexamethylenetetramine see (2); from o-chlorobenzylamine with formalin + hexamethylenetetramine see (41); for other misc. methods see Beil. VII-233].

Č with CrO₃ (16) or KMnO₄ (2) oxidizes to o-chlorobenzoic acid (3:4150), m.p. 141°. [For study of auto-oxidn. see (17).] — Č on cat. hydrogenation gives (yield: 96% (18); 50% (19)) o-chlorobenzyl alc., m.p. 69° (19), 64–65° (18). — Č with conc. alk. undergoes Cannizzaro reactn. (for study on dioxane soln. see (20)) although presumable products, o-chlorobenzyl alc. and o-chlorobenzoic acid, have not (by this reactn.) actually been isolated.

Č with dil. alc. KCN for 4 hrs. at 60° gives (21% yield (22)) 2,2'-dichlorobenzoin, m.p. 63-64° (22). — Č with KCN + HCl yields o-chloromandelonitrile which on hydrolysis with HCl gives o-chloromandelic acid, m.p. 84-85° (23).

Č on htg. with NaOAc + Ac₂O for 8 hrs. at 180-200° undergoes Perkin reactn. giving (71% yield (12)) o-chlorocinnamic acid, m.p. 211° (12). [This with Br₂ in CHCl₃ gives (24) o-chlorocinnamic acid dibromide, m.p. 183° (24).] — Č + malonic acid + pyridine gives (38) alm. quant. yield of o-chlorocinnamic ac., m.p. 211-212° (31). [In absence of pyridine reactn. gives 93% yield o-chlorobenzalmalonic acid, m.p. 192° (37).]

C on mononitration as specified (25) gives 2-chloro-5-nitrobenzaldehyde, cryst. from

dil. AcOH, m.p. 78-79° (25), 80° (26). [Oxime, m.p. 147-148° (26); corresp. acid, 2-chloro-5-nitrobenzoic acid, m.p. 165° (25).]

Č in alc. warmed at 58-60° for 2 hrs. with (NH₄)₂CO₃ + KCN as directed (37) gives 5-(o-chlorophenyl)hydantoin, m.p. 175.7-176.1° cor. (37).

[Č with hydrazine sulfate gives (91-95% yield (40)) o-chlorobenzaldazine, m.p. 143.5° cor., but Č with hydrazine hydrate gives (84% yield (40)) o-chlorobenzaldehyde hydrazone m.p. 33-34°, b.p. 165-170° at 14 mm.; note that latter on Wolff-Kishner reduction gives (35-82% yield (40)) o-chlorotoluene (3:8245).]

- ① o-Chlorobenzaldoxime (anti form): pr. from alc., m.p. 75-76° (1) (27). [From Č + NH₂OH.HCl + Na₂CO₃ (1); the sym. isomer has m.p. 98-102° (28), 101-103° (7).]
- O-Chlorobenzaldehyde phenylhydrazone: m.p. 86° (29), 84° (39).
- O-Chlorobenzaldehyde p-nitrophenylhydrazone: or. pl., m.p. 249° (30) (31); br.-red. ndls., 241° (32); red ndls. from alc., 237–238° (13).
- © o-Chlorobenzaldehyde 2,4-dinitrophenylhydrazone: or.-red. ndls. from xylene, m.p. 209° (33), 213.6° (34) 207° (41). [Use in detn. of C (11).]
- ① o-Chlorobenzaldehyde dimethone: ndls. from alc., m.p. 199° u.c., 205° cor. (35). [Corresp. anhydride, cryst. from alc., m.p. 224-226° cor. (35).]
- © o-Chlorobenzaldehyde semicarbazone: lfts. from MeOH, m.p. 229-230° (36), tbls. from pyridine, m.p. 225-226° (9), 226° (42).
- 3:6410 (1) Erdmann, Schwechten, Ann. 260, 55-58 (1890). (2) Mayer, English, Ann. 417, 78 (1918). (3) Kahovec, Kohlrausch, Z. physik. Chem. B-38, 138 (1937). (4) Hoechster Farbwerke, Ger. 207,157; Cent. 1909, I 962. (5) Asinger, Lock, Monatsh. 62, 333-334 (1933). (6) von Auwers, Ann. 422, 166 (1921). (7) Brady, Cosson, Roper, J. Chem. Soc. 127, 2428-2429 (1925). (8) Gilliard, Monet, Cartier, Ger. 101,221; Cent. 1899, I 960. (9) Law, Perkin, J. Chem. Soc. 93, 1636 (1908). (10) Stuart, Elliot, J. Chem. Soc. 53, 803 (1888).
- (11) Eitel, Lock. Monaish. 72, 388-389 (1939). (12) Bock, Lock, Schmidt, Monaish. 64, 406 (1934). (13) Zetsche, Zala, Helv. Chim. Acta 9, 288-290 (1926). (14) Erdmann, Kirchhoff, Ann. 247, 368 (1888). (15) Rosenmund, Zetsche, Ber. 54, 436-437 (1921). (16) Henry, Ber. 2, 136 (1869). (17) van der Beek, Rec. trav. chim. 51, 411-413 (1932). (18) Carothers, Adams, J. Am. Chem. Soc. 46, 1682 (1924). (19) Rosenmund, Jordan, Ber. 58, 162 (1925). (20) Eitel, Lock, Monaish 72, 407 (1939).
- (21) Olivier, Weber, Rec. trav. chim. 53, 881 (1934). (22) Weissberger et al., Ann. 478, 128 (1930); J. Chem. Soc. 1935, 225. (23) Karrer et al., Helv. Chim. Acta 4, 144 (1921). (24) Willstaedt, Ber. 64, 2690 (1931). (25) Hodgson, Beard, J. Chem. Soc. 1926, 151. (26) Erdmann, Ann. 272, 153-154 (1892). (27) Brady, McHugh, J. Chem. Soc. 125, 551 (1924). (28) Behrend, Niessen, Ann. 269, 400 (1892). (29) Fichter, Frohlich, Cent. 1903, II 427. (30) Chattaway, Clemo, J. Chem. Soc. 123, 3059-3060 (1923).
- (31) Hodgson, Beard, J. Soc. Chem. Ind. 45, T 91-93 (1926). (32) Busch, Lang, J. prakt. Chem. (2) 144, 312 (1936). (33) Blanksma, Wacker, Rec. trav. chim. 55, 658 (1936). (34) Ferrante, Bloom, Am. J. Pharm. 165, 381-384 (1933). (35) Vorländer, Z. anal. Chem. 77, 265 (1929). (36) Henderson, Heilbron, J. Chem. Soc. 107, 1749 (1915). (37) Henze, Speer, J. Am. Chem. Soc. 64, 522-523 (1942). (38) K. C. Pandya, R. B. Pandya, Proc. Indian Acad. Sci. 14-A, 112-122 (1941); C.A. 36, 1599 (1942). (39) Harvill, Herbst, J. Org. Chem. 9, 26 (1944). (40) Lock, Stach, Ber. 76, 1253-1255 (1943).
- (41) Graymore, Davies, J. Chem. Soc. 1945, 293-294. (42) Vogelsang, Rec. trav. chim. 62, 5-11 (1943): C.A. 39, 1394 (1945).

3:6420 1,2,4-TRICHLOROBENZENE Cl
$$C_6H_3Cl_3$$
 Beil. V - 204 $V_{1-}(112)$ $V_{2-}(156)$

B.P. M.P. 213° cor. (1) (17) 17–18° (8)
$$D_{25}^{25} = 1.4634$$
 (15) 212.9–213° (2) 17° (7) (9) cf. (7) 212–213° (3) 16–17° (4) $n_{\rm D}^{25} = 1.5524$ (15) 211° cor. at 742 mm. (4) 16.6° (10) 210° (5) (6) 16.5° (11) (12) 206° (7) 16° (1) (3) (13) 14.5° (14)

For thermal anal. of mixts. of \bar{C} with 1,2,3-trichlorobenzene (3:0990) or with 1,3,5-trichlorobenzene (3:1400) see (10) (the cutectic of \bar{C} with the former conts. 71% \bar{C} and melts 2.7° (10)); for m.p./compn. data on ternary mixt. of \bar{C} with the other two isomers see (10).

[For use of C in mfg. of elec. insulating material see (16).]

[For prepn. of \bar{C} from 2,4-dichloroaniline [Beil. XII-621; \bar{X} II₁-(309)] (1) (11), from 2,5-dichloroaniline [Beil. XII-625, XII₁-(311)] (6), or 3,4-dichloroaniline [Beil. XII-626 XII₁-(311)] (1) via diazotization and use of Cu_2Cl_2 reaction see indic. refs.; from 4-chloro-1,3-diaminobenzene [Beil. XIII-53, XIII₁-(15)] via tetrazotization and use of Cu_2Cl_2 reaction (62% yield) see (17); from p-dichlorobenzene (3:0980) with S_2Cl_2 in SO_2Cl_2 + AlCl₃ (58% yield \bar{C}) see (3) (18).]

[For formn. of Č from 2,3,6-trichlorobenzaldehyde (3:2287) by KOH fusion (88% yield (4)) or from 2,3,6-trichloroacetophenone by KOH fusion (82% yield (14)) see indic. refs.; from 2,4-dichlorophenol (3 0560) by htg. 7 hrs. with PCl₅ (25.5% yield) see (1); from 2-nitro-1,4-dichlorobenzene or from 4-chloro-3-nitrobenzenesulfonic acid by htg. with SOCl₂ in s.t. 10 hrs. at 160-180° see (19) (20); from 2-chlorobenzene-1,4-disulfonyl chloride with PCl₅ in s.t. 4 hrs. at 210° see (8); from 2,4-dichlorobenzenesulfonyl chloride by htg. with SOCl₂ in s.t. at 180° see (21).]

[For formn. of $\bar{\rm C}$ (together with other products) from ${\rm C_6H_6}$ with ${\rm Cl_2}$ in pres. of ${\rm I_2}$ (7) or of Fe (22) see indic. refs.; from o-dichlorobenzene (3:6055) and/or p-dichlorobenzene (3:0980) with ${\rm Cl_2}$ under various conditions see (22) (23) (24) (25) (9); from m-dichlorobenzene (3:5960) with ${\rm Cl_2}$ under various conditions see (9) (13) (23); from chlorobenzene (3:7903) or p-dichlorobenzene (3:0980) by boilg. with ${\rm FeCl_3}$ see (26); from α -benzene-hexachloride (3:4410) on htg. above its m.p. (158°) (28) (21) or htd. with aq. in s.t. at 200° (27), or on boilg. with ${\rm MeOH/KOH}$ (10), ${\rm EtOH/KOH}$ (10) (28) (5) (22), alc. KCN (27), or pyridine (10), or on htg. with quinoline at 105–110° (10), see indic. refs.; from β -benzene-hexachloride (3:4990) q.v. on boilg. with alc. KOH see (10).]

[\bar{C} with Cl₂ in pres. of Al/Hg yields exclusively (23) 1,2,4,5-tetrachlorobenzene (3:4115), m.p. 135-136° (23); \bar{C} with liq. Cl₂ in s.t. at room temp. for 10 days gives (29) (30) a mixt. of addn. products.]

[Č with NaOMe in MeOH under various conditions (31) (32) (33) (11) (34) yields 2,5-dichlorophenol (3:1190), m.p. 57°; for behavior with EtOH/KOH see (38).]

 $\ddot{\mathbf{C}}$ on mononitration, e.g., by soln. of $\ddot{\mathbf{C}}$ (1 g.) in 5 ml. fumg. HNO₈ (D=1.49) (35), then pouring onto ice (35), gives 100% yield (35) (1) (5) (15) (39) 1,2,4-trichloro-5-nitrobenzene [Beil. V-246], pr. from alc., m.p. 58° (1), 57° (7) (15), 56° (35); this prod. with piperidine as directed (36) yields 1,2-dichloro-4-piperidino-5-nitrobenzene, red pr. from alc., m.p. 64-65° (36).

 \bar{C} on dinitration, e.g., by soln. of \bar{C} (1 g.) in 5 ml. fumg. HNO₃ (D=1.49) + 5 ml. conc. H₂SO₄ and subsequent refluxing for 1 hr., then pouring into aq. (35), gives (100% yield (35)) (7) (37) 1,2,4-trichloro-3,5-dinitrobenzene [Beil. V-266], pr. from alc., m.p. 103.5° (7), 102.5-103.5° (35) (37); this prod. (1 g.) htd. 1 hr. at 100° with 5 g. aniline as directed (35) yields 1-chloro-2,4-dianilino-3,5-dinitrobenzene, m.p. 182° (35).

Note that the trinitration prod. to be expected from complete nitration of C has not been reported.

[\bar{C} with chlorosulfonic acid as directed (35) yields 1,2,4-trichlorobenzenesulfonyl chloride, m.p. 31-34° (35) which with $(NH_4)_2CO_3$ yields 1,2,4-trichlorobenzenesulfonamide, m.p. above 200° (35).]

3:6420 (1) Beilstein, Kurbatow, Ann. 192, 230-232 (1878). (2) Dadieu, Pongratz, Kohlrausch, Monatsh. 61, 433 (1932). (3) Silberrad, J. Chem. Soc. 121, 1015-1020 (1922). (4) Lock, Ber. 66, 1531 (1933). (5) Lesimple, Ann. 137, 122-124 (1866). (6) Noelting, Kopp, Ber. 38, 3509 (1905). (7) Jungfleisch, Ann. chim. (4) 15, 264-277 (1868). (8) Olivier, Rec. trav. chim. 39, 502 (1920). (9) Mouneyrat, Pouret, Compt. rend. 127, 1028 (1898). (10) van der Linden, Ber. 45, 231-247 (1912).

(11) van der Lande, Rec. trav. chim. 51, 104, 110 (1932). (12) Hassel, Naeshagen, Z. physik. Chem. B-12, 87 (1931) (13) Oliviei, Rec trav. chim. 39, 411-413 (1920). (14) Lock, Böck, Ber. 70, 924 (1937). (15) Tei, Koinatsu, Mem. Coll. Sci. Kyoto Imp. Univ. 10-A, 325-330 (1927); Cent. 1928, I 2370, C.A. 22, 1086 (1928). (16) Ford (to Westinghouse Electric and Mfg. Co.), U.S. 2,139,945-2,139,948, Dec. 13, 1938, Cent. 1939, I 2047; C.A. 33, 2253-2254 (1939). (17) Cohn, Fischer, Monatsh. 21, 278 (1900) (18) Roberts Co. & Silberrad, Brit. 193,200, March 15, 1923; Cent. 1925, I 904. (19) Meyer, Monatsh. 36, 724-725 (1915). (20) Kinzlberger and Co., Ger. 280,739, Cent. 1915, I 104.

(21) Quihco, Gazz. chim. ital. 57, 800 (1927), Cenl. 1928, I 1395, C.A. 22, 1765 (1928). (22) Zil'berman, Slobodnik, J. Applied Chem. (U.S.S.R.) 10, 1080-1085 (1937), Cenl. 1938, 1580 (1938); C.A. 32, 1664 (1938). (23) Cohen, Hartley, J. Chem. Soc. 87, 1363-1364 (1905). (24) Britton (to Dow Chem. Co.), U.S. 1,923,419, Aug. 22, 1933; Cent. 1933, II 3049, C.A. 27, 5086 (1933). (25) Slobodnik, Zil'berman, Russ. 48,285, Aug. 31, 1936; Cent. 1937, II 288. (26) Thomas, Compt. rend. 126, 1212 (1898). (27) Meunier, Ann. chim. (6) 10, 223-269 (1887). (28) Matthews, J. Chem. Soc. 59, 165-172 (1891). (29) van der Linden, Rec. trav. chim. 55, 315-324 (1936). (30) van der Linden, Rec. trav. chim. 57, 217-224 (1938).

(31) Holleman, Rec. trav. chim. 37, 201 (1918). (32) Kraay, Rec. trav. chim. 49, 1087 (1930). (33) de Crauw, Rec. trav. chim. 50, 787 (1931). (34) Aktien-Gesell, für Anilin Fabrikation, Ger. 349,794, March 9, 1922, Cent. 1922, IV 45 (35) Huntress, Carten, J. Am. Chem. Soc. 62, 512-514 (1940). (36) LeFevre, Turner, J. Chem. Soc. 1927, 1116-1117. (37) Huffer, Rec. trav. chim. 40, 452 (1920). (38) Clark, Crozier, Trans. Roy. Soc. Can. (3) 19, III 153-156 (1925). (39) Holleman, van Haeften, Rec. trav. chim. 40, 71 (1921).

See 3:0220. Division A: Solids.

3:6425 HEXACHLOROBUTADIENE-1,3 Cl Cl C₄Cl₆ Beil. S.N. 12 $Cl_2C=C-C=CCl_2$

B.P. M.P. 215° (1)
$$-21$$
° (1) (2) $D_4^{20} = 1.6820$ (1) $n_D^{20} = 1.5542$ (1) 211° at 710 mm. (2) -19 ° (5)

[See also octachlorocyclopentene (3:0422).]

Colorless oily liq. with weak turpentine-like odor.

[For prepn. of Č from butadiene-1,3 (1) (3) or butane, butene, or their chloro substitution products (3) (4) with Cl₂; or from hexachlorobutene (itself obtd. from dimerization (5) (2) of trichloroethylene (3:5170)) by cat. addn. of Cl₂ followed by cat. removal of 2 HCl or vice versa (1) (2); or from acetylene with Cl₂ (6) (note that tetrachloroethylene (3:5460) is also formed).]

Č on reduction with Zn + alc. gives (1) butadiene-1,3 (corresp. tetrabromide, m.p. 117°). Č behaves as if saturated: e.g., Č does not add Cl₂ (even in sunlight) (1); Č does not (1) react with maleic anhydride or benzoquinone-1,4; Č does not (1) polymerize (even at 100 atm.).

Č is stable toward acids and alkalies and (unlike some other highly chlorinated unsaturates) does not give a carboxylic acid on treatment with conc. H₂SO₄ (1).

Note that a product of m.p. 38° and b.p. 283° formerly regarded as \bar{C} is now thought to be octachlorocyclopentene (3:0390).

3:6425 (1) Fruhwirth, Ber. 74, 1700-1701 (1941). (2) Consortium für Elektrochem. Ind., French 836,719, Jan. 25, 1939; Cent. 1938, I 3256; [C.A. 33, 5548 (1939)]; Ger. 723,981, July 2, 1942; [C.A. 37, 5415 (1934)]. (3) Fruhwirth (to Donau-Chemie, A.G.), Ger. 736,884, May 20, 1943; C.A. 38, 2974 (1944). (4) Wimmer, Mugdan (to Consortium für Elektrochem. Ind.), Ger. 734,682, March 25, 1943; C.A. 38, 1245 (1944). (5) Mugdan, Wimmer (to Consortium für Elektrochem. Ind.), Ger. 704,179, Feb. 20, 1941; C.A. 36, 1116 (1942); U.S. 2,269,600, Jan. 13, 1942; C.A. 38, 2870 (1942). (6) Fruhwirth (to Donau-Chemie, A.G.), Ger. 734,722, March 25, 1943; C.A. 38, 1252 (1944).

3:6430 DICHLOROACETIC ACID ANHYDRIDE
$$C_4H_2O_3Cl_4$$
 Beil. II - 204 II_1 ... II_2 ... Cl_2CH ...

Note that the above name of C is so rendered to emphasize that it is the anhydride of dichloroacetic acid (not a dichlorinated acetic anhydride).

[For prepn. of \tilde{C} from dichloroacetyl chloride (3:5290) with Na \tilde{A} in POCl₃ in dry ether (1), or with Na \tilde{A} + AlCl₃ (4), or on boilg. with Na₂CO₃ (2) see indic. refs.; for formn. of \tilde{C} as by-product during reactn. of sodium dichloroacetate with acetyl chloride (3:7065) in dry ether see (3) (the other prod. is the mixed anhydride, acetic-dichloroacetic anhydride [Beil. II-204], b.p. 79-80° at 16 mm., $D_4^{20} = 1.5170$ (3).]

Č on hydrolysis with aq. yields dichloroactic acid (3:6208) q.v.; for the amide, anilide, p-toluidide, and other derivs. corresp. to Č see dichloroacetic acid (3:6208).

3:6430 (1) Anthoine, Jahresber. 1883, 1032. (2) Patterson, Ber. 38, 212-213 (1905). (3) Baroni, Gazz. chim. ital. 63, 30 (1933); Cent. 1933, I 3183; C.A. 27, 3447 (1933). (4) Strosacker, Schwegler (to Dow Chem. Co.), U.S. 1,713,104, May 14, 1929; Cent. 1929, II 1215; C.A. 23, 3234 (1929).

3:6445 m-CHLOROBENZYL CHLORIDE
$$C_7H_6Cl_2$$
 Beil. V — V_1 — V_2 —(231) B.P. 215-216° at 753 mm. (1) $D_4^{15} = 1.2695$ (1) 213-214° at 740 mm. (2) 111.0-111.2° at 25.4 mm. (3) 111-113° at 25 mm. (4) 110-111° at 25 mm. (5) 104° at 17 mm. (6)

[For prepn. from m-chlorobenzyl alc. [Beil. VI-444] with PCl₅ (1) or with SOCl₂ (yield: 87% (5), 78% (4)) see indic. refs.; from m-chlorotoluene (3:8275) with Cl₂ see (2) (3) (6) (7) (8) (9) see indic. refs.]

[Č with phenol in toluene yields (10) o-(m-chlorobenzyl)phenol, b.p. 192-194° at 14 mm. (benzoate, m.p. 67-67.4°), and m-chlorobenzyl phenyl ether, m.p. 36.0-36.4°; Č with 2,-4-dichlorophenol (3:0560) in toluene yields (10) 2-(m-chlorobenzyl)-4,6-dichlorophenol, m.p. 59.4-60.0° (benzoate, m.p. 63.5-64.0°, benzenesulfonate, m.p. 114.5-115.0°, p-toluenesulfonate, m.p. 125.4-126.0°), and m-chlorobenzyl 2,4-dichlorophenyl ether, m.p. 42-42.5°,

[Č with phenol + AlCl₃ yields (10) p-(m-chlorobenzyl)phenol, b.p. 145-148° at 3 mm. (benzoate, m.p. 57.5-58.0°); Č with 2,6-dichlorophenol (3:1595) yields (10) 4-(m-chlorobenzyl)-2,6-dichlorophenol, m.p. 79-80° (benzoate, m.p. 130-130.4°; p-toluenesulfonate, m.p. 104.5-105.0°).]

[C with Mg in dry ether yields (8) m-Cl.C₆H₄.CH₂Cl; this on treatment with CO₂ yields m-Cl.C₆H₄.CH₂.COOMgCl which on subsequent further treatment with various other RMgX cpds. undergoes abnormal reaction giving m-chlorophenylmalonic acid, m.p. 127–128° (8); the RMgCl cpd. with phenyl isocyanate as directed (13) for the p-isomer should yield m-chlorophenylacetanilide, m.p. 130° cor. (14), although this reaction has not been specifically reported for C.]

[For studies of rate of reaction of \tilde{C} with NaOEt see (1) (11) (5); with Na₂SO₃ see (4); with AlCl₃ + C₆H₆ see (12); for acid hydrolysis in acetone see (6); with KI in various solv. see (6); for reactn. of \tilde{C} with diethyl malonate see (2).]

3:6445 (1) Olivier, Rec. trav. chim. 41, 309 (1921). (2) Kenner, Witham, J. Chem. Soc. 119, 1460 (1921). (3) de Bruyne, Davis, Gross, J. Am. Chem. Soc. 55, 3938 (1933). (4) Sprung, J. Am. Chem. Soc. 52, 1643, 1649 (1930). (5) Franzen, Rosenberg, J. prakt. Chem. (2) 101, 334 (1921). (6) Bennett, Jones, J. Chem. Soc. 1935, 1818. (7) Jones, J. Chem. Soc. 1935, 1839. (8) Ivanov, Pchenitchny, Bull. soc. chim. (5) 1, 231 (1934). (9) Zelinsky, Schering-Kahlbaum, Ger. 478,084, June 20, 1929; Cent. 1929, II 1216. (10) Houston, Guile, Chen, Headley, Warren, Baur, Mate, J. Am. Chem. Soc. 55, 4639-4643 (1933).

(11) Olivier, Rec. trav. chim. 41, 650 (1921). (12) Olivier, Berger, Rec. trav. chim. 45, 717 (1926). (13) Underwood, Gale, J. Am. Chem. Soc. 56, 2117-2119 (1934). (14) Jenkins, J. Am. Chem. Soc. 55, 2898 (1933).

See 3:0255. Division A: Solids.

3:6480 1,1,1,2,3,3-HEXACHLOROPROPANE Cl
$$C_2H_2Cl_6$$
 Beil. I — (unsym.-Hexachloropropane) Cl_2HC — C — CCl_8 I_1 -(35) I_2 —

B.P. 216° (1)
$$D_4^{34} = 1.6980$$
 (1) $n_D^{17} = 1.5250$ (1) 145° cor, at 90 mm. (1)

Colorless liq. [For use as solvent for cellulose esters see (3) (4).]

[For prepn. of \overline{C} from chloroform (3.5050) + trichloroethylene (3:5170) + AlCl₃ (1) (2) or from CCl₄ (3:5100) + 1,2-dichloroethylene (3:5030) + AlCl₃ see (1) (2).]

Č with 1 ml. alc. KOH loses HCl yielding (1) (2) 1,1,2,3,3-pentachloropropene-1 (3:6075), b.p. 183° (1).

3:8460 (1) Prins, J. prakt. Chem. (2) 89, 417-419 (1914) (2) Prins, Ger. 261,689, March 2, 1912; Cent. 1913, II 394; C A. 7, 3641 (1913). (3) Spicers, Ltd. & Hands, Brit. 279,139, April 21, 1926; Cent. 1928, I 770, C.A. 22, 2840 (1928). (4) Spicers, Ltd. & Hands, French 625,165, Aug. 4, 1927; Cent. 1928, I 770.

3:6475
$$m$$
-CHLOROBENZALDEHYDE C_7H_6OCl Beil. VII - 234 VII_1 -(133)

Oil. — Volatile with steam. — C yields NaHSO₃ cpd.

[For prepn. of \bar{C} from *m*-nitrobenzaldehyde via reductn. with SnCl₂ to *m*-aminobenzaldehyde followed by diazotization and reactn. with CuCl (yield: 75-79% (4), 70-80% (3), 58-65% (7) (24) see indic. refs.; from *m*-chlorotoluene (3:8275) with CrO₂Cl₂ (44.5% yield) see (8); from *m*-chlorobenzyl alc. by oxidn. with HNO₃/H₂SO₄ see (9); for formn. (together with other products) during chlorination of benzaldehyde see (10); from *m*-chlorobenzylamine with formalin + hexamethylenetetramine see (25).]

 \tilde{C} is readily oxidized even by air (4); \tilde{C} with KMnO₄ yields m-chlorobenzoic acid (3:4392), m.p. 154°. [For study of auto-oxidn see (11).] — \tilde{C} with conc. NaOH undergoes Cannizzaro reactn. (for study in dioxane soln see (23)) although the presumable products, m-chlorobenzyl alc., b.p. 234°, and m-chlorobenzoic acid, m.p. 154°, have not (by this reactn.) actually been isolated.

Č with dil. alc. KCN at 60° for 5 hrs. in absence of air gives 22% yield of 3,3'-dichlorobenzoin, cryst. from lgr., m.p. 75-76° (12).

 \tilde{C} on htg. with NaOAc + Ac₂O for 8 hrs. at 180-200° undergoes Perkin reactn. giving (61.5% yield (13)) m-chlorocinnamic acid, m.p. 165° (13) (14). [This with Br₂ in CHCl₃ gives dibromide, m.p. 183° (15).] — \tilde{C} htd. with malonic acid + pyridine (24) gives alm. quant. yield (24) of m-chlorocinnamic acid, m.p. 163° (24). [In absence of pyridine reaction gives 100% yield m-chlorobenzalmalonic acid, m.p. 184-186° (24).]

Č on mononitration as specified (3) yields 3-chloro-6-nitrobenzaldehyde [Beil. VII-262], ndls. from dil. alc., m.p. 77.5° (3). [Oxime, tbls. from alc., m.p. 112° (3); phenylhydrazone, ndls. from alc., m.p. 180-181° (3).]

- m-Chlorobenzaldoxime (anti form): pr. from alc., m.p. 70-71° (2), 70° (16) (17). [From C + NH₂OH.HCl + Na₂CO₃ (2); the syn isomer (from the anti via ethereal HCl, then Na₂CO₃) has m.p. 115-116° rap. htg. (2), 118° (17).].
- ① m-Chlorobenzaldehyde phenyihydrazone: ndls. from abs. alc., m.p. 134-135° (3), 133-134° (18).
- m-Chlorobenzaldehyde p-nitrophenylhydrazone: cryst. from dil. AcOH, m.p. 216° (19), 214° (16). [For m.p./compn. data on mixt. of this deriv. with benzaldehyde p-nitrophenylhydrazone, m.p. 190°, see (16).]
- m-Chlorobenzaldehyde 2,4-dinitrophenylhydrazone: or.-yel. cryst., m.p. 256° (20), Bordeaux-red cryst. from xylene, m.p. 248° cor. (22), 245° (25). [Use in detn. of C (22).]
- m-Chlorobenzaldehyde semicarbazone: lfts. from MeOH (21) or pyridine (8), m.p. 230° (21), 228° (8). [This deriv. does not distinguish C from o- (3:6410) or p- (3:0765) isomers.]
- 3:6475 (1) Olivier, Weber, Rec. trav. chim. 53, 882 (1934). (2) Erdmann, Schwechten, Ann. 266, 58-62 (1890) (3) Eichengrun, Einhorn, Ann. 262, 134-137 (1891). (4) Buck, Ide, Org. Syntheses, Coll. Vol. 2 (1st ed.), 130-133 (1943). (5) Kahovec, Kohlrausch, Z. physik. Chem. B-38, 138 (1937). (6) von Auwers, Ann. 422, 166 (1921). (7) Asinger, Lock, Monatsh. 62, 335 (1933). (8) Law, Perkin, J. Chem. Soc. 93, 1636-1637 (1908). (9) Mettler, Ber. 38, 2812 (1905). (10) Gnehm, Banziger, Ann. 296, 65 (1897); Ber. 29, 875 (1896).
- (11) van der Beek, Rec. trav. chm. 51, 412-413 (1932). (12) Weissberger, J. Chem. Soc. 1935, 225. (13) Bock, Lock, Schmidt, Monatsh. 64, 406 (1934). (14) Reich, Araus, Potok, Tempel, Helv. Chim. Acta 3, 794 (1920). (15) Willstaedt, Ber. 64, 2693 (1931). (16) Shoppee, J. Chem. Soc. 1932, 701, 705. (17) Brady, McHugh, J. Chem. Soc. 125, 551 (1924). (18) Charlton, Earl, Kenner, Luciano, J. Chem. Soc. 1932, 40. (19) Hodgson, Beard, J. Soc. Chem. Ind. 45, T 91-93 (1926). (20) Blanksma, Wackers, Rec. trav. chim. 55, 658 (1936).
- (21) Henderson, Heilbron, J. Chem. Soc. 107, 1749 (1915). (22) Eitel, Lock, Monatsh. 72, 389-390 (1939) (23) Eitel, Lock, Monatsh. 72, 332-409 (1939). (24) Ushakov, Matusov, J.Gen. Chem. (U.S.S.R.) 14, 120-127 (1944), C.A. 39, 916 (1945). (25) Graymore, Davies, J. Chem. Soc. 1945, 293-294. (26) Vogelsang, Rec. trav chim 62, 5-11 (1943); C.A. 39, 1394 (1945).
- 3:6490 ISOAMYL TRICHLOROACETATE $C_7H_{11}O_2Cl_3$ Beil. II 209 iso- $C_5H_{11}O.CO.CCl_3$ II₁-(94) II₂-(200)
 - B.P. 217° (1) $D_4^{20} = 1.2314$ (2) cf. (3) $n_D^{20} = 1.4521$ (2)
- 3:6490 (1) Clermont, Bull. soc. chim (2) 40, 302 (1883). (2) Schjanberg, Z. physik. Chem. A-172, 229 (1935). (3) Livingston, Morgan, Kramer, J. Am. Chem. Soc. 35, 1836 (1913).

CHAPTER XV

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 1. D_4^{20} greater than 1.1500

(3:6500-3:6999)

C₅H₆O₂Cl₂

Beil. II - 634

II1-(273)

[For prepn. of C from glutaric acid (1:0440) with PCl₅ (1) (2) (3) or with SOCl₂ (80-88% vield (4)) (5) see indic. refs.]

Note that C may react in either sym. or unsym. form (6).

3:6500 GLUTARYL (DI)CHLORIDE

 $[\bar{C} \text{ with AlCl}_3 + C_6H_6 \text{ yields (7) (4) 1,5-diphenylpentanedione-1,5 (1,3-dibenzoylpropane)}$ [Beil. VII-775, VII₁-(403)], m.p. $62-63^{\circ}$ (7) (4); \bar{C} with AlCl₃ + m-xylene gives (8) 1,5di-m-xylylpentanedione-1,5, m.p. 60° (8), $+ \gamma$ -(m-xyloyl)-n-butyric acid, m.p. 118° (8); Č with AlCl₃ + mesitylene gives (72% yield (5)) 1,5-dimesitylpentanedione-1,5, m.p. 133-134° (5).]

 \tilde{C} on hydrolysis yields glutaric acid (1:0440), m.p. 98° (for the diamide, dianilide, di-ptoluidide, and other derivs. corresp. to \bar{C} see 1:0440).

3:6500 (1) Reboul, Ann. chim. (5) 14, 504 (1878). (2) von Auwers, Schmidt, Ber. 46, 479 (1913). (3) Meerburg, Rec. trav. chim. 18, 373 (1899). (4) Skraup, Guggenheimer, Ber. 58, 2493 (1925). (5) Kao, J. Chinese Chem. Soc. 3, 56-59 (1935). (6) Plant, Tomlinson, J. Chem. Soc. 1935, 856. (7) Auger, Ann. chim. (6) 22, 358 (1891). (8) Borsche, Ber. 52, 2080 (1919).

3:6510 \(\beta\)-CHLOROETHYL TRICHLOROACETATE C₄H₄O₂Cl₄ Beil. II - 209 Cl.CH₂.CH₂.O.CO.CCl_a II1---II.

B.P. 217° at 766 mm. (1)
$$D_4^{20} = 1.5357$$
 (1), cf. (4) 99.5–100.0° at 14 mm. (2) $n_D^{20} = 1.48133$ (1) cf. (4) 95–96° at 11 mm. (3) 68–69° at 1.6 mm. (4)

[For prepn. (45% yield (3)) from ethylene chlorohydrin (3:5552) + trichloroacetyl chloride (3:5420) + pyridine in ether see (3) (1); for prepn. (70% yield (3)) from Bhydroxyethyl trichloroacetate (3:9099) + SOCl₂ see (3).]

 \tilde{C} on shaking with aq. is smoothly saponified to β -chloroethanol (3:5552) + trichloroacetic ac. (3:1150), no chloride ion being formed (3).

3:6510 (1) Delacre, Bull. soc. chim. (2) 48, 708 (1887). (2) Palomaa, Salmi, Korte, Ber. 72, 797 (1939). (3) Meerwein, Sönke, Ber. 64, 2380 (1931). (4) Meerwein, Sönke, J. prakt. Chem. (2) 137, 309 (1933).

3:6517
$$\beta$$
-CHLORO- β' -HYDROXY-ISOPROPYL ACETATE $C_5H_9O_3Cl$ Beil. II - 142 (Glycerol α -chlorohydrin β -acetate; CH $_2Cl$ II₁-(67) β -aceto- α -chlorohydrin; H—C—O.CO.CH $_3$ CH $_2OH$

B.P. 218° (1) at 760 mm. (2) 108° at 12 mm. (3)

[See also glycerol α -chlorohydrin α' -acetate (3:6775).]

[For formn. of \bar{C} from 3-hydroxy-1,2-epoxypropane (glycidol) with AcCl (3:7065) (γ -hydroxy- β -chloro-n-propyl acetate is also formed) see (1); from epichlorohydrin (3:5358) with AcOH in s.t. at 180° see (1); from glycerol α , β -diacetate with PCl₅ see (3).]

Note that the homogeneity of all reported prepns. of $\bar{\mathbf{C}}$ is probably open to serious question.

3:6517 (1) Bigot, Ann. chim. (6) 22, 489-491 (1891). (2) Gibson, J. Soc. Chem. Ind. 59, 950 (1931). (3) Wegscheider, Zmerzlikar, Monatsh. 34, 1079-1080 (1913).

B.P. 218-219°

M.P. 53-54°

See 3:0990. Division A: Solids.

B.P. 219-220° at 740 mm.

M.P. 67°

See 3:1595. Division A: Solids.

B.P. 218.5° (1) $D_4^{34} = 1.7131$ (1) $n_D^{18} = 1.5262$ (1)

[For prepn. of \tilde{C} from 1,2,3,3-tetrachloropropene-1 (3:5920) + Cl_2 in sunlight at -30° see (1).] [The product obtd. by (4) from sym.-tetrachloroacetone (3:6050) + PCl_5 was probably very impure \tilde{C} .]

Č with alc. KOH loses HCl quant. yielding 1,1,2,3,3-pentachloropropene-1 (3:6075), b.p. 183° (1).

[For use as solvent for cellulose esters see (2) (3).]

3:6525 (1) Prins, J. prakt. Chem. (2) 89, 422 (1914). (2) Spicers, Ltd. & Hands, Brit. 279,139, April 21, 1926; Cent. 1928, I 770, C.A. 22, 2840 (1928). (3) Spicers, Ltd. & Hands, French 625,165, Aug. 4, 1927; Cent. 1928, I 770. (4) Levy, Curchod, Ann. 252, 335-338 (1889).

3:6535 m-TOLUYL CHLORIDE
$$C_8H_7OCl$$
 Beil. IX - 477 CH_3 CH_3 CH_3 CH_3 CH_7OCl CH_7OCl CH_8 CH_8

B.P.			M.P.	
219-220°	at 773 m	n. (1)	-25° (4)	$D_4^{20} = 1.173 (3)$
218.7-219.7°	at 760 m	n. (2)	-23° (1)	-
218°	at 724 m	n. (1)		
120°	at 38 m	n. (3)		
119-120°	at 36 m	n. (4)		
[136-138°	at 31 m	n. (5)]		
105°	at 20 mm	n. (6)		
109°	at 15 m	n. (7)		
109°	at 8 mm	n. (8)		
71.2°	at 4 m	n. (9)		

[For prepn. of \bar{C} from m-toluic acid (1:0705) with PCl₅ (83% yield (1)) (2) (10), with PCl₅ in CHCl₃ (70% yield (3)) (5), with PCl₃ (8), with SOCl₂ (95% yield (11)) (12) (6) (9), or with POCl₃ + NaCl (or KCl) (13) see indic. refs.; for formn. of \bar{C} from heptadiyne-1,6-carboxylic acid-4 (pseudo-m-toluic acid) with PCl₅ see (14).]

C with pyridine and excess K₂S₂O₅ yields (15) m-toluic anhydride, m.p. 70-71°.

[For reactn. of \bar{C} with AlCl₃ and various hydrocarbons to yield corresp. ketones, e.g., with C_6H_6 yielding (10) phenyl *m*-tolyl ketone [Beil. VII-440, VII₁-(235)], with toluene yielding (16) *m*-tolyl *p*-tolyl ketone [Beil. VII-451], with *m*-xylene yielding (17) *m*-tolyl *m*-xylyl ketone, see indic. refs.; note, however, that \bar{C} on htg. with AlCl₃ alone at 130-140° gives (17) (44-46% yield (18)) 2,6-dimethylanthraquinone [Beil. VII-815], m.p. 236°]

[\bar{C} with MeZnI (19) or Zn(CH₃)₂ (3) or MeMgBr + CdCl₂ (20) gives (yield: 83% (20), 43% (19)) *m*-methylacetophenone (1:5527), b.p. 220°.]

[$\bar{\mathbf{C}}$ with Cl₂ at 160-180° gives (90% yield (21)) (6) m-(chloromethyl)benzoyl chloride (ω -chloro-m-toluyl chloride), b.p. 149-150° at 20 mm. (21); $\bar{\mathbf{C}}$ with Br₂ at 185-195° gives (50% yield (22)) ω -bromo-m-toluyl bromide, b.p. 167° at 22 mm. (22).]

[Č with MeOH yields methyl m-toluate (1:3781), b.p. 221°; Č with EtOH yields ethyl m-toluate (1:3942), b.p. 234°; for study of rate of reactn. see {4}.]

 \bar{C} on hydrolysis yields *m*-toluic acid (1:0705), m.p. 110-111° (for study of rate see (23)). — For the amide, anilide, *p*-toluidide, and other derivs. corresp. to \bar{C} see *m*-toluic acid (1:0705).

3:6535 (1) van Scherpenzeel, Rec. trav. chim. 20, 162 (1901). (2) Kohlrausch, Pongratz, Stockmair, Monatsh. 67, 108 (1936). (3) Klages, Lickroth, Ber. 32, 1560 (1899). (4) Norris, Young, J. Am. Chem. Soc. 57, 1424 (1935). (5) Cohen, Dudley, J. Chem. Soc. 97, 1749 (1910). (6) Morgan, Parter, J. Chem. Soc. 1926, 1258. (7) Frankland, Aston, J. Chem. Soc. 75, 494 (1899). (8) Frankland, Wharton, J. Chem. Soc. 69, 1311 (1896). (9) Thompson, Norris, J. Am. Chem. Soc. 58, 1955 (1936). (10) Ador, Rilliet, Ber. 12, 2301 (1879).

(11) Maxim, Bul. Soc. Chim. România 11, 29-36 (1929); Cent. 1929, II 2324. (12) Shopee,

J. Chem. Soc. 1932, 700. (13) Kissling (to I.G.), Ger. 642,519, March 10, 1937; Cent. 1937, I, 3874; C.A. 31, 5816 (1937). (14) Perkin, Simonsen, J. Chem. Soc. 91, 847 (1907). (15) Gasopoulos, Praktika Akad. Athenon 6, 347-353 (1931); Cent 1932, I 3171. (16) Scharwin, Schorygin, Ber. 36, 2027 (1903). (17) Morgan, Coulson, J. Chem. Soc. 1929, 2213. (18) Seer, Monatsh. 32, 154-157 (1911). (19) Mauthner, J. prakt. Chem. (2) 103, 394 (1921/22). (20) Gilman, Nelson, Rec. trav. chim. 55, 528-530 (1936).

(21) Titley, J. Chem. Soc. 1928, 2582. (22) Davies, Perkin, J. Chem. Soc. 121, 2210 (1922).

(23) Berger, Olivier, Rec. trav. chim. 46, 524-527 (1927).

3:6540 BENZOTRICHLORIDE (Phenylchloroform,
$$\omega, \omega, \omega$$
-trichlorotoluene) CCl₃ C₇H₅Cl₃ Beil. V - 300 V₁-(152) V₂-(233) B.P. F.P. 220.5-221.5° (1) -4.4° (8) $D_4^{20} = 1.3741$ (8) 220.9° (2) -4.75° (3) 1.37563 (4) 220.7° at 761 mm. (3) -5.0° (9) (10) $n_D^{20} = 1.55789$ (8) 214-216° (4) -8.1° (7) 1.5579 (4) 213.0-213.5° (5) 1.55726 (11) 129° at 60 mm. (6) 105° at 25 mm. (7) 110.7° at 23 mm. (3) 89.0-89.5° at 10 mm. (8)

Colorless liquid insol. aq., sol. many org. solvents. — Ord. samples of \bar{C} may also cont. benzal (di)chloride (3:6327) or even benzyl chloride (3:8535). — \bar{C} when pure is stable in dry air, but ord. material (contg. dislvd. HCl) hydrolyzes rapidly in moist air (3). — The very high value (93) of molal f.p. lowering of \bar{C} prob. accounts for difficulty of earlier workers in attaining high f.p. values (3). — For removal of dislvd. HCl from \bar{C} by treat. with PbCO₃ see (9). — For purification of \bar{C} via crystallization see (10); for comml. purification see (12).

 $\bar{\mathbf{C}}$ forms const.-boilg. mixts. with various cpds., e.g., $\bar{\mathbf{C}}$ with *p*-dibromobenzene (b.p. 220.25°) forms an azeotrope, b.p. 219.6° at 760 mm., contg. 28 wt. % $\bar{\mathbf{C}}$ (2); $\bar{\mathbf{C}}$ with nitrobenzene (b.p. 210.75°) forms an azeotrope, b.p. 210.72° at 760 mm., contg. 1.5 wt. % $\bar{\mathbf{C}}$ (2); $\bar{\mathbf{C}}$ with *o*-nitrotoluene (b.p. 221.85°) forms an azeotrope, b.p. 219.55° at 760 mm., contg. 75.5 wt. % $\bar{\mathbf{C}}$ (13); $\bar{\mathbf{C}}$ with methyl salicylate (1:1750) (b.p. 222.35°) forms an azeotrope, b.p. 220.75° at 760 mm., contg. 97 wt. % $\bar{\mathbf{C}}$ (13).

 \tilde{C} is impt. intermediate in prepn. of benzoic acid (see below under hydrolysis), in prepn. of certain dyestuffs (see below), and in prepn. of acyl halides and anhydrides (see below); for use in prepn. of films of cellulose ethers see (14).

[For prepn. of \bar{C} from toluene with Cl₂ especially in pres. of light and/or other catalysts see (15) (16) (17) (18); with Cl₂ in pres. of PCl₃ (3) cf. (19); with SOCl₂ in s.t. at 220° for 18 hrs. (20) or at 230-250° (21) see indic. refs.; with NOCl at 350° see (22); for formn. of \bar{C} from benzal (di)chloride (3:6327) with Cl₂ (23) or with NOCl at 150° (24) see indic. refs.; from benzyl chloride (3:8535) by htg. with PbCl₄.2NH₄Cl see (25); from benzoyl chloride (3:6240) with PCl₅ see (26); from benzotrifluoride + acetyl chloride + AlCl₃ as directed see (8); from benzyl ethers with PCl₅ see (27).]

 $[\bar{C}]$ on reductn. in alc. soln. with H_2 in pres. of colloidal Pd (28) or Pd/CaCO₃ (29) reacts bimolecularly giving (75% yield (28)) tolane tetrachloride (diphenylacetylene tetrachloride) (3:4496), colorless cryst. from AcOH, m.p. 162–163° (28), also obtd. from \bar{C} by other treatments (see below); this prod. with $H_2 + Pd/CaCO_3$ in alc. KOH is further reduced yielding (29) dibenzyl (1:7149) (use in quant. detn. of its halogen (29)). — \bar{C} with hydra-

zine hydrate in MeOH/KOH in pres. of Pd/CaCO₃ refluxed for $1\frac{1}{2}$ hrs. gives (42% yield (30)) a mixt. of the two geom. isomeric tolane dichlorides consisting mainly of the α -isomer (3:4210), colorless tbls. from alc., m.p. 148° (30), with a little of the β -isomer (3:1380), m.p. 61° (30); despite their unsaturation these prods. reduce further only with difficulty.

[Č satd. with Cl₂ and stood in sunlight for 8 months or Č with liq. Cl₂ in sunlight for a few days adds 3 Cl₂ yielding (31) 1,2,3,4,5,6-hexachloro-1 (trichloromethyl) cyclohexane, cryst. from CHCl₃ or by sublimation, m.p. 103° (31); this may be accompanied by a little pentachlorotrichloromethylcyclohexene, m.p. 132-134° (31). — Č with Cl₂ in pres. of I₂ yields (32) a mixt. of mono- and di-chlorobenzotrichlorides.]

[Č on pyrogenic decompn. over Pt at red heat yields (32a) cf. (34) tolane tetrachloride (3:4496) together with its isomorphous mixt. with α -tolane dichloride (see above). — \tilde{C} with Na in liq. NH₃ yields (33) 5% dibenzyl (1:7149) accompanied by much nitrogenous tar. — \tilde{C} with Zn in ether soln. reacts vigorously yielding (35) a deep green soln. contg. tolane dichloride (see above). — \tilde{C} with equal wt. reduced Cu at 100° for 10 hrs. yields (36) tolane tetrachloride, m.p. 162° (3:4496); note that distn. of crude reactn. prod. leads to further reactn. and formation (36) (37) of α - and β -tolane dichlorides (see above). — \tilde{C} with C₆H₆ in pres. of powdered chromium metal at 100° for 5 hrs. gives (17% yield (38)) triphenylchloromethane (3:3410), m.p. 106° (38). — \tilde{C} with small proportion of AlCl₃ (0.1 mole) at 50-60° evolves HCl and gives a mixt. (39) contg. 40% α , α -dichloro-m-trichloromethyl-diphenylmethane, m.p. 59-61°, + 10% m-(α ', α '-dichloro-m'-trichloromethylbenzyl)- α , α -dichlorodiphenylmethane, oil, + 34% unchanged \tilde{C} . — \tilde{C} with AlCl₃ in C₆H₆ (39) or \tilde{C} with Al + HgCl₂ in C₆H₆ (40) gives (62% yield (39)) 9,9',10,10'-tetraphenyl-9,10-dihydroanthracene, cryst. from acetone or lgr., m.p. 159° (40), 157-158° (39).]

[Č with MeMgCl in ether gives two types of reactn. according to concn. (41); e.g., Č with dilute MeMgCl yields tolane tetrachloride (3:4496) + ethane + MgCl₂, while Č with conc. MeMgCl gives in 22% yield a mixt. of the two geom. isomers of tolane dichloride (see above) consisting of 5 pts. of the trans form (3:4210), m.p. 138-139° (41), together with 1 pt. of the cis form (3:1380), m.p. 63° (41), separable by fractional crystn. from alc. — For reactn. of Č with EtMgBr see (42). — Č does not (43) react with excess mercury di-p-tolyl.]

[\bar{C} with HF gas in Cu flask at 0° for 72 hrs. (44), or \bar{C} with SbF₃ (45) (46), or \bar{C} with SbF₃.2NaF at 130-140° (47), gives (yields: 75-95% (44), 75% (45), benzotrifluoride, b.p. 102.3°, m.p. -29° . — Note that \bar{C} with ZnF₂ in Cu flask at 120° for 6 hrs. gives (65% yield (57)) benzoyl fluoride, b.p. 155-156° (57), also that \bar{C} + KF in HCOOH gives (16% yield (68)) formyl fluoride, b.p. -26° at 750 mm. (68).]

 \bar{C} on complete hydrolysis yields benzoic acid (1:0715): e.g., \bar{C} on htg. with anhydrous HCOOH yields (48) BzOH + CO + HCl (use in detn. of side-chain halogen (49)); \bar{C} with aq. in s.t. at 150° (15) or with aq. at 90-95° in pres. of Fe salts (50), or with aq. vapor at 550-850° over cat. (51), or with aq. + ZnCl₂ at 110-115° under press. (52), or with aq. CaCO₃ at 90° followed by acidif. with minl. acid (53) yields BzOH; note, however, although \bar{C} in ether soln. is only slowly hydrolyzed by aq. at room temp. (54) yet \bar{C} adequately shaken with aq. at room temp. is completely hydrolyzed (use in detn. of \bar{C} + benzal (di-chloride + benzyl chloride by titration with std. alk. using thymolsulfonphthalein (55)) and \bar{C} if subjected to actn. of steam (as in steam distn. of mixt. with volatile cpds.) is partially hydrolyzed (8). — [For study of kinetics of hydrolysis of \bar{C} in aq. acetone at 30° in pres. of acids, bases, or salts see (1).]

[\tilde{C} on partial hydrolysis yields benzoyl chloride (3:6240): e.g., \tilde{C} with limited amt. aq. in pres. of H₂SO₄ or FeCl₃ (56), or \tilde{C} with ord. comml. ZnCl₂ at 120° (57) (58), or \tilde{C} with aq. vapor over tin phosphate at 240° (59), or \tilde{C} with pure ZnO at 100° (57), or \tilde{C} with benzoic

acid in boilg. nitrobenzene (60), yields BzCl; note, however, that C with pure ZnCl₂ fails to react but addn. of 1 mole aq. or initial use of tech. ZnCl₂ gives BzCl (57).]

[Č htd. with carboxylic acids or anhydrides especially in pres. of ZnCl₂ is often used to prepare a mixture of benzoyl chloride with the acid chloride of the acid employed, particularly in cases where the two acyl chlorides are readily separable: e.g., Č with phthalic anhydride (1:0725) (61) (62) or phthalic acid (1:0820) (62) + ZnCl₂ at 110-120° or above gives 96% yield BzCl (3:6240) + 93% sym.-phthalyl (di)chloride (3:6900); for other examples see under chloroacetyl chloride (3:5235), dichloroacetyl chloride (3:5290), trichloroacetyl chloride (3:5420), fumaryl (di)chloride (3:5875), and terephthalyl (di)chloride (3:2205). — Similarly Č with salts of sulfonic acids yields BzCl + the corresp. sulfonyl chloride: e.g., Č + sodium β-naphthalenesulfonate gives (63) 90% yield BzCl + 80% yield β-naphthalenesulfonyl chloride.]

[C under certain conditions may be converted to benzoic anhydride (1:0595): e.g., C with BzOH + trace Fe salts htd. 6 hrs. at 110-115° under reflux (64), or C with NaOBz (65), or C with ord. conc. H₂SO₄ (66), or C in AcOH in pres. of phosgene (67), yields Bz₂O₋]

 \bar{C} very readily undergoes alcoholysis: e.g., \bar{C} with EtOH in pres. of ZnCl₂ yields (69) ethyl benzoate (1:3721); note, however, that \bar{C} + abs. EtOH in s.t. at 130-140° (70) or \bar{C} + trace sublimed FeCl₃ treated at 80-110° with 95% alc. (71) yields benzoyl chloride (3:6240) + ethyl chloride (3:7015); furthermore that \bar{C} + ethyl acetate (2 moles) in pres. of ZnCl₂ yields (69) ethyl benzoate (1:3721) + acetyl chloride (3:7065) + ethyl chloride (3:7015).

C reacts with phenols to give various products according to circumstances: C with aq. (72) (74) or better alc. (73) sodium phenolate (3 moles) gives at 100° small yields of phenyl benzoate (1:2257), m.p. 71°, and of o-hydroxybenzophenone (1:1414), m.p. 41°, together with other prods. notably benzaurin (see below). — C with phenol in pres. of ZnO gives (75) phenyl benzoate (see above) + p-hydroxybenzophenone (1:1560), m.p. 134°. — C with phenol (2 moles) htd. at 100° and reactn. prod. treated with steam yields (76) (77) 4,4'-dihydroxytriphenylcarbinol (=phenolbenzein=4'-hydroxyfuchsone=bcnzaurin) [Beil. VI-1145, VIII₁-(589)], as red crystn. powder (diacetate, m.p. 119° (76) (77); dibenzoate, m.p. 183-184° (76)), accompanied by p-hydroxybenzophenone (see above). — [For corresp. reactns. of C with o-crosol (1:1400) yielding o-crosolbenzein (78) (79), with thymol (1:1430) yielding thymolbenzein (80), with resorcinol (1:1530) yielding resorcinolbenzein (76), or with pyrogallol (1:1555) yielding pyrogallolbenzein (81) see indic. refs. - For reactn. of \tilde{C} with α -naphthol (1:1500) (73) (94) (95) (or with 1-hydroxynaphthoic acid-2 (82) (83) (95)) yielding 4-(1-hydroxynaphthyl) phenyl ketone (or the corresp. 4-(1-hydroxy-2carboxynaphthyl) phenyl ketones) respectively see indic. refs.; for reactn. of \bar{C} with β naphthol (1:1540) see (84).]

Č with ammonia or amines gives varied reactns. — Č with liq. NH₃ (85) or with NH₄Cl in s.t. at 200° (86) gives (75% yield (85)) benzonitrile; Č with conc. aq. NH₄OH in s.t. at 130° yields (85) benzoic acid + benzamide + benzonitrile. — Č (1 mole) with aniline (2 moles) warmed together without solvent or with ZnCl₂ in AcOH soln. gives (87) N,N'-diphenylbenzamidine hydrochloride [Beil. XII-273, XII₁-(202)], the free base of which has m.p. 147°; note, however, that Č with aniline hydrochloride + nitrobenzene + Fe filings htd. at 180° for 3-4 hrs. yields (87) the dyestuff Doebner's Violet (the HCl reactn. prod. of 4,4'-diaminotriphenylcarbinol) [Beil. XIII-742, XIII₁-(293)]. — Č (1 mole) with dimethylaniline (2 moles) htd. at 100° preferably in pres. of ZnCl₂ yields (86) the dyestuff Malachite Green (the HCl reactn. prod. of 4,4'-dimethylaminotriphenylcarbinol) [Beil. XIII-743, XIII₁-(293)] (see ⊕ below); analogous dyestuffs from other tertiary amines cannot be discussed here.

[Č with excess phenylhydrazine in alc. does not react until Cu powder is added; the

solution then (89) rapidly turns or.-red. and on cooling soon ppts. a mixture of benzaldehydephenylhydrazone, m.p. 157° (see 1:0195) (doubtless accounted for by reductn. of $\bar{\mathbf{C}}$ to benzal (di)chloride (3:6327) at the expense of phenylhydrazine), together with phenylhydrazine hydrochloride. — $\bar{\mathbf{C}}$ + excess phenylhydrazine heated in alc. without Cu (89) turns dark red and ppts. a mixt. of "formazylbenzene" [Beil. XVI-17], red lfts. from alc., m.p. 173° (doubtless accounted for as above), and phenylhydrazine hydrochloride.]

[C with amides or ammonium salts gives on htg. mixtures of corresp. nitriles and acid halides: e.g., C with benzamide at 140° yields (90) benzonitrile + benzoyl chloride; C with p-toluamide at 140° yields (90) benzonitrile, p-toluntrile, benzoyl chloride, and p-toluyl chloride (3:6600). — For patents exemplifying this type of reactn. see (91) (92).]

 \bar{C} on mononitration, e.g., with 0.44 pt. fumg. HNO₃ + 0.44 pt. conc. H₂SO₄ at 25–30° for ½ hr. (4), gives 85% yield *m*-nitrobenzoic acid, m.p. 140° (4); very possibly hydrolysis here precedes nitration since \bar{C} on nitration with N₂O₅ in cold CCl₄ gives (32) (93) an oily mixt. of nitrobenzotrichlorides more stable to hydrolysis than original \bar{C} , but which on cleavage with alk. or conc. H₂SO₄ yields a mixt. of nitrobenzoic acids containing 70% *m*-nitrobenzoic acid (for other studies of nitration of \bar{C} see (5) (10)). — \bar{C} on dinitration by soln. in 5.4 pts. conc. H₂SO₄ and treatment with 6.8 pts. fumg. HNO₃ at 185° for 1 hr. gives (4) 33% yield of 3,5-dinitrobenzoic acid, m.p. 203–204° (4).

[Č cannot be sulfonated without hydrolysis of the —CCl₃ group; \bar{C} with conc. H₂SO₄ even at 30° yields (66) benzoic acid (or its anhydride). — However, \bar{C} with gaseous SO₃ at room temp. (6) gives on subsequent vac. distn. an oil (perhaps *m*-sulfobenzotrichloride) which with aq. yields *m*-sulfobenzoic acid [Beil. XI-384, XI₁-(98)], dihydrate, m.p. 97-98°, losing aq. at 160° yielding anhydrous acid, m.p. 140-141° (6).]

- Malachite Green formation. C

 (1 drop) + dimethylaniline (1 drop) warmed with 0.1 g. fused ZnCl₂ gives intense green color.
- Benzoic acid: C on refluxing with aq. NaOH soln., subsequently acidified, ppts. benzoic acid (1:0715), m.p. 121°.

3:6540 (1) Olivier, Weber, Rec. trav. chim. 53, 881, 884 (1934). (2) Lecat, Rec. trav. chim. 47, 14, 17 (1928). (3) Swarts, Bull. soc. chim. Belg. 31, 375-377 (1922). (4) Sah, Lei, Wang, Sci. Repts. Natl. Tsinghua Univ. A-2, 137-141 (1933); Cent. 1933, II 2977, C.A. 28, 118 (1934). (5) Flürscheim, Holmes, J. Chem. Soc. 1928, 1611-1615. (6) Lauer, J. prakt. Chem. (2) 142, 252-258 (1935); (2) 143, 127-138 (1935). (7) Timmermans, Bull. soc. chim. Belg. 25, 334-343 (1914); Cent. 1914, I 618. (8) Henne, Newman, J. Am. Chem. Soc. 60, 1698 (1938). (9) Sutton, Proc. Roy. Soc. London A-133, 673 (1931). (10) Holleman, de Mooy, Rec. trav. chim. 33, 25-27, 33-34 (1914).

(11) Dummer, Z. anorg. allgem. Chem. 101, 37 (1920). (12) Britton (to Dow Chem. Co.), U.S. 1,804,458, May 12, 1931; Cent. 1931, II 497. (13) Lecat, Ann. Soc. sci. Bruxelles 48, I 16, 116 (1928). (14) Donohue (to Eastman Kodak Co.), U.S. 1,552,798, Sept. 8, 1925; Cent. 1926, I 541. (15) Beilstein, Kuhlberg, Ann. 146, 330-333 (1868). (16) Selden Co. & Gibbs, Brit. 123,341, Oct. 22, 1917; C.A. 13, 1478 (1919); Swiss 87,961, Jan. 17, 1921; Cent. 1921, IV 354. (17) Conklin (to Solvay Process Co.), U.S. 1,828,858, U.S. 1,828,859, Oct. 27, 1931; Cent. 1932, I 1575. (18) I.G., French 798,727, May 25, 1936; Cent. 1936, II 3360. (19) Erdmann, Ann. 272, 150 (1892). (20) Pollak, Rudich, Monatsh. 43, 218 (1922).

(21) Meyer, Monalsh. 36, 729 (1915). (22) Moyer (to Solvay Process Co.), U.S. 2,152,357, March 3, 1939; Cent. 1939, II 1775; C.A. 33, 5001 (1939). (23) Limpricht, Ann. 139, 321-325 (1866). (24) Perrot, Compt. rend. 198, 1425 (1934). (25) Seyewetz, Trawitz, Compt. rend. 136, 241 (1903). (26) Limpricht, Ann. 134, 55-57 (1865). (27) Whitmore, Langlois, J. Am. Chem. Soc. 55, 1518 (1933). (28) Borshee, Heimburger, Ber. 48, 458 (1915). (29) Busch, Stöve, Rev. 49, 1087, 1068 (1916). (29) Busch, Weber J. renkt. Chem. (2) 46, 12-13, 50-52 (1936).

Soc. 55, 1518 (1933). (28) Borshce, Heimburger, Ber. 48, 458 (1915). (29) Busch, Stöve, Ber. 49, 1067-1068 (1916). (30) Busch, Weber, J. prakt. Chem. (2) 46, 12-13, 50-52 (1936). (31) van der Linden, Rec. trav. chim. 57, 1075-1080 (1938). (32) Spreckels, Ber. 52, 315-319 (1919). (32a) Löb, Ber. 36, 3060-3061 (1903). (33) Dean, Berchet, J. Am. Chem. Soc. 52, 2825 (1930). (34) Marckwald, Karcag, Ber. 40, 2994-2996 (1907). (35) Staudinger, Clar, Czako, Ber. 44, 1646 (1911). (36) Onufrowicz, Ber. 17, 833-835 (1884). (37) Hanhart, Ber. 15, 898-901 (1882). (38) Chakrabarty, Dutt, J. Indian Chem. Soc. 5, 514, 517 (1928). (39) Wohl, Wertyporoch, Ann. 481, 30-42 (1930). (40) Ray, J. Chem. Soc. 117, 1339 (1920).

(41) Fuson, Ross, J. Am. Chem. Soc. 55, 720-723 (1933). (42) Sanna, Cent. 1937, II 2345. (43) Whitmore, Thurman, J. Am. Chem. Soc. 51, 1497 (1929). (44) Simons, Lewis, J. Am. Chem. Soc. 60, 492 (1938). (45) Aelony, J. Am. Chem. Soc. 56, 2063 (1934). (46) Booth, Elsey, Burchfield, J. Am. Chem. Soc. 57, 2066-2069 (1935). (47) I.G., French 809,301, March 1, 1937; Cent. 1938, I 4863. (48) Heble, Nadkarin, Wheeler, J. Chem. Soc. 1938, 1322. (49) Gavankar, Heble, Wheeler, J. Univ. Bombay 6 (2), 112-113 (1937); Cent. 1938, I 4610; C.A. 32, 3757 (1938). (50) Schultze, Ger. 82,927, July 22, 1895, 85,493, Jan. 13, 1896; Friedländer 4, 143, 145.

(51) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994. (52) George (to Mathieson Alkali Works), U.S. 1,557,153, Oct. 13, 1925; Cent. 1926, I 1716. (53) Stockelbach (to Mathieson Alkali Works), U.S. 1,591,245, July 6, 1926; Cent. 1926, I I 1584. (54) Straus, Hussy, Ber 42, 2180-2181 (1909). (55) Lubs, Clark, J. Am. Chem. Soc. 49, 1449-1453 (1918). (56) B.A.S.F., Ger. 331,696, Jan. 10, 1921; Cent. 1921, II 558. (57) Davies, Dick, J. Chem. Soc. 1932, 2808-2809. (58) George (to Mathieson Alkali Works), U.S. 1,557,154, Oct. 13, 1925; Cent. 1926, I 1716-1717. (59) Abkin, Medvedev, J. Chem. Ind. (Moscow) 1934, No. 1, 30-34; Cent. 1935, I 2801; C.A. 28, 3051 (1934); Russ. 34,551, Feb. 28, 1934; C.A. 29, 2973 (1935). (60) British Dyestuff Corp. & Bunberg & Shepherdson, Brit. 293,924, Aug. 9, 1928; Cent. 1928, 11614.

(61) Kyrides, J. Am. Chem. Soc. 59, 207-208 (1937). (62) Kyrides (to Monsanto Chem. Co.), U.S. 1,963,748, 1,963,749, June 19, 1934; Cent. 1934, II 2900. (63) Kranzlein, Hopff (to I.G.), Ger. 574,836, April 20, 1933; Brit. 384,722, Jan. 5, 1933; Cent. 1933, II 1430; French 739,290, Jan. 9, 1933; Cent. 1933, I 2173. (64) British Dyestuffs Corp. & Payman & Hall, Brit. 280,373, Dec. 8, 1927; Cent. 1928 I 1460. (65) Wacker Soc. Chem. Ind. & Kaufler & Hormann, Brit. 165,747, Aug. 24, 1921; Cent. 1922, II 1218. (66) Jenssen, Ber. 12, 1495 (1879); Ger. 6,685, Oct. 30, 1878. (67) Béhal, Compt. rend. 148, 648 (1909). (68) Nesmeyanov, Kahn, Ber. 67, 370-373 (1934). (69) Jacobsen, Ger. 11,494; Friedländer 1, 24. (70) Limpricht, Ann. 135,

(71) Verein chem. metallurg. Prod., Ger. 472,422, Feb. 28, 1929; Cent. 1929, I 2823. (72)
Heiber, Ber. 24, 3684-3687 (1891). (73) Sen, Ray, J. Indian Chem. Soc. 9, 181-183 (1932).
(74) Hamada, Science Repts. Tohoku Imp. Univ., First Ser. 22, 55-60 (1933); Cent. 1933, II 871;
C.A. 27, 3928 (1933). (75) Doebner, Stackmann, Ber. 9, 1918-1920 (1876). (76) Meyer,
Gerloff, Ber. 56, 98-104 (1923); Ber. 57, 591-599 (1924). (77) Dobner, Ann. 217, 227-233 (1883).
(78) Orndorff, McNulty, J. Am. Chem. Soc. 49, 992-997 (1927). (79) Meyer, Funke, Ber. 57, 1360-1363 (1924). (80) Orndorff, Lacey, J. Am. Chem. Soc. 49, 818-826 (1927).

(81) Orndorff, Wang, J. Am. Chem. Soc. 47, 290-292 (1925); 49, 1284-1289 (1927).
(82) Soc. Chem. Ind. Basel, Ger. 355,115, June 21, 1922; Swiss 92,406, Feb. 16, 1922; Swiss 93,490-393,492, March 1, 1922; Cent. 1923, II 483-484.
(83) Soc. Chem Ind. Basel, Ger. 378,908, Aug. 7, 1923; Ger. 378,909, Aug. 11, 1923; Swiss 98,559, April 2, 1923; Cent. 1923, IV 593-594.
(84) Dilthey, Quint, Heinen, J. prakt. Chem. (2) 152, 66-68 (1939).
(85) Franklin, J. Am. Chem. Soc. 55, 4915 (1933).
(86) Fireman, J. Am. Chem. Soc. 52, 2951-2954 (1930).
(87) Doebner, Ann. 217, 239-249 (1883).
(88) Doebner, Ann. 217, 250-261 (1883).
(89) Bodforss, Ber. 59, 670 (1926).
(90) Titherly, Holden, J. Chem. Soc. 101, 1881-1889 (1912).

(91) I.G., Brit. 323,948, Feb. 6, 1930; Cent. 1930, I 2630. (92) Hopff (to I.G.), Ger. 517,760,
Feb. 13, 1931; Cent. 1931, I 2937: Ger. 524,715, May 11, 1931; Cent. 1931, II 497. (93) Vorlander,
Ber. 52, 273 (1919). (94) Soc. Chem. Ind. Basel, Swiss 105,396 June 16, 1924, Cent. 1925, I 1014.
(95) Soc. Chem. Ind. Basel & de Montmollin & Bonhote, Brit. 231,342, April 23, 1925; Cent. 1926.

II 614-615.

```
B.P.
                                   M.P.
                                   16°
                                                  D_4^{20} = 1.3621 (8)
221-221.5°
                             (1)
                                            (9)
                                                                    n_{\rm D}^{20} = 1.5790 \, (8)
                                   15°
220-222°
                   (2) (10) (12)
                                           (10)
119°
               at 27.5 mm. (3)
                                   14-16°
                                           (11)
109°
               at 18.5 mm. (3)
                                   13.5°
                                            (8)
111.5°
                                   13-14° (12)
               at
                   18 mm. (4)
109-111°
               at
                   18 mm.
                            (5)
104.5°
               at
                   15 mm.
                            (3)
105°
               at
                   14 mm.
100.0-100.4° at 12.5 mm. (7)
                   11 mm. (8)
99.6°
99°
               at 11.5 mm. (3)
               at 10.5 mm. (3)
97.5°
93.6-93.9°
                    9 mm. (33)
               at
79.5-79.7°
               at
                    2 mm. (19)
```

[For prepn. of \tilde{C} from p-chlorobenzoic acid (3:4940) with PCl₅ (80% yield (10)) (2) (13) (14), with SOCl₂ (11) (14) (6) (33), with SOCl₂ + AlCl₃ (15), or with p-chlorobenzotrichloride (3:6825) + ZnCl₂ (16) cf. (18) see indic. refs.; from NaĀ with oxalyl dichloride (3:5060) see (17); from p-toluenesulfonyl chloride with SOCl₂ in s.t. at 240° (95% yield) see (12); for formn. of \tilde{C} (2%) from benzoyl chloride (3:6240) with Cl₂ + FeCl₃ (together with 83.5% m- (3:6590) and 14.5% o- (3:6640) isomers see (3).]

 \bar{C} with MeOH yields (4) methyl p-chlorobenzoate (3:0535), m.p. 43°; \bar{C} with EtOH yields ethyl p-chlorobenzoate (3:6750), b.p. 238° (for study of rate of alcoholysis see (19) (20)); \bar{C} with isopropyl alc. yields isopropyl p-chlorobenzoate (for study of rate of reactn. see (21)).

 \bar{C} with Na \bar{A} (50% yield (22)) or \bar{C} with oxalyl dichloride (3:5060) in C_6H_6 (23) gives p-chlorobenzoic acid anhydride, ndls. from C_6H_6 or dil. acetone, m.p. 194.8° (22), 193–194° (23) (24). [This anhydride may form during various reactns. of \bar{C} espec. in pres. of terbases or Na₂CO₃.]

[For reactn. of \bar{C} with AlCl₃ + benzene yielding (25) p-chlorobenzophenone (3:1914), with AlCl₃ + toluene yielding (26) 4-chloro-4-methylbenzophenone, with AlCl₃ + biphenyl yielding (5) p-chlorophenyl p-xenyl ketone, with AlCl₃ + naphthalene yielding (27) p-chlorophenyl α -naphthyl ketone; with AlCl₃ + chlorobenzene yielding (9) 4,4'-dichlorobenzophenone (3:4270), with AlCl₃ + anisole yielding (6) (28) 4-chloro-4'-methoxybenzophenone, with AlCl₃ + phenetole yielding 4-chloro-4'-ethoxybenzophenone see indic. refs.]

[For reactn. of C with perylenetetracarboxylic acid diimide yielding vat dyes see (30); with 4,10-dichloroperylene + AlCl₃ see (31).]

[For reactn. of \tilde{C} with alk. H_2O_2 in acetone giving 4,4'-dichlorodibenzoyl peroxide, m.p. $137-138^\circ$ dec., see (32).]

 $\bar{\mathbf{C}}$ on hydrolysis yields p-chlorobenzoic acid (3:4940); for the amide, anilide, p-toluidide, and other derivs. corresp. to $\bar{\mathbf{C}}$ see p-chlorobenzoic acid (3:4940).

8:6550 (1) Norris, Fasce, Staud, J. Am. Chem. Soc. 57, 1415-1420 (1935). (2) Emmerling, Ber. 8, 881-883 (1875). (3) Hope, Riley, J. Chem. Soc. 121, 2510-2527 (1922); 123, 2470-2480 (1923). (4) Montagne, Rec. trav. chim. 19, 55, 61 (1900). (5) de Ceuster, Cent. 1932, II 1296; C.A. 26, 4323 (1932). (6) Bergmann, Bondi, Ber. 64, 1471 (1931). (7) Kohlrausch, Pongrats,

Stockmair, Monatch. 67, 108 (1935). (8) Martin, Partington, J. Chem. Soc. 1936, 1177. (9) Dittrich, Ann. 264, 175-177 (1891). (10) van Raalte, Rec. trav. chim. 18, 395 (1899).

(11) Meyer, Monatsh. 22, 778 (1901). (12) Pollak, Rudich, Monatsh. 43, 216-217 (1922). (13) Novello, Miriam, Sherwin, J. Biol. Chem. 67, 559 (1926). (14) Frankland, Carter, Adams, J. Chem. Soc. 101, 2476-2477 (1912). (15) Kissling, (to I.G.) Ger. 701,953 Jan. 2, 1940; C.A. 36, 99 (1942). (16) Scottish Dyes, Ltd., Bangham, Thomas, Brit. 308,231, April 18, 1929; Cent. 1929, II 1348. (17) Adams, Uhlich, J. Am. Chem. Soc. 42, 605-606 (1920). (18) Mills (to Dow Chem. Co.), U.S. 1,965,556, July 3, 1934; Cent. 1934, II 2899; C.A. 28, 5474 (1934). (19) Norris, Young, J. Am. Chem. Soc. 57, 1420-1424 (1935). (20) Berger, Olivier, Rec. trav. chim. 46, 516-527 (1927).

(21) Norris, Gregory, J. Am. Chem. Soc. 50, 1813-1816 (1928).
(22) Rule, Paterson, J. Chem. Soc. 125, 2161 (1924).
(23) Adams, Wirth, French, J. Am. Chem. Soc. 40, 427 (1918).
(24) Lockemann, Ber. 43, 2229 (1910).
(25) Demuth, Dittrich, Ber. 23, 3609 (1890).
(26) Blakey, Scarborough, J. Chem. Soc. 1928, 2495.
(27) Scholl, Seer, Ber. 55, 115 (1922).
(28) Jones, J. Chem. Soc. 1936, 1861.
(29) Montagne, Rec. trav. chim. 39, 346 (1920).
(30) Nawiasky (to B.A.S.F.), Ger. 411,594, April 2, 1925; Cent. 1925, I 2666.

(31) Zinke, Funke, Pongratz, Ber. 58, 802 (1925). (32) Gelissen, Hermans, Ber. 58, 292 (1925).

(33) Thompson, Norris, J. Am. Chem. Soc. 58, 1956 (1936).

3:6560 n-AMYL TRICHLOROACETATE $C_7H_{11}O_2Cl_3$ Beil. S.N. 160 n- C_8H_{11} -O.CO.CCl₃

B.P. 220.3-222.3° (1)
$$D_{20}^{20} = 1.2475$$
 (2) 218° at 756 mm. (2)

124.8-125° at 36 mm. (1) 118° at 30 mm. (2)

[For prepn. (91% yield (2)) from n-amyl alc. (1:6205) + trichloroacetic ac. (3:1150) see (2).]

3:6560 (1) Cheng, Z. physik. Chem. B-24, 309 (1934). (2) Liston, Dehn, J. Am. Chem. Soc. 60, 1264-1265 (1938).

3:6575 TRICHLOROACETIC ACID ANHYDRIDE
$$C_4O_3Cl_6$$
 Beil. II - 210 $II_1 II_2-$ (200)

Note that the above name of C is so rendered to emphasize that it is the anhydride of trichloroacetic acid (not a trichlorinated acetic anhydride).

[For prepn. of \tilde{C} from trichloroacetic acid (3:1150) with trichloroacetyl chloride (3:5420) and PCl₃ (2), P₂O₅ (1) or AlCl₃ (5) see indic. refs.; for prepn. of \tilde{C} from trichloroacetic acid (3:1150) with P₂O₅ at 200–215° (80% yield (6)) (4) see indic. refs.; for prepn. of \tilde{C} from sodium trichloroacetate with SO₂Cl₂ or SO₂ + Cl₂ in EtOAc (90–95% yield) see (7).]

[For behavior of \tilde{C} on htg. with SbF₃ + Br₂ see (6); for behavior with pure H₂O₂ see (4).] \tilde{C} is hydrolyzed with great speed by aq. or even moist air (2) (4) yielding trichloroacetic acid (3:1150) q.v.; for the amide, anilide, p-toluidide, and other derivatives corresp. to \tilde{C} see trichloroacetic acid (3:1150).

3:6575 (1) Clermont, Compt. rend. **86**, 337 (1878); Bull. soc. chim. (2) **30**, 505 (1878). (2) Buckney, Thomsen, Ber. **10**, 698-699 (1877). (3) Antoine, Jahresber. **1883**, 1032. (4) Fichter, Fritsch, Müller, Helv. Chim. Acta **6**, 503-504 (1923). (5) Strosacker, Schwegler (to Dow Chem. Co.),

U.S. 1,713,104, May 14, 1929; Cent. 1929, II 1215; C.A. 23, 3234 (1929). (6) Swarts, Bull. soc. chim. (3) 13, 992 (1895). (7) I.G., French 703,816, May 6, 1931; Cent. 1931, II 1347.

3:6582 DIMETHYL CHLOROFUMARATE
$$C_{0}H_{7}O_{4}Cl$$
 Beil. II - 744 Cl —C—COOCH₃ II₁-(302) II₂-(640) $CH_{3}OOC$ —CH

B.P. 224° (1) $D_{4}^{25}v_{ac} = 1.2899$ (2) 115.5° cor. at 18 mm. (2) $D_{4}^{20} = 1.300$ (3) $n_{He}^{20} = 1.471$ (3) 108° at 15 mm. (3) $D_{4}^{179} = 1.3028$ (3) $n_{He}^{19} = 1.47198$ (3)

[For prepn. of C from chlorofumaric acid (3:4853) in abs. MeOH with HCl gas (1) or conc. H₂SO₄ (3) see indic. refs.; from chlorofumaryl (di)chloride (3:6105) with MeOH under reflux see (1).]

3:6582 (1) Kauder, J. prakt. Chem (2) 31, 26-28, 32 (1885). (2) Walden, Swinne, Z. physik. Chem. 79, 741 (1912). (3) von Auwers, Harres, Ber. 62, 1679, 1686-1687 (1929).

[For prepn. of \bar{C} from *m*-chlorobenzoic acid (3:4392) with PCl₅ (76% yield (8)) (1) (5) or with SOCl₂ (10) (6) see indic. refs.; from benzoyl chloride (3:6240) with Cl₂ + FeCl₃ (83.5% \bar{C}) see (7) (11); from tetrahydroxybenzoic acid [Beil. X-535, X₁-(270)] with 5 moles PCl₅ see (12); from *o*-sulfobenzoic acid with 2 moles PCl₅ see (1) (13).]

[Note that for the isomeric p-chlorobenzoyl chloride (3:6550) htg with P_2O_5 in toluene yields (16) the corresp. anhydrides; although this reactn. is not recorded for \bar{C} yet the corresp. m-chlorobenzoic acid anhydride, ndls. from alc. (17) or from lt. pet. (16), m.p. 95.5° (16), 95° (17), has been obtd. from m-chlorobenzoic acid (3:4392) with P_2O_5 in boilg. toluene (30% yield (16)) or with oxalyl dichloride (3:5060) in boilg. C_6H_6 (17).]

[Č with MeOH yields (5) methyl m-chlorobenzoate (3:6670), b.p. 231°; Č with EtOH yields (1) ethyl m-chlorobenzoate (3:6770), b.p. 245°.] [For studies of rate of alcoholysis of Č see (14) (9).]

[\tilde{C} with C_6H_6 + AlCl₃ gives (65% yield (6)) (2) (4) *m*-chlorobenzophenone (3:2160), m.p. 82-83°; \tilde{C} with naphthalene + AlCl₃ in CS₂ gives (73% yield (15)) *m*-chlorophenyl α -naphthyl ketone, pale yel. pr. from alc., m.p. 77-79° (15).]

 $\tilde{\mathbf{C}}$ on hydrolysis (e.g., by boilg. with aq. (7)) yields m-chlorobenzoic acid (3:4392). — For the amide, anilide, p-toluidide, and other derivs. corresp. to $\tilde{\mathbf{C}}$ see m-chlorobenzoic acid (3:4392).

3:8590 (1) Limpricht, von Uslar, Ann. 102, 262-263 (1857). (2) Hantzsch, Ber. 24, 57 (1891). (3) Kohlrausch, Pongratz, Stockmair, Monatsh. 67, 108 (1935). (4) Norris, Blake, J. Am. Chem. Soc. 50, 1812. (5) Montagne, Rec. trav. chim. 19, 55, 58 (1900). (6) Bergmann, Bondi, Ber. 64, 1477 (1931). (7) Hope, Riley, J. Chem. Soc. 121, 2510-2527 (1922). (8) Novello, Miriam, Sherwin, J. Biol. Chem. 67, 558 (1926). (9) Norris, Young, J. Am. Chem. Soc. 57, 1420-1424 (1935). (10) Frankland, Carter, Adams, J. Chem. Soc. 101, 2476-2477 (1912).

Hope, Riley, J. Chem. Soc. 123, 2470-2480 (1923). (12) Graebe, Ann. 138, 200-202 (1866).
 Otto, Ann. 122, 156 (1862). (14) Berger, Olivier, Rec. trav. chim. 46, 516-527 (1927).
 Scholl, Seer, Ber. 55, 113 (1922). (16) Rule, Paterson, J. Chem. Soc. 125, 2161 (1924).
 Adams, Wirth, French, J. Am. Chem. Soc. 40, 427 (1919). (18) Thompson, Norris, J. Am. Chem. Soc. 58, 1956 (1936).

3:6600 p-TOLUYL CHLORIDE
$$C_8H_7OCl$$
 Beil. IX - 486 (p-Methylbenzoyl chloride) CH_3 $C=O$ Cl Cl

[For prepn. of \bar{C} from p-toluic acid (1:0795) with PCl₅ (100% yield (3)) (6) (10), with PCl₃ (11), with SOCl₂ (95% yield (12)) (2) (7) (13) (14), with POCl₃ + NaCl (KCl) (15) see indic. refs.]

[\bar{C} with pyridine and excess $K_2S_2O_5$ yields (16) p-toluic anhydride, m.p. 94° (also formed as by-product of prepn. of \bar{C} with PCl_5 (6)).]

[For reactn. of \bar{C} with AlCl₃ and various hydrocarbons to yield ketones, e.g., with C_6H_6 yielding (3) phenyl p-tolyl ketone (1:5160), with toluene yielding (17) di-p-tolyl ketone (1:5185), with biphenyl yielding (18) (13) p-tolyl p'-xenyl ketone, with naphthalene yielding (19) α -naphthyl p-tolyl ketone, with m-xylene yielding (14) p-tolyl m-xylyl ketone, with p-xylene yielding (14) p-tolyl p-xylyl ketone, with isopropylbenzene (cumene) yielding (20) p-cumyl p-tolyl ketone see indic. refs.]

 $[\tilde{\mathbf{C}}$ with EtZnI yields (21) ethyl p-tolyl ketone [Beil. VII-317, VII₁-(170)], b.p. 238°.]

 $[\bar{C}]$ with Cl_2 at elevated temp. yields (22) p-(chloromethyl)benzoyl chloride (a-chloro-p-toluyl chloride, b.p. 150–155° at 22 mm. (22); \bar{C} with Br_2 at 185–190° yields (23) a mixt. of p-(bromomethyl)benzoyl chloride, b.p. 155–156° at 20 mm., and p-(bromomethyl)benzoyl bromide, b.p. 170–171° at 20 mm., m.p. 56° (23).]

[C with MeOH yields methyl p-toluate (1:2071), m.p. 33°, b.p. 222.5°; C with EtOH yields ethyl p-toluate (1:3947), b.p. 234.5°; for study of rate of reactn. with MeOH see (24), with EtOH see (9), with isopropyl alc. see (25).]

 $\tilde{\mathbf{C}}$ on hydrolysis yields p-toluic acid (1:0795), m.p. 178°; for the amide, anilide, p-toluidide, and other derivs. corresp. to $\tilde{\mathbf{C}}$ see p-toluic acid (1:0795).

3:6600 (1) Kohlrausch, Pongratz, Stockmair, Monatsh. 67, 108 (1936). (2) Meyer, Monatsh. 22, 425 (1901). (3) Ador, Rilliet, Ber. 12, 2298-2299 (1879). (4) Frankland, Aston, J. Chem.

Soc. 75, 494 (1899). (5) Martin, Partington, J. Chem. Soc. 1936, 1177. (6) van Scherpenzeel,
 Rec. trav. chim. 20, 156 (1901). (7) Thompson, Norris, J. Am. Chem. Soc. 58, 1955 (1936).
 Branch, Nixon, J. Am. Chem. Soc. 58, 2500 (1936). (9) Norris, Young, J. Am. Chem. Soc. 57, 1424 (1935). (10) Cahours, Ann. 108, 316 (1858).

(11) Frankland, Wharton, J. Chem. Soc. 69, 1311 (1896). (12) Maxim, Bul. Soc. Chim. România 11, 29-36 (1929); Cent. 1929, II 2324. (13) Schlenk, Bergmann, Ann. 464, 32 (1928). (14) Morgan, Coulson, J. Chem. Soc. 1929, 2208-2211. (15) Kissling (to I.G.), Ger. 642,519, March 10, 1937; Cent. 1937, I 3874; C.A. 31, 5816 (1937). (16) Gasopoulos, Praktika Akad. Athenon 6, 347-353 (1931); Cent. 1932, I 3171. (17) Sommelet, Compt. rend. 180, 1349-1351 (1925). (18) Dilthey, J. prakt. Chem. (2) 109, 316 (1925). (19) Scholl, Seer, Ann. 394, 147 (1912). (20) Kozlov, Fedoseev, Drabkin, J. Gen. Chem. (U.S.S.R.), 6, 1686-1689 (1936); Cent. 1937, I 2369; C.A. 31, 2591 (1937).

(21) Mauthner, J. prakt. Chem. (2) 103, 294 (1921/22). (22) Badische Anilin- und Soda-Fabrik., Ger. 239,311, Oct. 10, 1911; Cent. 1911, II 1394; Ger. 240,835, Nov. 15, 1911; Cent. 1911, II 1394; Ger. 240,835, Nov. 15, 1911; Cent. 1911, II 1843. (23) Titley, J. Chem. Soc. 1928, 2581. (24) Norris, Fasce, Staud, J. Am. Chem. Soc. 57, 1415–1420 (1935). (25) Norris, Gregory, J. Am. Chem. Soc. 50, 1813–1816 (1928).

B.P. 226.5°

M.P. 56°

See 3:1020. Division A: Solids.

3:6615 o-CHLOROACETOPHENONE O C₈H₇OCl Beil. VII — VII₁-(151)

B.P.
$$228-229^{\circ}$$
 at 758 mm. (10) $D_{25}^{25}=1.1884$ (1) $n_{25}^{25}=1.685$ (1) $227-228^{\circ}$ at 738 mm. (1) $D_{4}^{20}=1.198$ (4) $n_{He}^{20}=1.5483$ (5) $n_{He}^{20}=1.5483$ (6) $n_{He}^{20}=1.5483$ (7) $n_{He}^{20}=1.5483$ (8) $n_{He}^{20}=1.5483$ (9) $n_{He}^{20}=1.5483$ (1) $n_{He}^{20}=1.5483$ (1) $n_{He}^{20}=1.5483$ (2) $n_{He}^{20}=1.5483$ (3) $n_{He}^{20}=1.5483$ (4) $n_{He}^{20}=1.5483$ (5) $n_{He}^{20}=1.5483$ (6) $n_{He}^{20}=1.5483$ (7) $n_{He}^{20}=1.5483$ (8) $n_{He}^{20}=1.5483$ (9) $n_{He}^{20}=1.5483$ (1) $n_{He}^{$

Colorless mobile liquid with agreeable odor.

[For prepn. of C from o-chlorophenyl-methyl-carbinol (4) (5) by oxidn. with CrO₃ see (4) (5); from methyl o-chlorobenzoylacetate (60% yield (2)) or from ethyl o-chlorobenzoylacetate (80% yield (1)) (54% from C (10)) on ketonic hydrol. with boilg. 20% H₂SO₄ for 10-12 hrs. see indic. refs.; from o-chlorobenzonitrile [Beil. IX-336] with MeMgI in ether (56% yield) see (3).]

[C with CuCN on htg. in mixt. of quinoline + pyridine as directed (6) gives 20% yield o-cyanoacetophenone, m.p. 48°, b.p. 148° at 12 mm. (6); for behavior of C on htg. with CuCN in quinoline at 210° or with CuCN + phthalonitrile in quinoline yielding coppercontg. pigments of the phthalocyanine type see (7).]

[C on htg. with 50% KOH as directed (8) gives small yield o-chlorobenzoic acid.]

[\overline{C} on mononitration with 10 pts. HNO₃ (D=1.52) at 0° gives (85% yield (1)) 2-chloro-4-nitroacetophenone, colorless pr. from alc., m.p. 62° (1) (for condens. of this prod. with arylamines to give substituted acridines see (9)).]

- O-Chloroacetophenone oxime: ndls. from aq., m.p. 112-113° (4), 103° (1).
- © o-Chloroacetophenone p-nitrophenylhydrazone: maroon cryst. from AcOH, m.p. 215° (2). (The phenylhydrazone of C is unstable (2).)
- O o-Chloroacetophenone 2,4-dinitrophenylhydrazone: dark yel. lfts. from AcOEt, m.p. 206° (3).
- © o-Chloroacetophenone semicarbazone: cryst. from MeOH, m.p. 178-179° (3), from 40% AcOH, m.p. 159-160° (2).

3:8615 (1) Thorp, Brunskill, J. Am. Chem. Soc. 37, 1260-1261 (1915). (2) Wahl, Rolland, Ann. chim. (10) 10, 28-29 (1928). (3) Borsche, Scriba, Ann. 541, 290 (1939). (4) von Auwers, Lechner, Bundesmann, Ber. 58, 49-50 (1925). (5) Ferbwerke Meister Lucius Brüning, Brit. 176,038, March 30, 1922; Cent. 1923, II 1252. (6) Helberger, von Rebay, Ann. 531, 283-284 (1937). (7) Helberger, Ann. 529, 216-217 (1937). (8) Lock, Böck, Ber. 76, 920 (1937). (9) Jensen, Rethwisch, J. Am. Chem. Soc. 50, 1145, 1149 (1928). (10) Sharp, Sutherland, Wilson, J. Chem. Soc. 1943, 346.

3:6625 o-CHLOROBENZAL (DI)CHLORIDE
$$C_7H_5Cl_3$$
 Beil. V - 300 (o-Chlorobenzylidene (di)chloride) $CHCl_2$ V_1 V_2 B.P. 228.5° (1) $D_{15}^{15} = 1.399$ (1) $n_D^{16} = 1.5670$ (4) 227-230° (2) 226-228° at 745 mm. (3) 100° at 10 mm. (3)

[For prepn. of \bar{C} from o-chlorobenzaldehyde (3:6410) with PCl₅ (86% yield (3)) (5) see indic. refs.; from o-toluenesulfonyl chloride with Cl₂ at 92° (73.5% yield (4)) or at 150–200° (6) see indic. refs.; from o-chlorotoluene (3:8245) with Cl₂ (1) in pres. of PCl₅ at 150–180° (7) or in pres. of PCl₅ at 102–105° (8) see indic. refs.; from o-hydroxybenzaldehyde (salicylaldehyde) (1:0205) with PCl₅ see (2); for formn. of \bar{C} (5–7%) from benzal dichloride (3:6327) with Cl₂ in pres. of I₂ (accompanied by 43% m- and 46–47% p-isomers) see (9).]

[For use of \bar{C} in prepn. of triphenylmethane dyes see (10) (11); for condensation with isoviolanthrone in prepn. of vat dyes see (12).]

Č on boilg. with water for 20 hrs. (3) or on htg. with aq. in s.t. at 170° (2) or with weakly fumg. H₂SO₄ at ord. temp. as directed (7) yields o-chlorobenzaldehyde (3:6410). [For studies of this hydrolysis under various other conditions see (13) (5).]

C on oxidn. with CrO₃ (2), or C on boilg. with aq. for 20 hrs. followed by treatment with cold conc. aq. KMnO₄ (3), gives (75% yield (3)) o-chlorobenzoic acid (3:4150), m.p. 141° (3).

[C in MeOH treated with molecular Ag + sand and htd. in s.t. for 6 hrs. at 95° yields (1) α,β -dichloro- α,β -bis-(o-chlorophenyl)ethane [Beil. V-601], cryst. from ether + lgr., m.p. 170.5° (1).]

3:6625 (1) Gill, Ber. 26, 650-652 (1893). (2) Henry, Ber. 2, 136 (1869). (3) Asinger, Lock, Monatsh. 62, 333-334 (1933). (4) Davies, Dick, J. Chem. Soc. 1932, 2045. (5) Olivier, Weber, Rec. trav. chim. 53, 881, 888 (1934). (6) Gilliard, Monnet, Cartier, Ger. 98,433, Dec. 12, 1896, Cent. 1898, II 800. (7) Erdmann, Ann. 272, 151-152 (1892). (8) Kyrides (to National Aniline and Chem. Co.), U.S. 1,733,268, Oct. 29, 1929; Cent. 1936, I 3831. (9) Wertyporoch, Ann. 493, 161-162 (1932). (10) Geigy and Co., Ger. 213,503, Oct. 14, 1909; Cent. 1909, II 1515.

(11) Weiler, Wenk, Stötter, Ger. 540,208, Dec. 12, 1931; Cent. 1932, I 3013. (12) Wuerts, Lycan (to du Pont Co.), U.S. 2,082,560, June 1, 1937; Cent. 1937, II 2077; C.A. 31, 5595 (1937).

(13) Lock, Asinger, Monatsh. 59, 157-160 (1932).

В.Р.	B.P. (cont.)		
229-230° at 773 mm. (1)	114.5°	at 19.75 mm. (15)	F.P4° (1)
235–238° (2)	110°	at 15 mm. (8)	
228-236° at 760 mm. (3)	108°	at 14.5 mm. (15)	
233° (4)	105°	at 12.75 mm. (15)	
227° (11)	104.8-105.2°	at 12.5 mm. (9)	
224–224.5° (5)	103.5°	at 12 mm. (15)	
224° (6)	101.5°	at 11 mm. (15)	
137-139° at 60 mm. (7)	93-95°	at 10 mm. (7)	
122° at 26.5 mm. (15)	87°	at 9 mm. (10)	
	78.9-79.2°	at 2 mm. (36)	

[For prepn. of \bar{C} from o-chlorobenzoic acid (3:4150) with PCl₅ (78% yield (11)) (2), with PCl₃ + ZnCl₂ (78% yield (11)), with SOCl₂ (yield: 90–98% (11), 87% (10)) (12) (13) (36), or with o-chlorobenzotrichloride (3 6880) + ZnCl₂ (14) see indic. refs.; from o-chlorobenzaldehyde (3:6410) with Cl₂ at 140–160° (70–72% yield) see (7); from toluene-o-sulfonyl chloride with SOCl₂ in s.t. at 240° (41% yield) see (4).]

[For formn. of \bar{C} (together with other products) from benzoyl chloride (3:6240) with $Cl_2 + FeCl_3$ (14.5% \bar{C}) (15) (16), from o-hydroxybenzoic acid (salicylic acid) (1:0780) with PCl_5 (17) (18) or with phospene (3:5000) + pyridine in toluene at 60-80° (19); from sodium salicylate with PCl_5 (18) (20); from o-sulfobenzoic acid dichloride by distn. at ord. press. (21) (8) (22) (3) see indic. refs.]

[C with MeOH yields (1) methyl o-chlorobenzoate (3:6695) (for study of rate of reaction see (6)); C with EtOH yields (23) ethyl o-chlorobenzoate (3:6800) (for study of rate of reaction see (5)).]

[\bar{C} with Na o-chlorobenzoate should yield o-chlorobenzoic acid anhydride, ndls. from lt. pet. (25) or alc. (26), m.p. 79.6° (25), 78–79° (26); this anhydride also results from o-chlorobenzoic acid with P_2O_5 in boilg. toluene (25) or with oxalyl dichloride (3:5060) in boilg. C_6H_6 (26).]

[C on cat. hydrogenation gives (70% yield (27)) (28) o-chlorobenzaldehyde (3:6410).]

[For reactn. of \ddot{C} with AlCl₃ + benzene yielding (29) o-chlorobenzophenone (3:0715), with AlCl₃ + o-chlorobluene yielding (30) 2,3-dichloro-4-methylbenzophenone, with AlCl₃ + p-dichlorobenzene yielding (31) 2,2',5'-trichlorobenzophenone, with AlCl₃ + naphthalene yielding (32) α -naphthyl o-chlorophenyl ketone, or with anisole + AlCl₃ (1:7445) yielding (33) 2-chloro-4-methoxybenzophenone see indic. refs.]

[For reactn. of C with perylenetetracarboxylic acid diimide (34) or with aminodibenzanthrones (35) yielding vat dyes see indic. refs.]

Č on hydrolysis yields o-chlorobenzoic acid (3:4150), m.p. 141°; for the amide, anilide, p-toluidide, and other derivs. corresp. to Č see o-chlorobenzoic acid (3:4150).

3:8640 (1) Montagne, Rec. trav. chim. 19, 55-56 (1900). (2) Emmerling, Ber. 8, 883 (1875).
(3) Davies, Dick, J. Chem. Soc. 1932, 2044. (4) Pollak, Rudich, Monatsh. 43, 217-218 (1922).
(5) Norris, Fasce, Staud, J. Am. Chem. Soc. 57, 1415-1420 (1935). (6) Norris, Young, J. Am. Chem. Soc. 57, 1420-1424 (1935). (7) Clarke, Taylor, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 155-156 (1941); (1st ed.), 148-149 (1932); 9, 34-35 (1929). (8) Fritsch, Ber. 29, 2299 (1896).
(9) Kohlrausch, Pongrats, Stockmair, Monatsh. 67, 108 (1935). (10) Novello, Miriam, Sherwin, J. Biol. Chem. 67, 557, (1926).

(11) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (12) Frankland, Carter, Adams, J. Chem. Soc. 101, 2476 (1912). (13) Meyer, Monatsh. 22, 427 (1901). (14) Scottish Dyes, Ltd., Bangham, Thomas, Brit. 308,231, April 18, 1929; Cent. 1929, II 1348; C.A. 24, 129 Dyes, Ltd., Balgham, Indias, Dr. 305, 121, 2510-252, (1920). (15) Hope, Riley, J. Chem. Soc. 123, 2470-2480 (1923). (17) Chiozza, Ann. 83, 317-318 (1852). (18) Kolbe, Lautermann, Ann. 115, 183-187 (1860). (19) Soc. Chem. Ind. Basel, Brit. 401,643, Dec. 14, 1933; Cent. 1834, II 2133; French 732,078, Sept. 13, 1932; Cent. 1934, I 287. (20) Reichenbach, Beilstein. Ann. 132, 311-313 (1864).

(21) Remsen, Kohler, Am. Chem. J. 17, 332-333 (1895). (22) List, Stein, Ber. 31, 1653-1654 (1898). (23) Kekulé, Ann. 117, 153-154 (1861). (24) Berger, Olivier, Rec. trav. chim. 46, 516-527 (1927). (25) Rule, Paterson, J. Chem. Soc. 125, 2161 (1924). (26) Adams, Wirth, 510-527 (1927). (20) Rule, Facision, J. Chem. Soc. 200, 241 (1927). (20) Annual, French, J. Am. Chem. Soc. 40, 427 (1918). (27) Rosenmund, Zetsche, Ber. 54, 436-437 (1921). (28) Zetsche, Swiss 92,404, Jan. 2, 1922, Cent. 1922, IV 889. (29) Mayer, Freund, Ber. 55, 2050-2051 (1922). (30) de Diesbach, Bulhard, Helv. Chim. Acta 7, 625 (1924). (31) Ganzmuller, J. prakt Chem. (2) 138, 311-312 (1933). (32) Scholl, Sier, Ber. 55, 113 (1922).

(33) Jones, J. Chem. Soc. 1936, 1861. (34) Nawiasky (to B.A.S.F.), Ger. 411,594, April 2, 1925; Cent. 1925, I 2666. (35) B.A.S.F., French 598,752, Dec. 24, 1925; Cent. 1926, I 1889. (36)

Thompson, Norris, J. Am. Chem. Soc. 58, 1956 (1936).

— 2,3,4-TRICHLOROTOLUENE

$$\begin{array}{ccccc} {\rm CH_{3}} & {\rm C_{7}H_{5}Cl_{3}} & {\rm Beil.} \ V - {\bf 298} \\ {\rm Cl} & & V_{1}-\\ {\rm Cl} & & V_{2}-({\bf 232}) \\ \end{array}$$

B.P. 231-232° at 716 mm.

M.P. 41°

See 3:0425. Division A: Solids.

- 2,3,5-TRICHLOROTOLUENE

$$CH_3$$
 $C_7H_5Cl_3$ Beil. $V-299$ $V_1 V_2-$

B.P. 229-231° at 757 mm.

M.P. 45-46°

See 3:0610. Division A: Solids.

— 2,4,5-TRICHLOROTOLUENE

$$\begin{array}{cccc} CH_3 & C_7H_5Cl_3 & \text{Beil. V - 299} \\ & & V_{1^-}(152) \\ & & V_{2^-}(232) \end{array}$$

B.P. 229-230° at 716 mm.

M.P. 82°

See 3:2100. Division A: Solids.

1,1,2,3,4-PENTACHLOROBUTANE C₄H₅Cl₅ Beil. S.N. 10 (Solid diastereoisomer) CH₂—CH—CH-

B.P. 230°

M.P. 49°

 $D_{-}^{53} = 1.539$ $n_{\rm D}^{53} = 1.5065$

See 3:0750. Division A: Solids.

[See also glycerol α-chlorohydrin α'-acetate (3:6775).]

[For prepn. of \tilde{C} from glycerol β -monochlorohydrin (3:9039) with Ac₂O (1:1015) see (3).]

[For formn. of $\bar{\mathbb{C}}$ from 3-hydroxy-1,2-epoxypropane (glycidol) with AcCl (3:7065) (note that γ -chloropropylene glycol β -acetate (3:6517) is also formed) see (1); from glycerol α,α' -diacetate with PCl₅ or S₂Cl₂ see (3); from allyl acetate by addn. of HOCl see (1).]

Note that the homogeneity of all reported prepns. of $\bar{\mathbf{C}}$ is probably open to serious question.

3:8648 (1) Bigot, Ann. chim. (6) 22, 490-493 (1891). (2) Gibson, J. Soc. Chem. Ind. 50, 950 (1931). (3) Wegscheider, Zmerzlikar, Monatsh. 34, 1071-1080 (1913).

3:6655 ETHYLENE GLYCOL bis- $(\beta$ -CHLOROETHYL) $C_{\delta}H_{12}O_{2}Cl_{2}$ Beil. S.N. 30 ETHER $CH_{2}O.CH_{2}.CH_{2}Cl_{2}$ CH₂.O.CH₂.CH₂Cl $(\beta(\beta$ -Chloroethoxy)ethyl β -chloroethyl ether; α,β -bis- $(\beta$ -chloroethoxy)ethane; $CH_{2}O.CH_{2}.CH_{2}Cl$ "triglycol dichloride")

B.P. 230°	at 760 mm. (1)	$D_{24}^{24}=1.196\ (4)$	
235°	· (2)		
118°	at 10 mm. (1)	$D_{20}^{20}=1.197(1)$	
80-85	o at 2 mm. (4)		

[For prepn. of \bar{C} from "triethylene glycol" (1:6538) + SOCl₂ (78.5% yield (4)) + dimethylaniline (2) or pyridine (4) see (2) (4); for prepn. from ethylene chlorohydrin (3:5552) + ethylene oxide (1:6105) see (1).]

[For reactn. of \bar{C} with phenols see (2) (3); with NaSCN see (5); for reactn. with metal polysulfides see (6).]

[For solubility of dichlorofluoromethane (refrigerating liquid) in \bar{C} see (4).] [For use in high-pressure lubrication see (1).]

3:8655 (1) Cox (to Carbide and Carbon Chem. Corp.), U.S. 2,017,811, Oct. 15, 1935; French 788,281, Oct. 7, 1935; Cent. 1936, I 3063; C.A. 29, 8320 (1935). (2) Röhm, Haas, French 822,326, Dec. 28, 1937; Cent. 1938, I 4384; C.A. 32, 4250-4251 (1938). (3) Rohm, Haas, French 824,887, Feb. 17, 1939; Cent. 1938, II 1861; C.A. 32, 6258 (1938). (4) Zellhoefer, Ind. Eng. Chem. 29, 548-551 (1937). (5) Hollander, Williams (to Röhm, Haas Co.), U.S. 2,077,478, 2,077,479, April 20, 1937; Cent. 1937, II 1650; C.A. 31, 4045-4046 (1937). (6) Patrick, Trans. Faraday Soc. 32, 347-358 (1935).

B.P. M.P. 231° at 763.5 mm. (1) 21° (2)
$$n_{\rm D}^{10.5} = 1.4923$$
 (5) 227° at 760 mm. (5) 20.0–20.5° (3) 114° at 18 mm. (2) 99.5–101.5° at 12 mm. (5)

[For prepn. of \bar{C} from *m*-chlorobenzoic acid (3:4392) with MeOH + Hcl (2) or with MeOH + H₂SO₄ (2) (3) see indic. refs.; from *m*-chlorobenzoyl chloride (3:6590) with MeOH see (1).]

 \tilde{C} on htg. with sirupy H_3PO_4 at 200° yields (4) m-chlorobenzoic acid (3:4392), chlorobenzene (3:7903), dimethyl ether, and CO_2 .

Č added to 5-6 pts. very conc. HNO₃ at 0°, then poured onto ice, yields (1) methyl 5-chloro-2-nitrobenzoate [Beil. IX-401], cryst. from MeOH, m.p. 48.5° (1).

[\ddot{C} with Na + methyl acetate condenses giving (65-70% yield (3)) methyl m-chlorobenzoylacetate, b.p. 165-169° at 11 mm. (3); this prod. with excess phenylhydrazine in alc. + AcOH yields 3-(m-chlorophenyl)-1-phenylpyrazolone-5, cryst. from alc., m.p. 144° (3); corresp. prod. from p-nitrophenylhydrazine, m.p. 189° (3).]

Č on hydrolysis (Sap. Eq. = 170.5) yields methyl alcohol (1:6120) and m-chlorobenzoic acid (3:4392). [For study of vel. of hydrol. with MeOH/KOH at 25° see (2).] — For the amide, anilide, p-toluidide, and other derivs. corresp. to Č see m-chlorobenzoic acid (3:4392).

3:6670 (1) Montagne, Rec. trav. chim. 19, 55-56, 58-61, 63-64 (1900). (2) Kellas, Z. physik. Chem. 24, 243-252 (1897). (3) Wahl, Rolland, Ann. chim. (10) 10, 9-18 (1928). (4) Raikow, Tischkow, Chem. Ztg. 29, 1269 (1905). (5) Kahovec, Wagner, Monatsh. 74, 285 (1943).

B.P. 231-233°

M.P. 57-58°

See 3:1145. Division A: Solids.

--- 3,5-DICHLOROPHENOL OH C₆H₄OCl₂ Beil. VI - 190 VI₁-(103) VI₂-(179)

B.P. 233° at 757 mm.

M.P. 68°

See 3:1670. Division A: Solids.

3:6685
$$d$$
, l -1,2-DICHLORO-1-PHENYLETHANE $C_8H_8Cl_2$ Beil. V - 354 V_1 —
styrene dichloride) $C_8H_8Cl_2$ V_1 —
 V_2 -(278)

B.P. 233-234° at 759 mm. (1)
$$D_4^{15} = 1.240$$
 (1) $n_D^{15} = 1.5544$ (1) 114.5-115.5° at 15 mm. (1) 93° at 5 mm. (2)

Limpid liq. with faint odor.

3:6695 METHYL o-CHLOROBENZOATE

[For prepn. of \tilde{C} from phenylethylene (styrene) (1:7435) with Cl₂ in CHCl₃ at 0° {1} cf. (3) or in CCl₄ at 40-50° (4) (note that some β -chlorostyrene (3:8717) is also formed (4)) see indic. refs.; for form. of \tilde{C} in reaction of styrene (1:7435) with NCl₃ in CCl₄ at -10° (5) or from ethylbenzene (1:7410) with Cl₂ in bright sunlight (6) see indic. refs.]

[\bar{C} with a mildly alkaline agent such as Na₂CO₃, NaOAc, CaO, or CaCO₃ (but not alkali hydroxide) as directed (7) undergoes hydrolysis of its α -chlorine atom giving chloromethyl-phenyl-carbinol (styrene chlorohydrin) (3:9570).]

[\bar{C} passed over activated Al₂O₃ at 360-400° and 85-105 mm. pres. (4) or \bar{C} with pyridine as directed (8) loses HCl giving (92% yield (4)) β -chlorostyrene (3.8717).]

[C with aq. alc. NaOH at 50-60° for 4 hrs. loses HCl (in the opposite sense from preceding paragraph) giving (89% yield (4)) \(\alpha \)-chlorostyrene (3:8715).]

3:6685 (1) Biltz, Ann. 296, 275-277 (1897). (2) Knorr (to I.G.), Ger. 559,521, Sept. 21, 1932; Cent. 1933, I 1843; C.A. 27, 736 (1933): French 735,000, Oct. 31, 1932, Cent. 1933, I 1843; C.A. 27, 1011 (1933). (3) Blyth, Hofmann, Ann. 53, 309-310 (1845). (4) Emerson, Agnew, J. Am. Chem. Soc. 67, 518-520 (1945). (5) Coleman, Campbell, J. Am. Chem. Soc. 50, 2754-2755 (1928). (6) Evans, Mabbott, Turner, J. Chem. Soc. 1927, 1163. (7) I G., French 735, 108, Nov. 3, 1932; Cent. 1933, II 1093; C.A. 27, 1011 (1933). (8) I.G., French, 729,730, July 30, 1932; Cent. 1932, II 3015; C.A. 27, 307 (1933).

C₈H₇O₂Cl

Beil. IX - 336

[For prepn. of \bar{C} from o-chlorobenzoic acid (3:4150) with MeOH + HCl (2) or MeOH + H₂SO₄ (2) (5) or MeOH + BF₃.Et₂O (70.6% yield (4)) see indic. refs.; from o-chlorobenzoyl chloride (3:6640) with MeOH see (1).]

 \tilde{C} on htg. with sirupy H_3PO_4 at 200° yields (6) o-chlorobenzoic acid (3:4150), chlorobenzene (3:7903), dimethyl ether $+ CO_2$.

Č added to 5-6 pts. very conc. HNO₃ at 0°, poured onto ice, yields (1) mainly methyl 2-chloro-5-nitrobenzoate [Beil. IX-403], ndls. from MeOH, m.p. 73° (1).

[C with Na + methyl acetate condenses giving (65-70% yield (5)) methyl o-chlorobenzoylacetate, b.p. 170-172° at 12 mm. (5); this prod. with excess phenylhydrazine in alc. + AcOH gives on htg. 3-(o-chlorophenyl)-1-phenylpyrazolone-5, colorless ndls. from MeOH, m.p. 113-114° (5); corresp. prod. from p-nitrophenylhydrazine, m.p. 203-204° (5).] Č on hydrolysis (Sap. Eq. = 170.5) yields methyl alcohol (1:6120) + o-chlorobenzoic acid (3:4150). [For studies of hydrolysis under various cond. see (2) (3) (7).] — For the amide, anilide, p-toluidide, and other derivs. corresp. to Č see o-chlorobenzoic acid (3:4150).

3:8695 (1) Montagne, Rec. trav. chim. 19, 55-58, 63-64 (1900). (2) Kellas, Z. physik. Chem. 24, 243-252 (1897). (3) Bergmann, Hirshberg, J. Chem. Soc. 1936, 334-336. (4) Sowa, Nieuwland, J. Am. Chem. Soc. 58, 272 (1936). (5) Wahl, Rolland, Ann. chim. (10) 10, 9-13, 17-18 (1928). (6) Raikow, Tischkow, Chem. Ztg 29, 1269 (1905). (7) Jones, McCombie, Scarborough, J. Chem. Soc. 123, 2695-2697 (1923); 125, 2593-2594 (1924). (8) Kahovec, Wagner, Monatch. 74, 284 (1943).

3:6697 DIETHYL CHLOROMALEATE
$$C_8H_{11}O_4Cl$$
 Beil. II - 753 Cl — C — $COOC_2H_5$ II₁-(305) II_{2} -(646)

B.P. 235° at 760 mm., sl. dec. (1) $D_4^{25}_{vac} = 1.1914$ (2) 189.5–190.5° at 210 mm. (1) 125.5° cor. at 19 mm. (2) $D_4^{20} = 1.174$ (4) (5) $n_{He}^{20} = 1.455$ (4) 122° at 15 mm. (3) 1.4549 (5) 120° at 12 mm. (5) $D_4^{10} = 1.1754$ (4) $n_{He}^{10} = 1.45532$ (4)

[See also diethyl chlorofumarate (3:6864).]

Colorless oil with pleasant odor.

[For prepn. of \bar{C} from chloromaleic anhydride (3:0280) in abs. EtOH with conc. H₂SO₄ in cold (4) or on refluxing several hrs. (6) or from silver salt of chloromaleic acid (3:3432) with EtI (1) (3) see indic. refs.]

 $[\bar{C}\ (1\ mole)\ with ethyl sodioacetoacetate (1\ mole)\ in abs. alc. refluxed <math>\frac{1}{2}$ hr. reacts readily yielding (3) (7) triethyl γ -acetylaconitate [Beil. III-860], yel. oil, b.p. 187-188° at 15 mm. (3), the same prod. as similarly obtd. from diethyl chlorofumarate (3:6864).]

[C with 6% alc. NH₃ (2 moles) at ord. temp. for 5-6 days reacts to yield (6) diethyl immosuccinate (diethyl aminobuten-2-dioate) [Beil. III-784], b.p. 144-145° at 25 mm. (6), identical with the prod. from similar treatment of the isomeric diethyl chlorofumarate (3:6864) q.v.]

3:6697 (1) Perkin, J. Chem. Soc. 53, 708 (1888). (2) Walden, Swinne, Z. physik. Chem. 79, 742 (1912). (3) Ruhemann, Taylor, J. Chem. Soc. 69, 532-535 (1896). (4) von Auwers, Harres, Ber. 62, 1681, 1686-1687 (1929). (5) von Auwers, Harres, Z. physik. Chem. A-143, 10 (1929). (6) Thomas-Mamert, Bull. soc. chim. (3) 13, 848-853 (1895). (7) Ruhemann, J. Chem. Soc. 71, 323-324 (1897).

[For prepn. of \tilde{C} from p-chlorobenzaldehyde (3:0765) with PCl₅ see (1) (4); from p-toluenesulfonyl chloride with SOCl₂ in s.t. at 140° for 18 hrs. (54% yield (3)) or with Cl₂ at 150-200° (accompanied by p-chlorobenzotrichloride (3:6825) (5)) see indic. refs.; for formn. of \tilde{C} (47% (6)) from benzal dichloride (3:6327) with Cl₂ in pres. of I₂ (6) (2) (accompanied by 5-7% o- and 43% m-isomers (6)) see indic. refs.]

[For use of C in prepn. of triphenylmethane dyes see (7).]

C on refluxing with aq. for 20 hrs. (1) or on htg. with aq. in s.t. at 170° (2) yields p-chlorobenzaldehyde (3:0765). [For studies of this hydrolysis under various other conditions see (4) (1).]

 \bar{C} on oxidn. with CrO₃ (2), or \bar{C} on refluxing with aq. for 20 hrs. followed by treatment with cold conc. aq. KMnO₄ (1), gives (85% yield (1)) p-chlorobenzoic acid (3:4940), m.p. 240° (1).

[For behavior of C with McMgCl see (8).]

3:6760 (1) Asinger, Lock, Monatsh. 62, 336 (1933). (2) Beilstein, Kuhlberg, Ann. 146, 327-329 (1868). (3) Pollak, Rudich, Monatsh. 43, 215-216 (1922). (4) Olivier, Weber, Rec. trav. chim. 53, 881, 888 (1934). (5) Gilliard, Monnet, Cartier, Ger. 98,433, Dec. 12, 1896, Cent. 1898, II 800. (6) Wertyporoch, Ann. 493, 161-162 (1932). (7) Weiler, Wenk, Stötter, Ger. 540,209, Dec. 12, 1931; Cent. 1932, I 3013. (8) Ellingboe, Fuson, J. Am. Chem. Soc. 55, 2964-2965 (1933).

—- 2,4-DICHLORO-3-METHYLPHENOL OH C₇H₆OCl₂ Beil. VI — VI₁— VI₂-(356)

B.P. 235-236° at 745 mm. M.P. 58-59°

See 3:1205. Division A: Solids.

B.P. 235–236°

M.P. 71-72°

See 3:1745. Division A: Solids.

3:6710 m-CHLOROBENZAL (DI)CHLORIDE C₇H₅Cl₃ Beil. S.N. 466 (m-Chlorobenzylidene dichloride) CHCl₂

B.P. 235-237° at 738 mm. (1) 105° at 11 mm. (1)

Colorless liq. with agreeable odor.

[For prepn. of \tilde{C} from m-chlorobenzaldehyde (3:6475) with PCl₅ (75% yield (1)) (2) see indic. refs.; for formn. of \tilde{C} from benzal dichloride (3:6327) with Cl₂ in pres. of I₂ (43% \tilde{C} together with 5-7% o- and 46% p-isomers) see (3).]

C on refluxing 20 hrs. with aq. then treated in cold with conc. aq. KMnO₄ gives (70% yield (1)) m-chlorobenzoic acid (3:4392), m.p. 158° (1).]

3:6710 (1) Asinger, Lock, *Monatsh.* **62**, 334-336 (1933). (2) Olivier, Weber, *Rec. trav. chim.* **53**, 882, 888 (1934). (3) Wertyporoch, *Ann.* **493**, 161-162 (1932).

3:6725-3:6735

$$\alpha,\alpha,\beta$$
-TRICHLORO- n -BUTYRIC ACID C₄H₅O₂Cl₃ Beil. II - 280 H Cl II₁-(124) CH₃-C COOH II₂-(255)

B.P. 236-238°

M.P. 60°

See 3:1280. Division A: Solids.

B.P. 235-240° (1)

[For prepn. of \tilde{C} from diisoamyl sulfide [Beil. I-405, I_1 -(200), I_2 -(435)] by actn. of Cl_2 see (1).]

 \bar{C} on htg. 7 hrs. at 110° in a s.t. with Ag₂O and aq. yields (1) CO₂ + isobutyric acid (1:1030) (as Ag \bar{A}).

3:6725 (1) Spring, Lecrenier, Bull. soc. chim. (2) 48, 627-628 (1887).

--- 3,5-DICHLOROBENZALDEHYDE C₇H₄OCl₂ Beil. S.N. 635

B.P. 235-240° at 748 mm.

M.P. 65°

See 3:1475. Division A: Solids.

3:6735 p-CHLOROACETOPHENONE

(<i>p</i> -	Chlorophenyl methyl ko	etone) Cl	C—CH ₃	VII ₁ -(151)
B.P.		M.P.	U	•
236.5°	cor. at 740 mm. (1)	20.5°	(10) (11) (12)	$D_{-}^{20} = 1.188 (2)$
232°	(2) (3) 20-21°	(5) (1)	
231-232°	(4) (17) 20°	(2)	
124-126°	at 24 mm. (5)	19.8°	(13)	
113°	at 14 mm. (3)	19°	(14)	
108-111°	at 13 mm. (6)	17.6-17.8°	(15)	
152°	at 12 mm. (7)			
99°	at 7 mm. (1)			
89.4-91°	at 5 mm. (8)			

C₈H₇OCl

Beil. VII - 281

Insol. aq.; misc. alc. or ether. — \bar{C} does not yield an addn. prod. with NaHSO₃. [For prepn. of \bar{C} from chlorobenzene (3:7903) with Ac₂O + AlCl₃ in CS₂ (yields: 83-79% (15), 78-74% (5), 68-66% (1)) (8) (9) or with acetyl chloride (3:7065) + AlCl₃ in absence

of solvent (poor yield (2)) or in CS_2 (yields: 80-90% (16), 81% (6), 41% (17)) see indicrefs.; from p-chlorobenzoylacetic acid on warming (18); from methyl p-chlorobenzoylacetate (4) on ketonic hydrolytic cleavage by boilg. 10-12 hrs. with 20% H₂SO₄ see (4).]

[Č in CS₂ treated with 1 mole Cl₂ yields (19) p-chlorophenacyl chloride (3:2990), m.p. 101°; Č with 2 moles Cl₂ at 50-60° without solv. (19) yields 4, ω , ω -trichloroacetophenone [Beil. VII-283], m.p. 57°. — Č with 1 mole Br₂ in CS₂ or AcOH yields (17) (20) p-chlorophenacyl bromide [Beil. VII-285], cryst. from alc., m.p. 96.5° (20), 96° (17) (for studies of rate of bromination see (13), of influence of light and other factors see (21)); Č with excess Br₂ directly (22), in AcOH (17), or in CCl₄ susp. of CaCO₃ (22) yields 4-chloro- ω , ω -dibromoacetophenone [Beil. VII-286], m.p. 93.5-94.5° (22), 92.5° (17).] [Note proximity of this m.p. to that (96°) of p-chlorophenacyl bromide (above).]

[\ddot{C} on monontration with mixt. of conc. $HNO_3 + conc.$ H_2SO_4 at -10° as directed (6) or added slowly to 10 pts. HNO_3 (D=1.5) at 0° (23) yields 4-chloro-3-nitroacetophenone, ndls. from alc., m.p. 104° (6), 99- 101° (23) (accompanied in the former case (6) by a little 4-chloro-3-nitrobenzoic acid, m.p. 181°).]

 \bar{C} in alk. medium readily condenses with aldehydes: e.g., \bar{C} in dil. alc. with a little alk. gives (yields: 96% (24), 93% (25), 83% (7)) benzal p-chloroacetophenone (p-chlorochalcone), cryst. from ether of CHCl₃, m.p. 101° (24), 98.5° (7), 96.4° (12), 96° (25) (for study of rate of condensation see (12)); similarly \bar{C} with salicylaldehyde (1:0205) yields (23) salicylidene-p-chloroacetophenone, yel. ndls. from alc., m.p. 151° (23); \bar{C} with p-dimethylaminobenzaldehyde yields (26) p-dimethylaminobenzal-p-chloroacetophenone, yel. ndls. from alc., m.p. 140-140.5° (26); for corresp. condensation of \bar{C} with p-chlorobenzaldehyde (3:0765) see (16), with o-nitrobenzaldehyde see (27) (28).

[$\bar{\mathbf{C}}$ also readily condenses with esters: e.g., $\bar{\mathbf{C}}$ in abs. alc. + NaOEt treated with ethyl formate (1:3000) gives (28) hydroxymethylene-p-chloroacetophenone, yel. ndls. from pet. eth., m.p. 48-49° (28); $\bar{\mathbf{C}}$ with ethyl phenylacetate (1:3872) in ether with Na gives (40% yield (29)) ω -(phenylacetyl)-p-chloroacetophenone.]

[\bar{C} with PCl₅ at 100° for 4 hrs. gives (60% yield (30)) p,α -dichlorostyrene, b.p. 115–116° at 20 mm., m.p. -6 to -5°, $D_{-}^{25} = 1.247$, $n_{D}^{25} = 1.5735$ (30); \bar{C} with selenium oxychloride (SeOCl₂) gives (50% yield (31)) bis-(p-chlorophenacyl)selenium dichloride, m.p. 126° (31); \bar{C} with K pyrosulfate + a little cone. H₂SO₄ htd. at 80° for 4 hrs. (46% yield (32)) or \bar{C} with 1% I₂ htd. 4 hrs. at 170° (32) gives 1,3,5-tris-(p-chlorophenyl)benzene, white ndls. from AcOEt, m.p. 238° (32); for behavior of \bar{C} with NOCl see (33) (14), with NaOEt + amyl nitrite in alc. see (34) (35).]

[$\bar{\mathbf{C}}$ htd. as directed with excess NH₄ formate and the intermediate formyl deriv. hydrolyzed with HCl gives (yields: 82% (36), 65% (37)) d, l- α -(p-chlorophenyl)ethylamine, b.p. 105° at 10 mm., $D_{20}^{20} = 1.1178$, $n_{D}^{25} = 1.5420$ (hydrochloride, m.p. 192–193°, N-benzoyl deriv., m.p. 144–145° (36)).]

[Č on htg. with 10% aq. NaOH + Cu at 190° for 5 hrs. under press. yields (38) p-hydroxy-acetophenone (1:1527), m.p. 109°; Č with conc. aq. NH₄OH in pres. of Cu₂O htd. 5 hrs. at 220° under press. yields (39) p-aminoacetophenone [Beil. XIV-46, XIV₁-(366)]; Č on htg. with 50% KOH as directed (40) gives small yield of p-chlorobenzoic acid. (3:4940); Č with alc. NaOEt htd. in s.t. at 130°-140° gives (41) p-chlorophenyl-methyl-carbinol, p-chlorobenzoic acid, and other prods.]

 \tilde{C} on oxidn. with KMnO₄ (2) or in MeOH soln. with NaOH + Cl₂ (93% yield (42)) or with CrO₃ + H₂SO₄ (95% yield (43)) or by cat. vapor-phase oxidn. (90% yield (44)) gives p-chlorobenzoic acid (3:4940), m.p. 242°. [Note that \tilde{C} in abs. alc. refluxed with SeO₂ gives (45) p-chlorophenylglyoxal, m.p. 122° (for study of rate see (46)).]

p-Chloroacetophenone oxime: ndls. from alc., m.p. 95° (17). [This prod. with conc.

- H_2SO_4 htd. at 100° rearranges to acet-p-chloroanilide [Beil. XII-611, XII₁-(306)], m.p. 172-173° (17).]
- p-Chloroacetophenone phenylhydrazone: m.p. 114° (17), 112-113° (48) (decomposes on stdg. 2 days (17) (4).)
- p-Chloroacetophenone p-nitrophenylhydrazone: maroon cryst. from AcOH, m.p.
 239° (4).
- p-Chloroacetophenone 2,4-dinitrophenylhydrazone: scarlet cryst., m.p. 231° cor. (47).
- p-Chloroacetophenone semicarbazone: white cryst. from 40% AcOH, m.p. 200-201° (4).
- 3:6735 (1) Noller, Adams, J. Am. Chem. Soc. 46, 1893 (1924). (2) Gautier, Ann. chim. (6) 14, 372-375 (1888). (3) Kahovec, Wagner, Proc. Indian Acad. Sci. A-8, 325 (1938). (4) Wahl, Rolland, Ann. chim. (10) 10, 27-31, 34-35 (1928). (5) Adams, Noller, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 111 (1941); (1st ed.), 105 (1932), 5, 19 (1925). (6) Mayer, Stark, Schön, Ber. 65, 1334 (1932). (7) Bergmann, Hampson, J. Chem. Soc. 1935, 991. (8) Groggins, U.S., 1,991,743, Feb. 19, 1935; Cent. 1936, I 883; C.A. 29, 2175 (1935). (9) Groggins, U.S. 2,008,418, July 16, 1935, Cent. 1936, I 1500; C.A. 29, 5856 (1935). (10) Hassel, Naeshagen, Z. physik. Chem. B-15, 419 (1932).
- (11) Evans, Morgan, Watson, J. Chem. Soc. 1935, 1172. (12) Coombs, Evans, J. Chem. Soc. 1949, 1295. (13) Nathan, Watson, J. Chem. Soc. 1933, 220. (14) Edkins, Linnell, Quart. J. Pharm. Pharmacol. 9, 75-109 (1936), Cent. 1937, I 4779, CA 30, 6349 (1936). (15) Groggins, Nagel, Ind. Eng. Chem. 26, 1316 (1934). (16) Straus, Ackermann, Ber. 42, 1812 (1909). (17) Collet, Bull. soc. chim. (3) 21, 68-70 (1899). (18) Throp, Brunskill, J. Am. Chem. Soc. 37, 1262 (1915). (19) Ref. 2, pp. 395-396, 402. (20) Judefind, Reid, J. Am. Chem. Soc. 42, 1044-1045 (1920).
- (21) Sampey, Hicks, J. Am. Chem. Soc. 63, 1098-1101 (1941).
 (22) Fisher, J. Am. Chem. Soc. 55, 4595 (1933).
 (23) C. G. LeFèvre, R. J. W. LeFèvre, J. Chem. Soc. 1932, 1989-1992.
 (24) Dilthey, J. prakt. Chem. (2) 101, 199 (1920).
 (25) Allen, Frame, Can J. Research 6, 605-613 (1932), Cent. 1932, II 3880, C.A. 26, 5086 (1932).
 (26) Pfeiffer, Kleu, Ber. 66, 1706 (1933).
 (27) Tanasescu, Baciu, Bull. soc. chim. (5) 4, 1748-1749; 1677-1678 (1937).
 (28) Benary, Ber. 61, 2253 (1928).
 (29) Kohler, Smith, J. Am. Chem. Soc. 44, 630 (1922).
 (30) Vaughn, Nieuwland, J. Am. Chem. Soc. 56, 1208 (1934).
- (31) Nelson, Jones, J. Am. Chem. Soc. 52, 1589 (1930). (32) Bernhauer, J. prakt. Chem. (2) 145, 305 (1936). (33) Rheinboldt, Schmitz-Dumont, Ann. 444, 129 (1925). (34) Avogadro, Gazz. chim. ttal. 53, 704-705 (1923). (35) Borsche, Ber. 62, 1365 (1929). (36) Ingersoll, Brown, Kim, Beauchamp, Jennings, J. Am. Chem. Soc. 58, 1810 (1936). (37) Ingersoll, Org. Syntheses, Coll. Vol. 2 (1st ed.), 505 (1943), 17, 78 (1937). (38) Britton (to Dow Chem. Co.), U.S. 1,961,630, April 10, 1934; Cent. 1934, II 1845; C.A. 28, 4744 (1934). (39) Britton, Bryner (to Dow Chem. Co.) U.S. 1,946,058; Feb. 6, 1934, Cent. 1934, I 3396; C.A. 28, 2364 (1934). (40) Lock, Böck, Ber. 70, 921 (1937).
- (41) Gastaldi, Cherchi, Gazz. chim. ital. 45, II 271-273 (1915). (42) von Arendonk, Cupery, J. Am. Chem. Soc. 53, 3184-3186 (1931). (43) Newton, Groggins, Ital. Eng. Chem. 27, 1397 (1935). (44) Stubbs, Sensemann, Ind. Eng. Chem. 28, 559-560 (1936). (45) Karrer, Musante, Helv. Chim. Acta 18, 1141-1142 (1935). (46) Mel'nikov, Rokitskaya, J. Gen. Chem. (U.S.S.R.) 10, 1439-1441 (1940); C.A. 35, 2400 (1941). (47) Allen, Richmond, J. Org. Chem. 2, 224 (1938). (48) Crowther, Mann, Purdiè, J. Chem. Soc. 1943, 67.

3	:6750 ETH	YL p-CHLOROBENZO	$\mathbf{ATE} \qquad \qquad \mathbf{C_9H_9O_2Cl}$	Beil. IX - 340
		•	Cl COOC ₂ H ₅	IX ₁ -(140)
	B.P.			
	238°	(1)	$D_4^{14.0} = 1.1873 (8)$	$n_{\rm D}^{14} = 1.52700 (8)$
	237.4-238.0)° (2)		
	142°	at 50 mm. (3)		
	121-122°	at 16 mm. (4)		
	122°	at 15 mm. (5)		
	120.1-120.2	e° at 15 mm. (2)		
	118°	at 15 mm. (6)		
	118°	at 14 mm. (7)		

[For prepn. of \bar{C} from p-chlorobenzoic acid (3:4940) with EtOH + H₂SO₄ see (1) (3); from p-chlorobenzoyl chloride (3:6550) with abs. EtOH see (2).]

 \bar{C} in alc. soln. on htg. with hydrazine hydrate yields (9) (10) p-chlorobenzhydrazide, white ndls. from alc., m.p. 162-163° (10). [This prod. with BzH yields benzal p-chlorobenzhydrazide, ndls. from 95% alc., m.p. 227-229° (10).] [For use of p-chlorobenzhydrazide as reagt. for identification of aldehydes and ketones see (10).]

[Č (1.5 moles) with NaOEt (0.3 mole) at 160-180° for 1 hr. gives (75% yield (15)) di-(p-chlorobenzoyl)methane, cryst. from MeOH, m.p. 158-159° (15).]

 \tilde{C} on hydrolysis (Sap. Eq. = 184.5) yields ethyl alcohol (1:6130) + p-chlorobenzoic acid (3:4940). [For studies of hydrolysis of \tilde{C} under various conditions see (7) (6) (11) (4) (12) (5) (13) (14).] For the amide, anilide, p-toluidide, and other derivs. corresp. to \tilde{C} see p-chlorobenzoic acid (3:4940).

3:6750 (1) van Raalte, Rec. trav. chim. 18, 398 (1899). (2) Kohlrausch, Stockmair, Monatsh. 66, 325 (1935). (3) Bergmann, Engel, Z. physik. Chem. B-15, 95 (1932). (4) Kındler, Ann. 456, 16 (1926). (5) Timm, Hinshelwood, J. Chem. Soc. 1938, 66-869. (6) Cashmore, McCombie, Scarborough, J. Chem. Soc. 121, 243-253 (1922). (7) McCombie, Scarborough, J. Chem. Soc. 107, 159 (1915). (8) von Auwers, Ann. 422, 166 (1921). (9) Kahl, Cent. 1904, II 1493. (10) Shih, Sah, Science Repts. Natl. Tsing-Hua Univ. A-2, 353-357 (1934); Cent. 1935, I 56-57; C.A. 29, 466 (1935).

(11) McCombie, Scarborough, Settle, J. Chem. Soc. 121, 2308-2318 (1922). (12) Blakey, McCombie, Scarborough, J. Chem. Soc. 1826, 2867. (13) Westheimer, J. Am. Chem. Soc. 62, 1893 (1940). (14) Price, Westheimer, J. Chem. Phys. 11, 150-153 (1943). (15) McElvain, Weber, J. Am. Chem. Soc. 63, 2196 (1941).

--- o-XYLYLENE (DI)CHLORIDE

CH₂Cl C₈H₈Cl₂ Beil. V - 364 V₁— V₂-(283)

B.P. 239-241° M.P. 55°

See 3:1040. Division A: Solids.

3:6770 ETHYL m-CHLOROBENZOATE $C_9H_9O_2Cl$ Beil. IX - 337 IX₁-(139)

B.P. $D_4^{15.4} = 1.1859 (7)$ $n_D^{15.4} = 1.52233 \ (7)$ 245° (1)] 239.3-241.7° (2) 130.0-130.5° at 20-21 mm. (3) 124° 21.5 mm. (4) at 20 mm. (5) 121° at 15 mm. (2) 114.6-116.2° at 119° 13 mm. (6)

[For prepn. of \bar{C} from m-chlorobenzoic acid (3:4392) with EtOH + H₂SO₄·(1) or with 5% EtOH/HCl (90% yield (8)) see indic. refs.; from m-chlorobenzoyl chloride (3:6590) with EtOH see (1) (2).]

[\tilde{C} on electrolytic reductn. in alc./ H_2SO_4 soln. yields (9) *m*-chlorobenzyl ethyl ether [Beil. VI-444], b.p. 219° (9).]

Č on refluxing with hydrazine hydrate gives (97% yield (8)) m-chlorobenzhydrazide, ndls. from aq. or alc., m.p. 158° (8), 157-158° (10). [This prod. in aq. soln. on htg. with BzH + a few drops AcOH yields benzal-m-chlorobenzhydrazide, flocks from alc., m.p. 118°

(8) (10).] [For study of prepn. and use of m-chlorobenzhydrazide as reagt. for identification of aldehydes and ketones see (10).]

 \tilde{C} on hydrolysis (Sap. Eq. = 184.5) yields ethyl alcohol (1:6130) + m-chlorobenzoic acid (3:4392). [For studies of hydrol. of \tilde{C} under various cond. see (6) (11) (5).] — For the amide, anilide, p-toluidide, and other derivs. corresp. to \tilde{C} see m-chlorobenzoic acid (3:4392).

3:6770 (1) Limpricht, von Uslar, Ann. 102, 262 (1857). (2) Kohlrausch, Stockmair, Monatsh. 66, 324 (1935). (3) Kindler, Ann. 450, 17 (1926). (4) Curtius, Melsbach, J. prakt. Chem. (2) 81, 536 (1910). (5) Evans, Gordon, Watson, J. Chem. Soc. 1937, 1430-1432. (6) McCombie, Scarborough, J. Chem. Soc. 107, 159 (1915). (7) von Auwers, Ann. 422, 166 (1921). (8) Curtius, Foerster, J. prakt. Chem. (2) 64, 326-328 (1901). (9) Mettler, Ber. 37, 3693 (1904). (10) Sah, Wu, Science Repts. Natl. Tsing-Hua Univ. A-3, 443-449 (1936); Cent. 1936, II 2130; C.A. 38, 8148 (1936).

(11) Blakey, McCombie, Scarborough, J. Chem. Soc. 1926, 2867.

3:6775
$$\gamma$$
-CHLORO- β -HYDROXY- n -PROPYL ACETATE $C_5H_9O_3Cl$ Beil. II - 142 (Glycerol α -chlorohydrin CH2Cl II_1-(67) α' -acetate; γ -aceto- α -chlorohydrin; γ -chloropropylene glycol α -acetate) H—C—OH

CH2O.CO.CH4

[See also glycerol α -chlorohydrin β -acetate (3:6517).]

[For prepn. of \bar{C} from epichlorohydrin (3:5358) with AcOH in s.t. at 180° for 24 hrs. (1) (2) or in pres. of anhydr. FeCl₃ at room temp. (4) cf. (5); note, however, that the isomeric glycerol α -chlorohydrin β -acetate (3:6517) is also formed.]

Note that the homogeneity of all reported prepns of \tilde{C} is probably open to serious question.

3:6775 (1) Reboul, Ann. Suppl. 1, 232 (1861). (2) Bigot, Ann. chim. (6) 22, 491 (1891). (3) Gibson, J. Soc. Chem. Ind. 50, 950 (1931). (4) Knoevenagel, Ann. 402, 136-138 (1914). (5) Delaby, Dubois, Bull. soc. chim. (4) 47, 573 (1930).

3:6780
$$\beta$$
-HYDROXYETHYL CHLOROACETATE $C_4H_7O_3Cl$ Beil. S.N. 160 (Ethylene glycol mono-(chloroacetate)) $CH_2.CO.O.CH_2.CH_2$ Cl OH

B.P.			
240° d	ec. at 760 mm. (1)	$D_4^{20} = 1.330 (2)$	$n_{\rm D}^{25} = 1.4585 (1)$
86°	at 1.6 mm. (2)	1.324 (2)	
85°	at 0.15 mm. (1)		$n_{\rm D}^{20} = 1.46090 (2)$
84°	at 0.95 mm. (2)		1.46049 (2)
83°	at 0.08 mm. (1)		

Colorless odorless liq. — Miscible with aq. [dif. from ethylene glycol bis-(chloroacetate) (3:0720)].

[For prepn. of C from ethylene oxide (1:6105) with chloroacetic acid (3:1370) in dry ether at 0° for 4 days (1) or at 50° for 6 days (2) see indic. refs.; from mono-sodium deriv. of ethylene glycol (1:6465) (1) or from ethylene glycol directly with chloroacetyl chloride (3:5235) in dry ether (1) or dioxane (2) see indic. refs.]

C on stdg. in ord. glass gradually disproportionates into ethylene glycol (1:6105) and

ethylene glycol bis-(chloroacetate) (3:0720) (1); this disproportionation may also occur during reactions of C and thus lead to numerous by-prods. (see below).

[\bar{C} with diazomethane gives (19% yield (1)) β -methoxyethyl chloroacetate (3:9285) accompanied by methyl chloroacetate (3:5585) and ethylene glycol bis-(chloroacetate) (3:0720).]

Č on long stdg. with aq. is slowly hydrolyzed into ethylene glycol (1:6465) and chloro-acetic acid (3:1370) (2).

3:6780 (1) Allen, Hibbert, J. Am. Chem. Soc. **56**, 1398-1399 (1934). (2) Meerwein, Sonke, J. prakt. Chem. (2) **137**, 316-319 (1933).

3:6790 DI-
$$(\beta$$
-CHLOROETHYL) CARBONATE $C_5H_8O_3Cl_2$ Beil. III — $(\beta,\beta'$ -Dichloroethyl $Cl.CH_2CH_2O$ CO III_1 — III_2 — III

B.P. M.P. 240-241° (1)
$$+8.5$$
° (1) $D_4^{20} = 1.3506$ (1) $n_D^{20} = 1.4610$ (1) 115° at 8 mm. (1)

Colorless odorless liq. — Insol. in boil. aq. and not decomposed thereby. — Volatile with steam $\{1\}$. — Requires solid CO_2 + ether for solidification.

[For prepn. from β -chloroethyl chloroformate (3:5780) + ethylene chlorohydrin (3:5552) (70% yield) see (1).]

Hydrolyzes, but very slowly, even with warm alk. (1).

[For use as industrial solvent see (2) (3).]

3:6790 (1) Nekrassow, Komissarow, J. prakt. Chem. (2) **123**, 164 (1929). (2) I.G., French 785,705, Aug. 17, 1935; Cent. **1936**, I 1134. (3) I.G., Brit. 257,258, Aug. 11, 1926; Cent. **1927**, I 820.

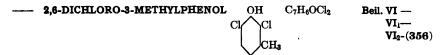
3:6795 3,4-DICHLOROBENZYL CHLORIDE
$$C_7H_5Cl_3$$
 Beil. V - 300 Cl CH_2Cl V_1 V_2

B.P. 241° (1)

[For prepn. of \bar{C} from 3,4-dichlorotoluene (3:6355) at b.p. or from benzyl chloride (3:8535) in pres. of I_2 on treatment with Cl_2 see (1).]

C on oxidn. with CrO₃ yields (2) 3,4-dichlorobenzoic acid (3:4925) q.v.

3:6795 (1) Beilstein, Kuhlberg, *Ann.* **146**, 326–327 (1868). (2) Beilstein, Kuhlberg, *Ann.* **152**, 224–226 (1869).



B.P. 241° M.P. 27°

See 3:0150. Division A: Solids.

B.P. 242.7–244.1°	at 760 mm. (1)
242-243°	at 733 mm. (2) (3)
148°	at 24 mm. (4)
122-123°	at 16 mm. (5)
123-125°	at 15 mm. (6)
123°	at 11 mm. (1)
110.8-111.0°	at 8.5 mm. (7)
81.5-82.0°	at 1 mm. (8)

[For prepn. of C from m-methoxybenzoic acid (1:0703) with PCl₅ (2) or with SOCl₂ (yields: 92% (6), 86% (4), 78% (5)) (1) (7) see indic. refs.]

[Although 2-methoxybenzoyl chloride (3:6870) with anhydrous Na₂CO₃ + pyridine gives the corresp. anhydride, this reactn. is not specifically recorded for \bar{C} ; however, 3-methoxybenzoic acid anhydride, cryst. from pet. eth., m.p. 66.6° (9), has been reported from 3-methoxybenzoic acid (1:0703) with P₂O₅ (9).]

[\bar{C} with C_6H_6 + AlCl₃ (2) (said to be unsatisfactory because of autocondensation of \bar{C} to anthracene derivs. (3)) or better with C_6H_5ZnBr (62% yield (6)) yields 3-methoxybenzophenone (1:5141), m.p. 37° (6) (2), b.p. 342-343° at 730 mm. (2), 192° at 14 mm. (6). — \bar{C} with anisole (1:7445) + AlCl₃ in CS₂ (3) or in tetrachloroethane (5) gives (yields: 100% (5), 35% (3)) 3,4-dimethoxybenzophenone, pr. from alc., m.p. 58-59° (5), 55° (3).]

[\bar{C} with ethyl sodioacetoacetate gives (61% yield (4) (10) ethyl m-methoxybenzoylacetoacetate; \bar{C} with methyl sodio- α -ethylacetoacetate gives (10) methyl α -ethyl- α -(m-methoxybenzoyl)acetoacetate; \bar{C} with ethyl sodio- α , γ -dimethoxyacetoacetate gives (11) ethyl α , γ -dimethoxy- α -(m-methoxybenzoyl)acetoacetate (for ketonic cleavage of these substacetoacetates see indic. refs.).]

[For reactn. of C with 1,4-diaminoanthraquinone in prepn. of vat dyes see (12) (13).]

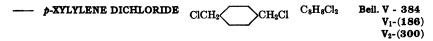
 $[\bar{C}]$ with MeOH yields methyl m-methoxybenzoate (1:4111), b.p. 252°; \bar{C} with EtOH yields ethyl m-methoxybenzoate (1:4131), b.p. 260° (for study of rate of reactn. of \bar{C} with EtOH at 0° see (14) (8)).]

C on hydrolysis yields m-methoxybenzoic acid (1:0703), m.p. 109-110°.

3:6797 (1) Kahovec, Kohlrausch, Z. physik. Chem. B-38, 136 (1938). (2) Ullmann, Goldberg, Ber. 35, 2813-2814 (1902). (3) Lea, Robinson, J. Chem. Soc. 1926, 2354-2355. (4) Robinson, Rose, J. Chem. Soc. 1933, 1472. (5) Blicke, Weinkauff, J. Am. Chem. Soc. 54, 1449 (1932). (6) Martynoff, Ann. chim. (11) 7, 437-438 (1937). (7) Thompson, Norris, J. Am. Chem. Soc. 58, 1956 (1936). (8) Norris, Young, J. Am. Chem. Soc. 57, 1424 (1936). (9) Rule, Patterson, J. Chem. Soc. 125, 2161-2162. (10) Furukawa, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 24, 320-324 (1934); Cent. 1935, I 1071.

(11) Pratt, Robinson, J. Chem. Soc. 127, 1185 (1925). (12) I.G., Swiss 136,249, Jan. 16, 1930; Cent. 1930, II 3462. (13) B.A.S.F., French 604,347, May 3, 1926; Cent. 1926, II 2358. (14)

Norris, Fasce, Staud, J. Am. Chem. Soc. 57, 1415-1420 (1935).



B.P. 240-245° dec.

M.P. 100°

122.5°

3:6800 ETHYL o-CHLOROBENZOATE
$$C_9H_9O_2Cl$$
 Beil. IX - 336 IX_1 —

B.P. 242.8-244.0° (1) $D_4^{15.4} = 1.1942$ (9) $n_D^{15.4} = 1.52470$ (9) 243° (2) (3) 242° (4) 238-242° (5) 130° at 20 mm. (6) 124.8-125.1° at 20 mm. (1)

[For prepn. of \bar{C} from o-chlorobenzoic acid (3:4150) with EtOH + HCl see (2); from o-chlorobenzoyl chloride (3:6640) with abs. EtOH see (5) (1).]

at 15 mm. (7) (8)

[C on electrolytic reductn. in alc./H₂SO₄ soln. yields (10) mainly o-chlorobenzyl ethyl ether [Beil. VI-444; VI₁-(222)], b.p. 212° (10), together with a little o-chlorobenzyl alc. [Beil. VI-444; VI₁-(222)], ndls. from dil. alc., m.p. 72° (10).]

[$\bar{\mathbf{C}}$ with C_6H_5MgBr in ether as directed (11) yields α,α' -bis-(o-chlorophenyl)- α,α' -diphenyl-ethylene glycol (sym.-2,2'-dichlorobenzpinacol) [Beil. VI₁-(523)].]

Č in alc. on refluxing with hydrazine hydrate yields (14) (15) o-chlorobenzhydrazide, white ndls. from alc., m.p. 117-118° (15), 109-110° (14). [This prod. with BzH yields benzal-o-chlorobenzhydrazide, white ndls. from 95% alc., m.p. 162° (15).] [For use of o-chlorobenzhydrazide as reagt. for identification of aldehydes and ketones see (15).]

 \tilde{C} on hydrolysis (Sap. Eq. = 184.5) yields ethyl alcohol (1:6130) + o-chlorobenzoic acid (3:4150). [For studies of hydrolysis of \tilde{C} under various conditions see (7) (8) (12) (13) (6).] — For the amide, anilide, p-toluidide, and other derivs. corresp. to \tilde{C} see o-chlorobenzoic acid (3:4150).

8:6800 (1) Kohlrausch, Stockmair, Monatsh. 66, 324 (1935). (2) Glutz, Ann. 143, 196 (1867).
 (3) Kindler, Ann. 464, 287 (1928). (4) Vavon, Barbier, Thiebaut, Bull. soc. chim. (5) 1, 813 (1934). (5) Kekulé, Ann. 117, 163-154 (1861). (6) Evans, Gordon, Watson, J. Chem. Soc. 1937, 1430-1432. (7) McCombie, Scarborough, J. Chem. Soc. 107, 159 (1915). (8) Cashmore, McCombie, Scarborough, J. Chem. Soc. 121, 249 (1922). (9) von Auwers, Ann. 422, 166 (1921). (10) Mettler, Ber. 37, 3696 (1904).

(11) Hatt, J. Chem. Soc. 1929, 1628. (12) McCombie, Scarborough, Settle, J. Chem. Soc. 121, 2314 (1922). (13) Blakey, McCombie, Scarborough, J. Chem. Soc. 1926, 2867. (14) Kalb, Gross, Ber. 59, 732 (1926). (15) Sun, Sah, Science Repts. Natl. Tsing Hua Univ. A-2, 359-363 (1934); Cent. 1935, I 57; C.A. 29, 466 (1935).

--- 1,2,4,5-TETRACHLOROBENZENE Cl
$$C_6H_2Cl_4$$
 Beil. V - 205 V_1 -(113) V_2 -(157)

B.P. 243-246° cor. M.P. 141°

See 3:4115. Division A: Solids.

--- 1,2,3,5-TETRACHLOROBENZENE Cl
$$C_6H_2Cl_4$$
 Beil. V - 204 V_1 -(113) V_2 -(157)

B.P. 246° cor. M.P. 51° See 3:0915. Division A: Solids.

227-229° (2)

127-131° at 30 mm. (3)

at 11 mm. (4) 113°

Colorless liq. with aromatic odor. — Volatile with steam.

[For prepn. of C from m-chlorophenyl-phenyl-carbinol (2) by oxidn. with CrO₃/AcOH (90% yield) see (2); from m-aminoacetophenone [Beil. XIV-45, XIV₁-(365)] via diazotization and use of Cu₂Cl₂ reactn. (45% yield (4)) see (4) (3); from methyl m-chlorobenzoylacetate (2) by hydrolysis with 20% H₂SO₄ for 12 hrs. (65% yield) see (2).]

[For study of rate of reactn. with Br2 see (4).]

C on htg. with 50% KOH as directed (1) gives 14% yield m-chlorobenzoic acid (3:4392).

- m-Chloroacetophenone oxime: cryst. from AcOH, m.p. 88° (2) (1).
- D m-Chloroacetophenone p-nitrophenylhydrazone: maroon cryst. from AcOH, m.p. 175-176° (2). (The phenylhydrazone of C is unstable (2).)
- m-Chloroacetophenone semicarbazone: cryst. from alc., m.p. 232° (3).

3:6815 (1) Lock, Böck, Ber. 70, 920-921 (1937). (2) Wahl, Rolland, Ann. chim. (10) 10, 29-30 (1928). (3) Edkins, Linnell, Quart. J. Pharm. Pharmacol. 9 75-109; Cent. 1937, I 4780; C.A. 30, 6349 (1936). (4) Evans, Morgan, Watson, J. Chem. Soc. 1935, 1172.

[For prepn. of \bar{C} from p-hydroxybenzoic acid (1:0840) (3) (or the "p-hydroxybenzid" [Beil. X-154] obtd. from it by htg. (4)) with PCl₅ see indic. refs.; from p-toluenesulfonyl chloride [Beil, XI-103, XI₁-(26)] with Cl₂ at 150-200° see (5); from p-chlorotoluene (3:8287) with Cl₂ at high temp. in u.v. light see (2); for formn. of C (together with other products) from benzotrichloride (3:6540) with Cl2 under various circumstances see (1) (6) (7); for purification of C see (8).]

[For use of C with NaOAc in prepn. of acetic anhydride see (9); for use of C htd. with p-chlorobenzoic acid (3:4940) + ZnCl₂ + FeCl₃ in prepn. of p-chlorobenzoyl chloride (3:6550) see (10); for use of \bar{C} with dichloroacetic acid $(3:6208) + H_2SO_4$ in prepn. of a mixt. of p-chlorobenzovl chloride (3:6550) and dichloroacetyl chloride (3:5290) see (11).

[For condens. of C with 1-hydroxynaphthoic acid-2 [Beil. X-331, X₁-(144)] in prepn. of dyestuff intermediates see (12); for react. of \bar{C} with α -naphthol (1:1500) to yield 1-hydroxy-4-(p-chlorobenzoyl)naphthalene see (13).]

[C htd. with 99% HF (14) (15) or with 2SbF₃.NH₄HF₂ at 150-160° (16) gives (86% yield (14)) p-chlorobenzotrifluoride, b.p. 137-138° (15).]

Č on hydrolysis, e.g., by htg. with aq. in s.t. at 200° (1), yields p-chlorobenzoic acid (3:4940) q.v.

3:6825 (1) Beilstein, Kuhlberg, Ann. 150, 295-296 (1869). (2) Maryott, Hobbs, Gross, J. Am. Chem. Soc. 62, 2321 (1940). (3) Anschütz, Moore, Ann. 239, 346-348 (1887). (4) Klepl, J. prakt. Chem. (2) 28, 204-205 (1883). (5) Gilliard, Monnet, Cartier, Ger. 98,433, Dec. 12, 1896; Cent. 1898, II 800. (6) Spreckels, Ber. 52, 319 (1919). (7) Wertyporoch, Ann. 493, 157-161 (1932). (8) Britton (to Dow Chem. Co.), U.S. 1,804,458, May 12, 1931; Cent. 1931, II 497; C.A. 25, 3668 (1931). (9) Dr. A. Wacker Ges. fur Elektrochem. Ind., Kaufler, Hormann, Brit. 165,747, June 30, 1921; Cent. 1922, II 1218. (10) Scottish Dyes, Ltd., Bangham, Thomas, Brit. 308,231, April 18, 1929; Cent. 1929, II 1348.

(11) Mills (to Dow Chem. Co.), U.S. 1,965,556, July 3, 1934; Cent. 1934, II 2899; C.A. 28, 5474 (1934). (12) Soc. Chem. Ind. Basel, Ger. 355,115, June 21, 1922; Swiss 92,406, Feb. 16, 1923; Cent. 1923, II 484. (13) Soc. Chem. Ind. Basel, Ger. 418,033, Aug. 26, 1925; Cent. 1925, II 2095. (14) Osswald, Muller, Steinhauser (to I.G.), Ger. 575,593, May 22, 1933; Cent. 1933, II 609. (15) I.G., French 745,293, May 8, 1933; Cent. 1933, II 2061. (16) I.G., French 809,301, March 1, 1937; Cent. 1937, I 4863; C.A. 31, 6675 (1937).

3:6835 ω,ω-DICHLOROACETO		8H6OCl2	Beil. VII - 282
		CO.CHCl ₂	VII ₁ -(152)
B.P.	M.P.		
245° at 760 mm. (1)	20-21.5°	(7)	
247-248° dec. (2)	19°	(2)	
249° (3)	Not frozen at -10°	(1)	
143° at 25 mm. (2)			
142-144° at 25 mm. (11)			
138-140° at 13 mm. (5)			
132-134° at 13 mm. (11)			
131-132° at 11 mm. (6)			
128-129° at 14 mm. (4)			
121-122° at 10 mm. (1)			

Lachrymatory oil.

[For prepn. from acetophenone (1:5515) by actn. of Cl₂ (100% yield (4) (8)) in AcOH (80-94% yield (11)) see (4) (2) (11) or of sulfuryl chloride see (1); from phenylacetylene (1:7425) by actn. of HOCl (7), CH₃OCl (6), or C₂H₅OCl (5) see (7) (6) (5); from C₆H₆ + dichloroacetyl chloride (3:5290) (2) or dichloroacetonitrile (4) + AlCl₃ see (2) (4).]

 \bar{C} is almost unchanged by boiling with aq. (2). — \bar{C} on shaking with 20 pts. 2 N aq. NaOH dissolves in 1–2 min.; after boiling under reflux for a few min. and acidifying, extraction with ether gives in 95% yield (8) 85–90% yield (11) d,l-mandelic ac. (1:0465), cryst. from CHCl₃ + pet. eth., m.p. 118.5° (8).

 \tilde{C} on oxidn. with alk. KMnO₄ yields (1) (2) (3) (5) (6) benzoic ac. (1:0715), m.p. 121°. [\tilde{C} on treatment with NaOH + NaOCl in the cold yields benzoic ac. (1:0715) and chloroform in proportions depending upon conditions (9).] [Note that d,l-mandelic ac. (see above) may also be formed owing to actn. of alk. upon \tilde{C} cf. (9).]

 \bar{C} on nitration yields m-nitro- ω , ω -dichloroacetophenone, m.p. 57-58° (10).

Č in alc. treated with excess alk. NH₂OH for 7-10 hrs. yields (6) phenylglyoxaldioxime [Beil. VII-672], cryst. from CHCl₃, m.p. 168° (6). [The product, m.p. 150-152°, so obtd. by (5) may have been a mixt. of the high-melting stereoisomer, m.p. 180°, with the low-melting stereoisomer. m.p. 168°.]

3:6835 (1) Durrans, J. Chem. Soc. 121, 46 (1922). (2) Gautier, Ann. chim. (6) 14, 345-347, 385-387 (1888). (3) Béhal, Bull. soc. chim. (2) 50, 634 (1888). (4) Houben, Fischer, Ber. 64, 2647-2648 (1931). (5) Goldschmidt, Endres, Dirsch, Ber. 58, 575-576 (1925). (6) Jackson, J. Am. Chem. Soc. 56, 977-978 (1934). (7) Wittorf, J. Russ. Phys.-Chem. Soc. 32, 88-117 (1900); Cent. 1900, II 30. (8) Houben, Fischer, Ber. 64, 2644-2645 (1931). (9) Aston, Newkirk, Dorsky, Jenkins, J. Am. Chem. Soc. 64, 1413-1416 (1942). (10) Rabcewicz-Zubkowsi, Roczniki Chem. 9, 532-537 (1929); C.A. 24, 92 (1930).

(11) Aston, Newkirk, Jenkins, Dorsky, Org. Syntheses 23, 48-51 (1943).

3:6840	3-CHLOROPROPANEDIOL-1,2 DIACETATE	C ₇ H ₁₁ O ₄ Cl	Beil. II - 142
	(γ-Chloropropylene glycol diacetate,	CH ₂ Cl	II ₁ -(67)
•	glycerol a-monochlorohydrin diacetate, "a-monochlorohydrin" diacetate)	нс-ооссиз	П2
		CH2OOCCH3	

B.P.								
245°	at	740	mm.	(1)	$D_4^{25} = 1.199 (5)$	$n_{ m D}^{25}$:	= 1.4386 (5)
145-150°	at	40	mm.	(2)				
142-149°	at	40	mm.	(3)		$n_{ m D}^{20}$	= 1.4407 (8)
116°	at	12	mm.	(4)				
116-118°	at	11	mm.	(10)				
115-117°	at	10	mm.	(5)				
113-114°	at	9	mm.	(6)				
102-105°	at	6	mm.	(7)				
96.5-97°	at	0.	4-0.6 mm.	. (7)				
90-91°	at	0.	8 mm.	(8)				

[For prepn. of \bar{C} from glycerol α -monochlorohydrin (3:9038) with Ac₂O (1:1015) (75% yield (6)) cf. (9) in pres. of a trace of H₂SO₄ (100% yield (4)) see indic. refs.; from epichlorohydrin (3:5358) with Ac₂O (1:1015) at 180° (1) (5) or in pres. of anhydrous FeCl₃ at ord. temp. (10) see indic. refs.; from 3-hydroxy-1,2-epoxypropane (glycidol) with large excess AcCl (3:7065) on htg. as directed (69% yield (7)) or from glyceryl-glycidol with AcCl (3:7065) at 60° for 2 hrs. (37% yield (8)) see indic. refs.]

[For prepn. of \tilde{C} from glycerol (1:6540) with AcOH + HCl see (11); from glyceryl α,α' -diacetate with Ac₂O + HCl see (3); from glyceryl triacetate (triacetin) in dry ether at 0° with HCl gas (2) (3) cf. (4) see indic. refs.]

[\bar{C} in MeOH contg. 1% HCl at 60° for 6 hrs. gives (80% yield (8)) 3-chloropropanediol-1.2 (glycerol α -monochlorohydrin) (3:9038).]

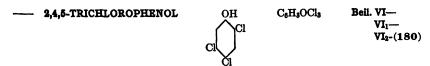
3:6840 (1) Truchot, Compt. rend. 61, 1170 (1865); Ann. 138, 299 (1866). (2) de la Acena, Compt. rend. 139, 868 (1904). (3) Seelig, Ber. 24, 3469-3471 (1891). (4) Wegscheider, Zmerzlikar, Monatsh. 34, 1068-1071 (1913). (5) Gibson, J. Soc. Chem. Ind. 50, 949-954 (1931). (6) Nivière, Compt. rend. 156, 1777 (1913); Bull. soc. chim. (4) 15, 82-83 (1914). (7) Rider, J. Am. Chem. Soc. 54, 775 (1932). (8) Sjöberg, Svensk Kem. Tid. 53, 454-457 (1941); Cent. 1942, II 25; C.A. 37, 4363 (1943). (9) Abderhalden, Eichwald, Ber. 47, 1859 (1914). (10) Knoevenagel, Ann. 402, 135-136 (1914).

(11) Berthelot, de Luca, Ann. chim. (3) 52, 461 (1858).)

--- 3,4,5-TRICHLOROTOLUENE CH₃ C₇H₅Cl₃ Beil. V - 299
V₁--- V₂---

B.P. 245.5-247° at 768 mm. M.P. 44.5-45.5°

See 3:0580. Division A: Solids.



B.P. 244-248° at 746 mm.

M.P. 67-68°

See 3:1620. Division A: Solids.

--- 1,1,1,2,2,3,3-HEPTACHLOROPROPANE C_3HCl_7 Beil. I - 108 I_{1-} (35) I_{1-} (35) I_{2-} (73) I_{2-} (73) I_{2-} (73) Beil. Beil. I - 108 I_{3-} (73) I_{3-} (74) I_{3-} (74) I_{3-} (75) $I_$

See 3:0200. Division A: Solids.

3,4-DICHLOROBENZALDEHYDE $C_7H_4OCl_2$ Beil. VII - 238 VII_1 -(134)

B.P. 247-248°

M.P. 43-44°

See 3:0550. Division A: Solids.

3:6845 m-CHLOROBENZOTRICHLORIDE C₇H₄Cl₄ Beil. V -303 V₁— V₂—

B.P. 247-250° (1)

[For prepn. from m-hydroxybenzoic acid (1:0825) (1) or from m-sulfobenzoic acid [Beil. XI-384, XI₁-(98)] (2) with PCl₅ see indic. refs.; for studies on formn. of \bar{C} from benzotrichloride (3:6540) with Cl₂ see (3) (4); for purification of \bar{C} see (5).]

[For condens. of C with 1-hydroxynaphthoic acid-2 [Beil. X-331, XI₁-(144)] in prepn. of dyestuff intermediates see (6).]

C on hydrolysis presumably yields m-chlorobenzoic acid (3:4392) q.v.

3:6845 (1) Anschütz, Moore, Ann. 239, 342 (1887). (2) Kämmerer, Carius, Ann. 131, 158 (1864). (3) Wertyporoch, Ann. 493, 157-161 (1932). (4) Spreckels, Ber. 52, 319 (1919). (5) Britton (to Dow Chem. Co.), U.S. 1,804,458, May 12, 1931; Cent. 1931, II 497; C.A. 25, 3668 (1931). (6) Soc. Chem. Ind. Basel, Ger. 355,115, June 21, 1922; Swiss, 92,406, Feb. 16, 1923; Cent. 1923, II 484.

249° (1) 11-11.5° (1) $D_4^{34} = 1.7921$ (1) 165° at 90 mm. (1) $n_D^{21} = 1.5427$ (1) 126-132° at 20 mm. (2)

Oil with disagreeable odor.

[For prepn. from trichloroethylene $(3:5170) + CCl_4 + AlCl_3$ (49% yield (2)) by stdg. 48 hrs. at 20-30° (2) see (2) (1).]

Č dislvd. in CCl₄ and heated at 60-70° with AlCl₃ evolves HCl and gives (83% yield (3)) hexachloropropene (3:6370).

Č in alc. on titration with alk. gives (3) an apparent Neut. Eq. of 285.5 by loss of 1 HCl and formation of hexachloropropene (3:6370).

3:6860 (1) Prins, J. prakt. Chem. (2) 89, 417 (1914). (2) Henne, Ladd, J. Am. Chem. Soc. 60, 2494-2495 (1938). (3) Prins, Rec. trav. chim. 54, 251 (1935).

3:6864 DIETHYL CHLOROFUMARATE
$$C_8H_{11}O_4CI$$
 Beil. II - 745 $CI-C-COOC_2H_5$ II₁-(302) II_2 -(640)

B.P. 250° at 760 mm., sl. dec. (1) $D_-^{24} = 1.19517$ (7) $n_D^{24} = 1.4598$ (7) 243-245° u.c. at 735 mm. (10) 202-203° at 210 mm. (1) $D_4^{20} = 1.188$ (8) $n_D^{20} = 1.4571$ (8) 136.5° cor. at 19 mm. (2) 1.187 (8) 1.4564 (8) 135-136° at 17 mm. (8) 1.183 (4) 127° at 10 mm. (3) 119° at 12 mm. (4) $D_4^{18.3} = 1.1890$ (8) $n_D^{18.3} = 1.45782$ (8) 117° at 7 mm. (5) 108° at 15 mm. (6) $D_4^{18.2} = 1.1903$ (8) $n_D^{18.2} = 1.45723$ (8) $D_4^{16.3} = 1.1822$ (4) $n_{He}^{16.3} = 1.45979$ (4)

[See also diethyl chloromaleate (3:6697).]

Colorless liq. with irritating actn. on skin and whose vapor strongly attacks the eyes. — Insol. cold aq., eas. sol. alc., ether; volatile with steam.

[For prepn. of \bar{C} from chlorofumaric acid (3:4853) in abs. EtOH with HCl gas (1) or conc. H₂SO₄ (4) see indic. refs.; from chlorofumaryl (di)chloride (3:6105) with EtOH see (10) (1) (9) (3).]

[For form. of \tilde{C} from diethyl d-tartrate (1:4256) with PCl₅ see (11) (note that ethyl hydrogen chlorofumarate, cryst. from pet. ether, m.p. $52-53^{\circ}$, has also been obtd. (12) as one of the prods. of this reactn.); from diethyl $d,l(?)-\alpha,\alpha$ -dichlorosuccinate by loss of HCl under actn. of dimethylaniline see (5).]

 $[\bar{C}\ (1\ mole)\)$ with diethyl sodio-malonate (1 mole) is said (13) to yield tetraethyl cyclopropane-1,1,2,3-tetracarboxylate [Beil. IX-991] although no details are given; in the presence of excess NaOEt in cold alc. for 12 hrs., however, the same components give (15-20% yield (14)) (15) triethyl γ -carbethoxyaconitate [Beil. II-876], b.p. 205-207° at 16 mm. (14); for reactn. of $\bar{C}\ (1\ mole)$ with diethyl mono- and di-substituted malonates yielding triethyl corresp. subst. aconitates see (13). — $\bar{C}\ (1\ mole)$ with ethyl sodioaceto-acetate (1 mole) in abs. alc. refluxed for ½ hr. gives (72% yield (3)) (16) triethyl γ -acetylaconitate [Beil. III-860], yel. oil, b.p. 187-188° at 15 mm. (3), the same as similarly obtd. (3) from diethyl chloromaleate (3:6697).]

[\bar{C} with o-chlorophenol (3:5980) or its Na deriv. in boilg. xylene for 2 hrs. gives (77% yield (17)) diethyl o-chlorophenoxyfumarate, b.p. 203-204° at 14 mm. (17). — \bar{C} with p-chlorophenol (3:0475) + NaOEt gives (17) diethyl p-chlorophenoxyfumarate, b.p. 199-200° at 12 mm. (17).]

The reactn. of C with NH₃ under various circumstances is disputed and confused and cannot profitably be discussed here; for refs. see Beil. II-745.

Č (1 mole) with hydrazine hydrate (2 moles) directly (18) or in alc. or AcOH (9) yields ethyl pyrazolone-5 (or 3)-carboxylate-3 (or 5) [Beil. XXV-206, XXV₁-(567)], ndls. from boilg. aq., m.p. 184-185° (18); 178° (9); note that in the direct treatment with just 2 moles of hydrazine hydrate much heat is evolved and the product ppts. on cooling; if excess base is employed (in which the prod. is soluble) neutralization with acid is necessary.

[Č with phenylhydrazine reacts much more slowly; however, after several hrs. at 100° phenylhydrazine HCl ppts. leaving an oil from which a cryst. prod. spar. sol. in boilg. AcOH but sepg. from it in colorless ndls., m.p. 272° dec., can be obtd. (18); this prod. is not, however, the ethyl 1-phenylpyrazolone-5(or 3)-carboxylate-3(or 5) which might be expected, but is regarded [Beil. XXVI-578] (18) as a 4,4'-bis derivative of it.

C on boilg, with 1:1 HCl and subsequent evapn, to dryness undergoes hydrolysis yielding (4) chlorofumaric acid (3:4853), m.p. 191.5° (4).

3:6864 (1) Perkin, J. Chem. Soc. 53, 700-703 (1888). (2) Walden, Swinne, Z. physik. Chem. 79, 742 (1912). (3) Ruhemann, Tyler, J. Chem. Soc. 69, 532-535 (1896). (4) von Auwers, Harres, Ber. 62, 1679, 1685-1687 (1929). (5) Darzens, Sejourne, Compt. rend. 154, 1617 (1912). (6) von Auwers, Harres, Z. physik. Chem. A-143, 10 (1929). (7) Gladstone, J. Chem. Soc. 59, 293 (1891). (8) von Auwers, Schmidt, Ber. 46, 481 (1913). (9) Ruggli, Hartmann, Helv. Chim. Acta 3, 513 (1920). (10) Claus, Ann. 191, 80-93 (1878).

(11) Henry, Ann. 156, 178-179 (1870).
(12) Patterson, Todd, J. Chem. Soc. 1929, 1768-1770.
(13) Ruhemann, J. Chem. Soc. 81, 1212-1214 (1902).
(14) Desai, J. Chem. Soc. 1932, 1089-1090.
(15) Bland, Thorpe, Proc. Chem. Soc. 28, 131 (1912).
(16) Ruhemann, J. Chem. Soc. 71, 323-324 (1897).
(17) Ruhemann, Ber. 54, 916-918 (1921).
(18) Ruhemann, J. Chem. Soc. 69, 1394-1397 (1896).

--- 2,3,6-TRICHLOROPHENOL

 $\begin{array}{cccc} & & & & & \text{C}_6\text{H}_3\text{OCl}_3 & & \text{Beil. VI - 190} \\ & & & & & \text{VI}_1\text{--} \\ & & & & & \text{VI}_2\text{-}(180) \\ \end{array}$

B.P. 252-253° u.c.

M.P. 58°

See 3:1160. Division A: Solids.

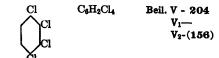
—— 3,4-DICHLOROPHENOL

B.P. 253.5° at 767 mm.

M.P. 65°

See 3:1460. Division A: Solids.

--- 1,2,3,4-TETRACHLOROBENZENE



B.P. 254° cor. at 761 mm.

M.P. 45-46°

See 3:0655. Division A: Solids.

3:6870 2-METHOXYBENZOYL CHLORIDE Cl C₃H₇O₂Cl Beil. X - 85 (o-Anisoyl chloride; Salicyloyl chloride methyl ether) CH₃ CCH₃

B.P. 254° u.c. at 760 mm. (1) 133° at 19 mm. (2) 145° cor. at 17 mm. (3) 136° 12 mm. (4) 128° 11 mm. (5) 128.8-129.0° 8 mm. (6) at 119.6° 1 mm. (7) 105-106° at 1 mm.

Colorless liquid.

[For prepn. of \bar{C} from o-methoxybenzoic acid (o-anisic acid) (1:0685) with PCl₅ (1) (4) (9) (10) (11) (every trace of salicylic acid must first be removed (9)) or with SOCl₂ (2) (3) (4) (5) (6) (7) (12) (prolonged heating tends to demethylate product (4)) see indic. refs.; note that for none of the prepns. is the yield recorded.]

[C on cat. reductn. at 280° with H₂ at ord. press. in press of Pd gives (11), not the expected o-methoxybenzaldehyde, but instead o-methoxytoluene (methyl o-tolyl ether) (1:7480).]

Č with anhydrous Na₂CO₃ in pyridine shaken for ½ hr., poured onto ice, yields (13) o-methoxybenzoic acid anhydrude, ndls. from pct. ether, m.p. 72.4° (13).

[\bar{C} with $C_6H_6+AlCl_3$ gives (14) (9) (2) (12) o-hydroxybenzophenone (1:1414) (note demethylation of intermediate o-methoxybenzophenone (1:5142) and also the formn. in small amt. (12) of 2-hydroxy-5-(2'-hydroxybenzoyl)benzophenone, m.p. 131-132° (12)).]

[\bar{C} with Et₂Zn gives (87% yield (3)) ethyl 2-methoxyphenyl ketone [Beil. VIII-102], b.p. 137° cor. at 16 mm. (3).]

[For reaction of \bar{C} with ethyl sodio-acetoacetate (5), with ethyl sodio- α -methylacetoacetate (15), with ethyl sodio- α -allylacetoacetate (16), or with ethyl sodio- α , dimethoxyacetoacetate (17) (together with hydrolytic cleavage of the resulting products to ketones and/or acids) see indic. refs.; for reactn. of \bar{C} with Na phenylacetylene and ring closure of intermediate to corresp. 2-methoxyflavone see (18).]

[C (1 mole) with HCN (4 moles) in dry ether + pyridine gives (4) o-methoxybenzoyl cyanide, yel. ndls. from lgr., m.p. 56°, b.p. 161° at 12 mm. (4).]

[\bar{C} with urea refluxed in C_6H_6 for 15 hrs. gives (19) N-(o-methoxybenzoyl)urea, ndls. from hot aq. or toluene, m.p. 192° (19).]

[Č with methyl salicylate gives (20) methyl O-(2-methoxybenzoyl)salicylate, m.p. 102–104° (20); Č with salicylamide in pyridine gives (21) N-(2-methoxybenzoyl)salicylamide, m.p. 189° (21).]

[C with MeOH yields methyl o-methoxybenzoate (1:4091), b.p. 248°; C with EtOH yields ethyl o-methoxybenzoate (1:4151), b.p. 261°; for study of rate of reactn. of C with EtOH at 0° see (22) (8).]

 \bar{C} on hydrolysis yields o-methoxybenzoic acid (1:0685), m.p. 100-101°; for the amide, anilide, and other derivs. corresp. to \bar{C} see o-methoxybenzoic acid (1:0685).

3:6870 (1) Pinnow, Müller, Ber. 28, 158 (1895).
 (2) Staudinger, Kon, Ann. 384, 99 (1911).
 (3) Fischer, Slimmer, Ber. 36, 2585-2586 (1903).
 (4) Marsh, Stephen, J. Chem. Soc. 127, 1635 (1925).
 (5) von Auwers, Ber. 52, 126-127 (1919).
 (6) Kahovec, Kohlrausch, Z. physik. Chem. B-38, 136 (1938).
 (7) Thompson, Norris, J. Am. Chem. Soc. 58, 1956 (1936).
 (8) Norris, Young, J. Am. Chem. Soc. 57, 1424 (1935).
 (9) Ullmann, Goldberg, Ber. 35, 2811-2812 (1902).
 (10) Cohen, Dudley, J. Chem. Soc. 97, 1739 (1910).

(11) Fröschl, Danoff, J. prakt. Chem. (2) 144, 224 (1936). (12) Blicke, Weinkauff, J. Am. Chem. Soc. 54, 1448 (1932). (13) Rule, Patterson, J. Chem. Soc. 125, 2161 (1924). (14) Graebe, Ullmann, Ber. 29, 824-825 (1896). (15) Robertson, Sandrock, Hendry, J. Chem. Soc. 1931, 2428. (16) Helferich, Keiner, Ber. 57, 1617-1618 (1924). (17) Pratt, Robinson, J. Chem. Soc. 127, 1184-1185 (1925). (18) Simonis, Z. angew Chem. 39, 1462 (1926). (19) Kaufmann, Arch. Pharm. 265, 236 (1927). (20) Lewicka, Bull. acad. sci. Cracovie, 1927-A; Cent. 1928, I 190; C.A. 22, 4515 (1928).

(21) Anschütz et al., Ann. 442, 33 (1925). (22) Norris, Fasce, Staud, J. Am. Chem Soc. 57, 1415-1420 (1935).

m-XYLYLENE DICHLORIDE

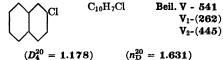
$$\begin{array}{cccc} CH_{2}Cl & C_{8}H_{8}Cl_{2} & \text{Beil. V - 373} \\ & V_{1}-\\ & V_{2}-(\mathbf{291}) \end{array}$$

B.P. 250-255°

M.P. 34°

See 3:0310. Division A: Solids.

2-CHLORONAPHTHALENE

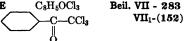


B.P. 256°

M.P. 60°

Division A: Solids. See 3:1285.

ω,ω,ω-TRICHLOROACETOPHENONE 3:6874 (Phenyl trichloromethyl ketone)



 $D_{-}^{16} = 1.425 (2)$ B.P. 256-257° (1) 249° (2)145° at 25 mm. (2) 120-121° at 15 mm. (3) 128-132° at 14 mm. (4) at 14 mm. (5)

Colorless liq. with agreeable odor. — \bar{C} has no lachrymatory or hypnotic props.

[For prepn. of C from acetophenone (1:5515) with Cl₂ at 100-200° in sunlight see (2); from phenyl-trichloromethyl-carbinol by oxidn. with CrO₃ (6) or K₂Cr₂O₇ + H₂SO₄ (72% yield (4)) see indic. refs.; from ω , ω -dichloroacetophenone (3:6835) in AcOH + NaOAc with Cl₂ at 95-100° (79% yield (7)) cf. (2) see indic. refs.; from trichloroacetyl chloride (3:5420) with C₆H₆ + AlCl₃ (47% yield (1)) (5) (2) or from trichloroacetonitrile with C₆H₆ + AlCl₃ + HCl gas (70% yield (3)) see indic. refs.]

[For study of behavior of C with Cl2 or Br2 see (8).]

 \ddot{C} with 3 pts. fumg. HNO₃ gives (96% yield (8)) m-nitro- ω, ω, ω -trichloroacetophenone, yel. oil, b.p. 200-201° at 26 mm., 192-193° at 18 mm. (8); this prod. with aq. alk. splits smoothly and quant. to m-nitrobenzoic acid, m.p. 137-141° (8).

[C with alcohols in pres. of corresp. Na alcoholate gives high yields (9) (10) of corresp. benzoates; e.g., \bar{C} with MeOH + NaOMe gives (92-94% yield (9)) methyl benzoate (1:3586), Č with EtOH + EtONa gives (85% yield (9)) ethyl benzoate (1:3721) (for corresp. results with isopropyl alc. (9), benzyl alc. (9), linalool (1:6260) (9), menthol (1:5940) (9) (10), ethylene glycol (9), glycerol (9), and cetyl alc. (1:5945) (10) see indic. refs.); \bar{C} with phenols in pres. of KOAc gives corresp. benzoates; e.g., \bar{C} with phenol + KOAc gives (80% yield (10)) phenyl benzoate (1:2257), m.p. 70°; \bar{C} with o-cresol + KOAc gives (80% yield (10)) o-tolyl benzoate (1:4371); \bar{C} with p-cresol + KOAc gives (90% yield (10)) p-tolyl benzoate (1:2279), m.p. 71°.]

C with boilg. aq. is scarcely affected (2), but C refluxed 16 hrs. with 10 pts. aq. contg. a little KOAc, or C in acctone contg. a little aq. KOAc refluxed 4 hrs., gives (90-96% yield (10)) benzoic acid (1:0715), m.p. 121°.

Č with cold dil. alk. (3) (7) (5) readily splits yielding benzoic acid (1:0715) and chloroform (3:5050).

3:6874 (1) Biltz, J. prakt. Chem. (2) 142, 196-197 (1935). (2) Gautier, Ann. chim. (6) 14, 396-402 (1888). (3) Houben, Fischer, J. prakt. Chem. (2) 123, 318-319 (1929). (4) Florence, Bull. soc. chim. (4) 49, 926-927 (1931). (5) Staudinger, Kon, Ann. 384, 112 (1911). (6) Dinesmann, Compt. rend. 141, 202 (1905). (7) Aston, Newkirk, Dorsky, Jenkins, J. Am. Chem. Soc. 64, 1415 (1942). (8) Houben, Fischer, Ber. 64, 2651-2653 (1931). (9) Houben, Fischer, Ber. 64, 244-247 (1931). (10) Houben, Fischer, Ber. 64, 2639-2645 (1931).

Oil, sol. alc., ether, C6H6, or AcOH.

[For prepn. of \bar{C} from 3,4-dichlorotoluene (3:6355) at its b.p. with Cl_2 (1) (5) or with dry Cl_2 in pres. of 2-3% PCl_5 (2); no yields or details are given, and no further record of prepn. of \bar{C} is made.]

 \tilde{C} on hydrolysis with aq. in s.t. at 220° (3) (4), or with 4 wt. pts. of a mixt. of equal parts fumg. H₂SO₄ (10% SO₃) + conc. H₂SO₄ at 30-40° (yields: 66% (4), 36% (5)) cf. (6), or with 98% H₂SO₄ (no yield stated (2)), or with aq. + CaCO₃ on refluxing 9 hrs. (40% yield (5)) gives 3,4-dichlorobenzaldehyde (3:0550) q.v.

C on oxidn. (5) with chromic acid (1) slowly yields 3,4-dichlorobenzoic acid (3:4925) q.v.

3:6876 (1) Beilstein, Kuhlberg, Ann. 150, 291-295 (1869). (2) Ruggli, Zaeslin, Lang, Helv. Chim. Acta 21, 1248 (1938); Erdmann, Ann. 272, 149-150 (1892). (3) Beilstein, Kuhlberg, Ann. 152, 228-229 (1869). (4) Erdmann, Schwechten, Ann. 260, 67, 72 (1890). (5) Kraay, Rec. trav. chim. 49, 1086 (1930). (6) B.A.S.F., Ger. 32,238, March 28, 1884; Ber. 18 (Referate), 470 (1885).

— CINNAMOYL CHLORIDE
$$C_9H_7OCl$$
 Beil. IX - 587 IX₁-(233)

B.P. 257.5° at 760 mm. M.P. 35-36° $D_4^{45.3} = 1.1617$ $n_D^{42.5} = 1.61364$

See 3:0330. Division A: Solids.

```
B.P.
                                    F.P.
                                                    D_4^{25} = 1.192
[263°
                                    -2.3°
                                             (9)
                                                                     (6)
                             (1)
[259-262°
                                    -2.5^{\circ}
                             (2)
                                            (6)
                                                    D_4^{21.6} = 1.1906 (7)
259.4-260.3° at 760 mm.
                             (3)
                                    -4°
                                           (12)
259.3°
                at 760 mm.
                             (4)(5)
                                                                 n_{\rm D}^{21.6} = 1.63184
                                                                                       (7)
258.8°
                at 753 mm.
                             (6)
258° cor.
                             (7)
                                                    D_4^{20} = 1.19382 (4)
255.5-256.0°
                             (8)
                                                           1.192
255.6° cor.
                at 752 mm.
                             (9)
248.6°
                at 600 mm.
                             (4)
                                                                   n_{\rm D}^{20} = 1.63321 (4) (7)
                at 400 mm.
230.8°
                at 200 mm.
204.2°
 180.4°
                at 100 mm.
                                                    D_{15}^{15} = 1.1966 \quad (9)
 171.4°
                at 75 mm.
                             (4)
 159.3°
                at
                    50 mm.
                             (4)
 144.0-146.5° at
                    29 mm. (10)
 140.3°
                    25 mm. (4)
 129.54°
                    16 mm. (5)
 125.4°
                    16 mm. (11)
 127.97°
                    15 mm. (5)
 126.25°
                at
                    14 mm.
 122.0-122.2° at
                    13 mm.
                             (3)
 118.6°
                at
                    10 mm.
                             (4)
104.8°
                     5 mm. (4)
85.3°
                at 1.5 mm. (4)
```

Colorless oil, volatile with steam. — Note that presence of as much as 10% of 2-chloronaphthalene (3:1285) has no effect upon density of \bar{C} (9). — Note also that addn. of 1,4-dichloronaphthalene (3:1655), m.p. 68°, or of 1,6-dichloronaphthalene (3:0810), m.p. 48°, lowers m.p. of \bar{C} (9).

[For sepn. of mixts. of \bar{C} with the isomeric 2-chloronaphthalene by fractional freezing of their soln. in appropriate solvents see (6). — For purification of tech. \bar{C} by treatment with 1-2% alk. at 150° under reduced press. see (13). — For sepn. of \bar{C} from dichloronaphthalenes by means of its const.-boil. mixt. (b.p. 99°) with aq. see (18).]

[For prepn. of \tilde{C} from α -naphthylamine [Beil. XII-1212, XII₁-(519)] via diazotization and use of Cu₂Cl₂ reactn. (70-75% yield (9)) (8) (7) or even by warming diazo soln. with HCl (10-20% yield (14)) or from diazonium/ZnCl₂ cpd. on addn. to phenol at 60° (46% \tilde{C} + 29% hydroxybiphenyl + 20% diphenyl ether (62)) see indic. refs.; from α -naphthalenesulfonyl chloride [Beil. XI-157, XI₁-(37)] (2), or from 1-nitronaphthalene [Beil. V-553, V₁-(264)] (15), or from β -naphthol (1:1500) (16) with PCl₅ as directed see indic. refs.; for formn. of \tilde{C} from 1-nitronaphthalene with Cl₂ see (17).]

[For prepn. of C from naphthalene with Cl₂ in boilg. naphthalene (19) (48), in vapor phase (20) (22) (27), in various solvents (21) (22) (23) (24) (25) (26) see indic. refs.; from naphthalene with HCl gas + air in pres. of cat. see (28); from naphthalene with PbCl₄-2NH₄Cl at 140-150° (29) or with SO₂Cl₂ + AlCl₃ (79% yield (30)) see indic. refs.; from

naphthalene dichloride [Beil. V-519] with boilg, alc. KOH (31) cf. (32) or by distn. (33) cf. (34) see indic. refs.]

[For thermal anal. of systems of \tilde{C} with SbBr₅ see (35); with PkOH see (36); with 2,4,6-trinitroresorcinol (styphnic acid) see (37).]

[C with Cl₂ in cold or C with Cl₂ in lt. pet. yields (38) 1-chloronaphthalene tetrachloride, m.p. 131° (38), and 1,4-dichloronaphthalene (3:1655), m.p. 68° (38); C with Cl₂ in CHCl₃ yields (38) the above 1-chloronaphthalene tetrachloride and 1,4-dichloronaphthalene tetrachloride, m.p. 172° (38); C with Cl₂ in CS₂ gives (38) a new dichloronaphthalene tetrachloride, m.p. 158° (38).]

[C on chloromethylation with paraformaldehyde + HCl gas + H₃PO₄ in AcOH gives (81) 1-chloro-4-(chloromethyl)naphthalene, m.p. 78-79° (81).]

[\bar{C} is not reduced with excess 5% Na/Hg in alc. even after 5 hrs. (39) nor by HI + P at 182° for 10 hrs. (42); however, \bar{C} in boilg. AmOH treated with Na yields (40) 1,4-dihydronaphthalene [Beil. V-518, V₁-(249)] (identified by addn. of Br₂ giving dibromide, m.p. 74° (40)) and 1,2,3,4-tetrahydronaphthalene (1:7550) q.v.; furthermore, \bar{C} with Mg in boilg. MeOH evolves gas and upon acidification and pouring into aq. gives alm. quant. yield (41) naphthalene (1:7200), m.p. 80°.]

 $[\bar{C}$ on cat. oxidn. with air at 250-300° gives (43) 97% phthalic anhydride (1:0725) + 3% 3-chlorophthalic anhydride (3:3900).

[\bar{C} with Li in s.t. 17½ hrs. at 263° followed by treatment with aq. gives (444) naphthalene (1:7200) + 1,1'-binaphthyl [Beil. V-725, V₁-(358)], m.p. 156°. — \bar{C} with Li in dry ether yields soln. of α -naphthyl-lithium which with Me₂SO₄ gives (77% yield (45)) 1-methyl-naphthalene (1:7600), the reactn. of \bar{C} with Li occurring even more readily (46) than with Mg.]

[\tilde{C} with Mg at 200-220° reacts very energetically and is complete within a few minutes; naphthalene sublimes abundantly, and yield of α -C₁₀H₇MgCl is only 10-13% (47).]

[\bar{C} with AlCl₃ at 100° gives small amts. (50) naphthalene (1:7200) + 2-chloronaphthalene (3:1285).]

[\bar{C} with CuCN in pyridine htd. 24 hrs. in bath at 245–250° (92% yield (10)) or \bar{C} with K₄Fe(CN)₆ + pyridine at 270° for 18 hrs. (49) gives α -naphthonitrile [Beil. IX-649, IX₁-(275)], b.p. 299° cor., b.p. 173–174° at 27 mm., 166–169° at 18 mm. (10).]

[C does not with Ag 3,5-dinitrobenzoate yield corresp. ester (80).]

[\bar{C} with 15% aq. NaOH above 300° for 12 hrs. gives (46% yield (51)) α-naphthol (1:1500); \bar{C} with 5 moles 3-25% aq. NaOH at 350-360° under pressure in pres. of Cu for 1 hr. gives (52) a mixt. of α-naphthol (1:1500) + β-naphthol (1:1540). — \bar{C} with aq. Na₂CO₃ + Cu at 300° under press. (53) or \bar{O} with aq. Na₂CO₃, Na₂HPO₄, or Na₂B₄O₇ at 325° and 280 atm. (54) yields α-naphthol (1:1500). — \bar{C} with aq. vapor over cat. at 300-400° yields (55) α-naphthol (1:1500).]

[\bar{C} with conc. aq. NH₄OH + CuO at 150-250° under press. (56) or \bar{C} with conc. aq. NH₄OH + Cu₂Cl₂ + Ca(OH)₂ at 225-230° under press. (57) cf. (58) yields α -naphthylamine (for study rate of reactn. see (58) (61); under suitable conditions the main prod. may be di- α -naphthylamine (60).]

[Č with KNH₂ in liq. NH₃ at -33° gives (82) only 2-3% α -naphthylamine, the main prod. (43-53%) being β -naphthylamine; for behavior of \bar{C} with LiNEt₂ see (83).]

[C on mononitration, e.g., with a mixt. of conc. HNO₃ (D = 1.4) (1 mole) + conc. H₂SO₄ (2 moles) at 0° (63) cf. (64) (65) (66) gives a mixt. of three mono nitro derivs., viz., 1-chloro-4-nitronaphthalene [Beil. V-555, V₁-(264)], pale yel. ndls. from alc., m.p. 85° (66) (63), 87-87.5° (67); 1-chloro-5-nitronaphthalene [Beil. V-556], m.p. 111° (63) (68); and 1-chloro-8-nitronaphthalene [Beil. V-556], ndls. from AcOH or C₆H₆, m.p. 94° (63), 93-94° (69). (Note that the relative proportions of these three mononitration products

vary rather widely acc. to conds. (63); that thermal anal. of various combinations of these three isomers have been recorded (65); and that of the other possible isomers the only ones reported are 1-chloro-2-nitronaphthalene, pale yel. ndls. from lt. pet., m.p. 80.5-81° (67), 76° (70) (71), and 1-chloro-6-nitronaphthalene, m.p. 118-120° (72), both prepd. indirectly.)]

[C on dinitration, e.g., with warm conc. HNO₃ (66) or fumg. HNO₃ (66), or 1-chloro-8-nitronaphthalene (above) on further nitr. (73) gives 1-chloro-4,8-dinitronaphthalene [Beil. V-561], m.p. 138° (73), and 1-chloro-4,5-dinitronaphthalene [Beil. V-561], m.p. 180° (66) (68); note that the only other recorded isomer, viz., 1-chloro-2,4-dinitronaphthalene [Beil. V-561, V₁-(265)], m.p. 146.5° cor., is obtd. only by indirect means, i.e., from 2,4-dinitronaphthol-1 with p-toluenesulfonyl chloride in diethylanline (74).]

[No record can be found of direct trinitration of \bar{C} ; the only two recorded 1-chlorotrinitronaphthalenes, viz., 1-chloro-2,4,5-trinitronaphthalene [Beil. V_{1} -(265)], m.p. 143-144°, and 1-chloro-2,4,8-trinitronaphthalene [Beil. V_{1} -(265)], m.p. 118-126°, have been obtd. from nitration (75) of 1-chloro-2,4-dinitronaphthalene (above).]

[\bar{C} with conc. H₂SO₄ at 140° yields (76) (77) mainly 1-chloronaphthalenesulfonic acid-4 [Beil. XI-160] (see also below).]

- ₱ 1-Chloronaphthalenesulfonamide-4 (4-chloronaphthalenesulfonamide-1): cryst. from dil. alc., m.p. 185–186° u.c. (78). [From \(\bar{C}\) with chlorosulfonic acid as directed, followed by conversion of the intermediate 1-chloronaphthalenesulfonyl chloride-4, m.p. 92–93° u.c., with (NH₄)₂CO₃ to the desired sulfonamide (78).]
- ---- 1-Chloronaphthalene picrate: m.p. 137° (50), 135° (11), 125.7° (36). [Note that this cpd. with PkOH forms a cutectic, m.p. 104.7°, contg. 16.3% (36).]
- ---- 1-Chloronaphthalene styphnate: m.p. 126-128° (79), 109.8° (37). [From Č (1 mole) + 2,4,6-trinitroresorcinol (1 mole) (styphnic acid) in hot alc. (79); Neut. Eq. calcd. 203.8, found (79) 207.8.]
- 3:8878 (1) Widman, Bull. soc. chim. (2) 28, 509 (1877). (2) Carius, Ann. 114, 145-146 (1860). (3) Gockel, Z. physik. Chem. B-29, 85 (1935). (4) Kahlbaum, Arndt, Z. physik. Chem. 26, 628, 646, 655 (1898). (5) von Rechenberg, J. prakt. Chem. (2) 101, 117 (1920). (6) Britton, Reed (to Dow Chem. Co.), U.S. 1,917,822, July 11, 1933; Cent. 1933, II 2194; CA. 27, 4547 (1933). (7) von Auwers, Frühling, Ann. 422, 194, 200,202 (1921). (8) Hampson, Weissberger, J. Chem. Soc. 1936, 394. (9) Zil'berman, Rashevskaya, Martyntseva, J. Applied Chem. (U.S.S.R.) 9, 1832-1840 (1936); C.A. 31, 2597 (1937). (10) Newman, J. Am. Chem. Soc. 59, 2472 (1937); Org. Syntheses 21, 89-91 (espec. Note 10) (1941).
- (11) L. Klemm, W. Klemm, Schiemann, Z. physik. Chem. A-165, 382 (1933). (12) Parts, Z. physik. Chem. B-16, 265 (1930). (13) Hanson, Brown (to Halowax Corp.), U.S. 2,025,742, Dec. 31, 1935; Cent. 1936, I 4841; C.A. 36, 1068 (1936). (14) Gasiorowski, Wayss, Ber. 18, 1939-1940 (1885). (15) de Koninck, Marquart, Ber. 5, 11 (1872). (16) Claus, Öhler, Ber. 15, 312, Note 2 (1882). (17) Atterberg, Ber. 9, 317, 927 (1876). (18) Buchheim (to Chem. Fabrik. von Heyden), Ger. 616,596, Aug. 1, 1935; Cent. 1935, II 3703. (19) Rymarenko, J. Russ. Phys.-Chem. Soc. 8, 141 (1876). (20) Ferrero, Wunenburger, Helv. Chim. Acta 11, 416-425 (1928).
- (21) Traubenberg, Wasserman, J. prakt. Chem. (2) 120, 177-178 (1928). (22) Ferrero, Fehlmann, J. prakt. Chem. (2) 122, 340-343 (1929). (23) Ferrero, Fehlmann, Helv. Chim. Acta 12, 583-593 (1929). (24) Ferrero, Corbaz, Helv. Chim. Acta 13, 1009-1025 (1930). (25) Ferrero, Fehlmann, Swiss 134,089, Sept. 16, 1929; Cent. 1930, I 2165; C.A. 24, 1652 (1930). (26) Britton, Reed (to Dow Chem. Co.), U.S. 1,784,267, Dec. 9, 1930; Cent. 1931, I 1970-1971. (27) I.G., French 823,021, Jan. 12, 1938; Cent. 1938, I 4719. (28) Prahl, Mathes (to F. Raschig), Ger. 575, 765, May 3, 1933; Cent. 1933, II 134. (29) Seyewetz, Biot, Compt. rend. 135, 1122 (1902). (30) Töhl, Eberhard, Ber. 26, 2945 (1893).
- (31) Laurent, Gmelin-Kraut (7th ed.) 4, 35, 38. (32) Faust, Saame, Ann. 160, 66-68 (1871). (33) Fischer, Ber. 11, 738 (1878). (34) Laurent, Ann. chim. (2) 59, 199 (1835). (35) Menschutkin, J. Russ. Phys.-Chem. Soc. 44, 1082 (1912); Cent. 1912, III 1436. (36) Jefremov, J. Russ. Phys.-Chem. Soc. 56, 381 (1918); Cent. 1923, III 379. (37) Jefremov, J. Russ. Phys.-Chem. Soc. 51, 359 (1909); Cent. 1923, III 770. (38) Turner, Wynne, J. Chem. Soc. 1941, 244-245.

(39) Franzen, Stäuble, J. prakt. Chem. (2) 103, 389 (1922). (40) Grien, Rowe, J. Chem. Soc. 112, 970 (1918).

(41) Zechmeister, Rom, Ann. 468, 128 (1929). (42) Klages Liecke, J. prakt. Chem. (2) 61, 323 (1900). (43) Pongratz, Bassi, Fuchs, Süss, Wüstner, Schober, Angew. Chem. 54, 22-26 (1941); C.A. 35, 3248 (1941). (44) Spencer, Price, J. Chem. Soc. 97, 388 (1910). (45) Vesley, Stursa, Collection Czechoslov. Chem. Commun. 4, 141-142 (1932). (46) Gilman, Zoellner, Selby, J. Am. Chem. Soc. 55, 1255 (1933). (47) Shoruigin, Isagulyantz, Guseva, Ber. 66, 1427 (1933). (48) DeWitt, Ekely, Univ. Colorado Studies 18, 119-121 (1931); C.A. 26, 2974 (1932). (49) A.G.F.A., Ger. 293,094, July 12, 1916; Cent. 1916, II 288-289. (50) Roux, Ann. chim. (6) 12, 347-349 (1887) Bull. soc. chim. (2) 45, 515 (1886).

(51) Meyer, Bergius, Ber. 47, 3159 (1914). (52) Britton, Stearns (to Dow Chem. Co.), U.S. 1,996,745, April 9, 1935; Cent. 1935, II 2126; C.A. 29, 3354 (1935). (53) Britton (to Dow Chem. Co.), U.S. 1,959,283, May 15, 1934; Cent. 1934, II 1688. (54) Hale, Britton (to Dow Chem. Co.), U.S. 1,882,824, 1,882,825, 1,882,826, Oct. 18, 1932; Cent. 1933, 1309; C.A. 27, 731 (1933). (55) Dreyfus, French 709,184, Aug. 4, 1931; Cent. 1931, II 12933. (56) Williams (to Dow Chem. Co.), U.S. 1,775,360, Sept. 9, 1930; Cent. 1931, II 1195. (57) Booth (to Swann Research, Inc.), U.S. 1,954,469, April 10, 1934; Cent. 1934, II 1846. (58) Federal Phosphorus Co., Brit. 370,774, May 5, 1932; Cent. 1932, II 1237. (59) Groggins, Stirton, Ind. Eng. Chem. 28, 1054 (1936). (60) Hale (to Dow Chem. Co.), U.S. 1,804,466, May 12, 1931; Cent. 1931, II 1195.

(61) Vorozhtsov, Kobelev, J. Gen. Chem. (U.S.S.R.), 9, 1569-1576 (0939); C.A. 34, 2688-2689 (1940).
(62) Hodgson, Foster, J. Chem. Soc. 1942, 582-583.
(63) Ferrero, Caflisch, Helv. Chim. Acta 11, 795-812 (1928).
(64) Franzen, Helwert, Ber. 53, 319-322 (1920).
(65) Assoks, Bull. Tokyo Ind. Research Inst. 23, (9) 1-26 (1928); C.A. 23, 3923 (1929).
(66) Atterberg, Ber. 9, 926-928 (1876).
(67) Hodgson, Leigh, J. Chem. Soc. 1937, 1352.
(68) Friedländer, Karamessinis, Schenk, Ber. 55, 47, 52 (1922).
(69) Woroshtzow, Koslow, Ber. 69, 413-415 (1926).
(70) Hodgson, Kilner, J. Chem. Soc. 1926, 7.

(71) Hoogeveen, Rec. trav. chim. 50, 38-39 (1931). (72) Hodgson, Turner, J. Chem. Soc. 1943, 391-392. (73) Ullmann, Consonno, Ber. 35, 2810 (1902). (74) Ullmann, Bruck, Ber. 41, 3932-3933 (1908). (75) Rindl, J. Chem. Soc. 103, 1912-1913 (1913). (76) Zinin, J. prakt. Chem. (1) 33, 36-37 (1844). (77) Arnell, Bull. soc. chim. (2) 39, 62-63 (1883). (78) Huntress, Carten, J. Am Chem. Soc. 62, 511-513 (1940). (79) Ma, Hsia, Sah, Science Repts. Natl. Tsing Hua Univ. 2, 150-156 (1933). (80) Tseng, Chu, Natl. Central Univ. (Nanking), Sci. Repts. A-1, No. 2, 5-7 (1931); C.A. 26, 2166 (1932).

(81) Horn, Warren, J. Chem. Soc. 1946, 144. (82) Urner, Bergstrom, J. Am. Chem. Soc. 67, 2108-2109 (1945). (83) Gilman, Crounse, Massie, Benkaser, Spatz, J. Am. Chem. Soc. 67, 2107 (1945).

3:6880 o-CHLOROBENZOTRICHLORIDE $C_7H_4Cl_4$ Beil. V - 302 $V_{1-}(153)$ $V_{2-}(234)$

B.P.	M.P.	
260° (1) (2)	30° (1) (2) (4)	$D_{-}^{-}=1.51 (1)$
129.5° at 13 mm. (2)	29–30° (5)	
115-118° at 5-6 mm. (3)		

Colorless liq. with faint but not disagreeable odor.

[For prepn. of \bar{C} from salicylic acid (1:0780) with PCl₅ see (1) (4); from o-chlorobenzoyl chloride (3:6640) with PCl₅ in s.t. at 200° for several days see (2); from o-chlorotoluene (3:8245) with Cl₂ at 130° (5) in pres. of PCl₃ (9), or from o-chlorotoluene- α -sulfonyl chloride (3) with Cl₂ at 150–180° (3), see indic. refs.; for formn. of \bar{C} from benzotrichloride (3:6540) with Cl₂ see (6) (7); for purification see (8).]

[For condens. of \tilde{C} with 1-hydroxynaphthoic acid-2 [Beil. X-331, X₁-(144)] to yield 1-hydroxy-4-(o-chlorobenzoyl)naphthoic acid-2, m.p. 213° (11), see (10) (11) (12); for reactn. of \tilde{C} with o-chlorobenzoic acid (3:4150) + ZnCl₂ to yield o-chlorobenzoyl chloride (3:6640) see (13); for reactn. of \tilde{C} with 99% HF yielding o-chlorobenzotrifluoride, b.p. 149-152°, see (14).]

Beil. X - 163

[\bar{C} on htg. with Cu powder in C₆H₆ for 25 hrs. gives (5) a mixt. of the two stereoisomeric forms of 1,2-bis-(o-chlorophenyl)-1,2-dichloroethylene, [Beil. V-635]; by repeated cryst. from pet. ether this mixt. is separable into 3 pts. higher-melting stereoisomer, m.p. 172° (5), and 1 pt. lower-melting stereoisomer, m.p. 129° (5).]

Č on hydrolysis, e.g., by htg. with aq. in s.t. at 150° (1) or by boilg. with conc. HNO₃ (2), yields o-chlorobenzoic acid (3:4150) q.v.

3:6880 (1) Kolbe, Lautemann, Ann. 115, 183-185, 195-196 (1860). (2) Anschutz, Ann. 454, 95-99 (1927). (3) Meister Lucius Bruning, Ger. 229,873, Jan. 6, 1911, Cent. 1911, I 358. (4) Anschütz, Moore, Ann. 239, 321-322 (1887). (5) Fox, Ber. 26, 653-656 (1893). (6) Spreckels, Ber. 52, 319 (1919). (7) Wertyporoch, Ann. 493, 157-161 (1932). (8) Britton (to Dow Chem. Co.), U.S. 1,804,458, May 12, 1931; Cent. 1931, II 497; C.A. 25, 3668 (1931). (9) Kyrides (to Nat. Aniline and Chem. Co.), U.S. 1,733,268, Oct. 29, 1929; Cent. 1930, I 3831. (10) Soc. Chem. Ind. Basel, Ger. 355,115, June 21, 1922; Swiss, 92,406, Feb. 16, 1923; Cent. 1923, II 484.

(11) Soc. Chem. Ind. Basel, Ger. 378,908, Aug. 7, 1923; Ger. 378,909, Aug. 11, 1923; Swiss 98,559, April 2, 1923; Cent. 1923, IV 593. (12) Soc. Chem. Ind. Basel, Ger. 418,033, Aug. 26, 1925; Cent. 1925, II 2095. (13) Scottish Dyes, Ltd., Bangam, Thomas, Brit. 308,231, April 18, 1929; Cent. 1929, II 1348. (14) I.G., French 745,293, May 8, 1933; Cent. 1933, II 2061.

('sH₇O₂Cl

3:6890 4-METHOXYBENZOYL CHLORIDE

$$(p\text{-Anisoyl chloride}) \qquad \qquad \text{CH}_3\text{O} \qquad \text{C} = \text{O} \qquad \text{X}_{1^-}(\ 77)$$
 B.P.
$$262-263^\circ \text{ sl. dec.} \qquad (1) \qquad 24^\circ \qquad (7) \qquad D_4^{20} = 1.2609 \ (6) \qquad n_D^{20} = 1.5802 \ (6)$$

$$262^\circ \qquad (9) \qquad 22^\circ \ (4) \ (15)$$

$$258.4-260.5^\circ \qquad (2) \qquad 21^\circ \qquad (8)$$

$$161-168^\circ \qquad \text{at } 38 \text{ mm. } (3)$$

$$160-164^\circ \qquad \text{at } 35 \text{ mm. } (4)$$

$$152-153^\circ \qquad \text{at } 24 \text{ mm. } (4)$$

$$148-153^\circ \qquad \text{at } 20 \text{ mm. } (5)$$

$$145^\circ \qquad \text{at } 14 \text{ mm. } (4)$$

$$137.6-137.8^\circ \text{ at } 14 \text{ mm. } (2)$$

$$90.8^\circ \qquad \text{at } 1 \text{ mm. } (6)$$

[For prepn. of \bar{C} from p-methoxybenzoic acid (p-anisic acid) (1:0805) with PCl₅ (93% yield (3)) (4) (9) (10) (11) or with SOCl₂ (6) (7) (12) (13) see indic. refs.; from sodium p-anisate with oxally chloride (3:5060) in $C_0H_6(75-90\%$ yield) see (14).]

[\bar{C} with 3% H_2O_2 in acetone + pyridine at 0° yields (15) di-p-anisyl peroxide, cryst. from AcOEt or pet. eth., m.p. 128° (15); for reactn. of \bar{C} with H_2S_2 + ZnCl₂ giving (60% yield) di-p-anisyl disulfide see (30).]

[$\bar{\mathbf{C}}$ on cat. reductn. with \mathbf{H}_2 and cat. as directed gives (81% yield (16)) p-methoxybenzaldehyde (1:0240) (under some conds. (17) reductn. goes to p-methoxytoluene (methylp-tolyl ether) (1:7495)).]

[Although 2-methoxybenzoyl chloride (3:6870) with anhydrous Na₂CO₃ + pyridine gives the corresp. anhydride, this reactn. is not specifically reported for Č; however, Č + a tertiary amine (pyridine) in C₆H₆ with excess K₂S₂O₅ yields (18) p-methoxybenzoic acid anhydride, m.p. 99-100° (18).]

[Č with C₆H₆ + AlCl₃ yields (1) p-methoxybenzophenone (1:5170); Č with toluene + AlCl₃ gives (40% yield (11)) 4-methoxy-4'-methylbenzophenone, cryst. from alc., m.p. 89° (11); Č with perylene + AlCl₃ in CS₂ gives (19) 3,9-bis-(p-methoxybenzoyl)perylene, m.p. 319.5° (19).]

[C condenses with many phenol ethers in pres. of AlCl₃; e.g., for reactn. of C with anisole

yielding 4,4'-dimethoxybenzophenone [Beil. VIII-317, VIII₁-(641)], m.p. 143-144° (20), see (20) (21); for \tilde{C} with phenetole yielding 4-methoxy-4'-ethoxybenzophenone, m.p. 112° (13), 111° (20), see indic. refs.; for \tilde{C} with pyrocatechol dimethyl ether (veratrole) (1:7560) yielding 3,4,4'-trimethoxybenzophenone [Beil. VIII-422], m.p. 98-99°, see (22); for \tilde{C} with resorcinol dimethyl ether (1:7570) yielding 2,4,4'-trimethoxybenzophenone [Beil. VIII-(702)], m.p. 70-71° (23), see (23); for \tilde{C} with phloroglucinol trimethyl ether (1:7148) yielding 2,4,6,4'-tetramethoxybenzophenone [Beil. VIII-496], m.p. 146°, see (22); for \tilde{C} with many other phenol ethers see (20).]

[\bar{C} with MeZnI (24) or better with Me₂Cd (25) gives (yields: 25% (24), 84% (25)) p-methoxyphenyl methyl ketone (p-methoxyacetophenone) (1:5140), m.p. 38°; \bar{C} with C₆H₅ZnBr gives (65% yield (26)) p-methoxybenzophenone, (1:5170), m.p. 61°, b.p. 202° at 14 mm. (26).]

[\bar{C} with ethyl sodioacetoacetate yields (4) ethyl α -(p-methoxybenzoyl)acetoacetate [Beil. X-1004]; \bar{C} with ethyl sodio- α , γ -dimethoxyacetoacetate yields (27) ethyl α , γ -dimethoxy- α -(p-anisoyl)acetoacetate (which on ketonic hydrolytic cleavage yields (27) ω ,4-dimethoxyacetophenone).]

[Č (1 mole) with HCN (4 moles) in dry ether + pyridine gives (12) p-methoxybenzoyl cyanide, m.p. 63°, b.p. 150° at 12 mm. (12); Č with KCN + quinoline yields (28) 1-(p-anisoyl)-2-cyano-1,2-dihydroquinoline, m.p. 120°, which upon acid hydrolysis gives (57% yield (28)) p-methoxybenzaldehyde (p-anisaldehyde) (1:0240).]

[\bar{C} with urea refluxed in C₆H₆ for 15 hrs. yields (29) N-(p-methoxybenzoyl)urea, ndls. from alc., m.p. 215° (29).]

[For reactn. of \tilde{C} with K_2S in alc. + ether yielding K salt of p-methoxythiobenzoic acid see (30); for reactn. of \tilde{C} with sodium phenylacetylene see (31); for reactn. of \tilde{C} with diphenylketene see (32); for reactn. of \tilde{C} with d-glucose and other carbohydrates see (33); for reactn. of \tilde{C} with 3,4-dimethoxyphenylethylamine (34) or with β -(n-butylamino)ethanol (3) see indic. refs.]

 \tilde{C} with MeOH yields methyl p-methoxybenzoate (methyl p-anisate) (1:2128), m.p. 49°; \tilde{C} with EtOH yields ethyl p-anisate (1.4191), b.p. 269°, m.p. $+7^{\circ}$ (for study of rate of reactn. of \tilde{C} with EtOH see (8) (35)).

 \bar{C} on hydrolysis yields p-methoxybenzoic acid (1.0805), m.p. 184°; for the amide, anilide, p-toluidide, and other derivs. corresp. to \bar{C} see p-methoxybenzoic acid (1.0805).

3:6890 (1) Ullmann, Goldberg, Ber. 35, 2814 (1902) (2) Kohlerusch, Pongratz, Stockmair Monatsh. 67, 110 (1935). (3) Pierce, Salsbury, Fredericksen, J. Am. Chem. Soc. 64, 1691-1694 (1942). (4) Schoonjans, Bull. acad. roy. Betg. (3) 33, 810-820 (1897); Cent. 1897, II 616. (5) de Ceuster, Natuurw. Tydschr 14, Nos. 3-6, 188-202 (1932), Cent. 1932, II 1296. (6) Thompson, Norris, J. Am. Chem. Soc. 58, 1956 (1936). (7) Meyer, Monatsh. 22, 428 (1901). (8) Branch, Nixon, J. Am Chem. Soc. 58, 2499-2504 (1936). (9) Cahours, Ann. chim. (3) 23, 350-354 (1848), Ann. 70, 47-48 (1849). (10) Lossen, Ann. 175, 284, Note (1875).

(11) Orechow, Brouty, Bull. soc. chrm. (4) 47, 623 (1930). (12) Marsh, Stephen, J. Chem. Soc. 127, 1635 (1925). (13) Schonberg, Schutz, Nickel, Ber. 61, 1380 (1927). (14) Adams, Uhlich, J. Am. Chem. Soc. 42, 606 (1920). (15) Vanno, Uhlfelder, Ber. 37, 3624 (1904). (16) Rosenmund, Zetsche, Ber. 56, 1483 (1923). (17) Rosenmund, Zetsche, Ber. 54, 641 (1921). (18) Gasopoulos, Praktika Akad. Athenon 6, 347-353 (1931); Cent. 1932, I 3172. (19) Zinke, Funke, Ber. 58, 2225 (1925). (20) Jones, J. Chem. Soc. 1936, 1860.

(21) Schnackenberg, Schell, Ber. 36, 654 (1903). (22) von Kostanecki, Tambor, Ber. 39, 4024, 4026 (1906). (23) Ziegler, Ochs, Ber. 55, 2273 (1922). (24) Mauthner, J. prakt. Chem. (2) 103, 392, 396 (1922). (25) Gilman, Nelson, Rec. trav. chrm. 55, 528-529 (1936). (26) Martynoff, Ann. chim. (11) 7, 439 (1937). (27) Pratt, Robinson, J. Chem. Soc. 127, 169 (1925). (28) Sugasawa, Tsuda, J. Pharm. Soc. Japan, 56, 103-105 (1936); Cent. 1936, II 3670. (29) Kaufmann, Arch. Pharm. 265, 236 (1927). (30) Block, Bergmann, Ber. 53, 974-975 (1920).

(31) Weygand, Bauer, Ann. 459, 141 (1927). (32) Staudinger, Kon, Ann. 384, 117 (1911). (3) Oden, Arkiv Kemi, Mineral. Geol. 7, No. 16, 1-16 (1918); Cent. 1923, III 254-256; C.A. 14, 2171 (1920). (34) Ahluwalia, Narang, Ray, J. Chem. Soc. 1931, 2058. (35) Norris, Fasce, Staud, J. Am. Chem. Soc. 57, 1415-1420 (1935).

TEREPHTHALYL (DI)CHLORIDE
$$C_8H_4O_2Cl_2$$
 Beil. IX₁-
$$C=O$$
 IX₁-

Beil. IX1- 844 IX₁-(376)

B.P. 263°

M.P. 83°

See 3:2205. Division A: Solids.

2,4,6-TRICHLORO-3-METHYLPHENOL C7H5OCl3 Beil. VI ---VI₂-(356)

B.P. 265°

M.P. 46°

See 3:0618. Division A: Solids.

3:6895 DI-(\gamma-CHLOROPROPYL) CARBONATE $\mathrm{C_7H_{12}O_3Cl_2}$ Beil. III -Ш1--- $(\gamma, \gamma$ -Dichloropropyl carbonate) Cl.CH₂CH₂CH₂O III_{2} -(5) Cl.CH₂CH₂CH₂CH₂C

B.P. 265-270° at 740 mm. (1)

[Obtd. as by-product in prepn. of γ -chloropropyl chloroformate (3:6010) from phospene and trimethylene chlorohydrin (3:8285) (1).]

3:6895 (1) Pierce, Adams, J. Am. Chem. Soc. 45, 791-792 (1923).

 OCTACHLOROPROPANE Beil. I - 108 I_{1} -(35)

B.P. 268-269° at 734 mm.

M.P. 160° (?)

See 3:4450. Division A: Solids.

p-CHLOROPHENACYL CHLORIDE C₈H₆OCl₂ Beil. VII - 282 -CH₂Cl VII₁-(152)

B.P. 270°

M.P. 101-102°

See 3:2990. Division A: Solids.

M.P. 101°

B.P. 276°

M.P. 43°

See 3:0520. Division A: Solids.

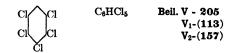
--- 3,4,5-TRICHLOROPHENOL

$$\begin{array}{cccc} \text{OH} & \text{C}_6\text{H}_5\text{OCl}_2 & \text{Beil. VI} - \\ & & \text{VI}_1 - \\ & & \text{VI}_2\text{-}(\mathbf{181}) \end{array}$$

B.P. 271-277° u.c. at 746 mm.

See 3:2885. Division A. Solids.

--- PENTACHLOROBENZENE



B.P. 275-277° M.P. 86-87°

See 3:2290. Division A: Solids.

[See also unsym.-o-phthalyl dichloride (3:2395).]

The m.p. of ord. samples of \bar{C} is usually abt. 12°, but distr. at ord. press. (7) yields a prod. with m.p. 16°. The chem. of \bar{C} is closely connected with that of the isomeric unsym.-o-phthalyl dichloride (3:2395) q.v.; for f.p./compn. curve for mixts. of the two isomers see (8).

[For prepn. of \bar{C} from phthalic anhydride (1:0725) with PCl₅ (92% yield (7)) (1) (3) (9) (10), with PCl₃ + Cl₂ (12), with benzotrichloride (3:6540) + a little ZnCl₂ (13), with a little ZnCl₂ at 220° by grad. addn. of SOCl₂ (100% yield (14)) (15), or with CCl₄ (etc.) + 2% ZnCl₂ at 250-280° (16) see indic. refs.; from phthalic acid (1:0820) with benzotrichloride + a little ZnCl₂ see (17).]

[For prepn. of \tilde{C} from unsym.-o-phthalyl dichloride (3:2395) by htg. at 150° for 1 hr. see (5); from thiophthalic anhydride [Beil. XVII-486, XVII₁-(256)] with dry Cl₂ at 245° see (18); for formn. as by-product of action of Cl₂ on o-toluoyl chloride (3:8740) see (19).] [For purification of \tilde{C} by treatment with MgO or CaO see (20).]

C on htg. with AlCl₃ (½ mole), then deeg. cpd. with aq. and extracting with pet. ether, isomerizes (72% yield (7)) (1) (21) to unsym.-o-phthalyl dichloride (3,3-dichlorophthalide) (3:2395), m.p. 89°.

[C with Cl₂ at 120-170° in pres. of Fe yields (22) tetrachlorophthalic acid (3:4946).]

[\bar{C} on reduction with Zn + HCl (23) (24) or HI + P in CS₂ (23) (25) yields phthalide (1:4920); \bar{C} on boilg. with AcOH + Na/Hg yields (26) phthalyl alcohol (o-xylylene glycol) [Beil. VI-910].]

 \bar{C} on heating with K in xylene (27), or with ter-bases + $K_2S_2O_5$ (28), or with $ZnCl_2$ + SO_2 at 200° (14) yields phthalic anhydride (1:0725). [Note that last reaction is the reverse of an impt. method (15) of prepn. of \bar{C} .]

[C on shaking for 20 min. at 60° in glass flask with ZnF₂, then extracting with pet. eth. yields (29) o-phthalyl difluoride, m.p. 42-43°, b.p. 224-236° at 760 mm. (29); C with HBr gas at 150-160° gives (50% yield (30)) sym-o-phthalyl dibromide, m.p. 78-81° rap. htg., b.p. 191° at 24 mm., 134° at 2 mm. (30).]

[C htd. with a little ZnCl₂ and diethyl ether (31) or diethyl phthalate (32) gives (80% yield (31)) ethyl chloride (3:7015).] [Use in mfg. of alkyl chlorides (33).]

[For reactn. of \bar{C} with glycols see (34); for use of \bar{C} in acylation of cellulose see (35).]

[For behavior of \bar{C} with H_2O_2 yielding phthalyl peroxide see (36); with PCl_5 see (37); with NaN_3 see (38) (39); with C_6H_5MgBr see (40).]

 $\bar{\mathbf{C}}$ on treatment with cold conc. NH₄OH followed by acidification yields (41) (42) o-cyanobenzoic acid [Beil. IX-814, IX₁-(365)], m.p. 190° dec., converted by htg. to phthal-imide, m.p. 228.5° u.c. [For reactn. of $\bar{\mathbf{C}}$ with dimethylamine yielding N,N,N',N'-tetramethyl-o-phthaldiamide, m.p. 121-122°, see (43); with diethylamine yielding (44) (45) corresp. N,N,N',N'-tetra-ethyl-o-phthaldiamide, m.p. 36° (44), 39° (45) see indic. refs.]

C htd. with 1 mole acetamide until no more HCl is evolved gives in good yield (46) N-acetylphthalimide, cryst. from toluene, m.p. 135-136° (46); similarly benzamide gives N-benzoylphthalimide, m.p. 168° (46).

 \bar{C} reacts instantly with aniline yielding (29) sym.-phthalyldianilide, m.p. 253-255°. [Note that when \bar{C} is treated with aniline in ether or C_6H_6 and stood for some time the prod. has m.p. about 231°; when recrystd. from EtOH, however, the m.p. rises to 253-255°. This apparent anomaly is attributable to the pres. in most samples of \bar{C} of some phthalic anhydride whose slower reactn. with aniline contaminates the main prod. but is removed by recrystn. from alc. If, on reactn. of ord. \bar{C} with aniline, the resultant ppt. is filtered at once (before the anhydride has reacted), washed with C_6H_6 , alc., and then aq., the prod. shows m.p. 253-255° without recrystn. (29).]

Č on hydrolysis yields o-phthalic acid (1:0825) q.v.

3:6900 (1) Ott, Ann. 392, 273-277 (1912). (2) Brühl, Ann. 235, 13-14 (1886). (3) Claus. Hoch, Ber. 19, 1187-1194 (1886). (4) von Auwers, Schmidt, Ber. 46, 483 (1913). (5) Garner, Sugden, J. Chem. Soc. 1927, 2878, 2881. (6) Martin, Partington, J. Chem. Soc. 1936, 1181. (7) Ott, Org. Syntheses, Coll. Vol. 2 (1st ed.), 528-530 (1943); 11, 88-91 (1931). (8) Csanyi, Monatsh. 40, 81-92 (1919). (9) Auger, Ann. chim. (6) 22, 295-302 (1891). (10) Tingle, Cram, Am. Chem. J. 37, 603-604 (1907).

(11) Graebe, Ann. 238, 329 Note (1887). (12) Clemmensen, Miller (to Monsanto Chem. Co.), U.S. 1,974,845, Sept. 25, 1934; Cenl. 1935, I 960; C.A. 28, 7285 (1934). (13) Kyrides (to Monsanto Chem. Co.), U.S. 1,963,749, June 19, 1934, Cenl. 1934, II 2900; C.A. 28, 5079 (1934). (14) Kyrides, J. Am. Chem. Soc 59, 206-208 (1937). (15) Kyrides (to Monsanto Chem. Co.), U.S. 1,951,364, Mar. 20, 1934; Cenl. 1934, II 333; C.A. 28, 3424 (1934). (16) Mares (to Monsanto Chem. Co.), U.S. 2,051,096, Aug. 18, 1936; Cenl. 1936, II 3594, C.A. 30, 6762 (1936). (17) Kyrides (to Monsanto Chem. Co.), U.S. 1,963,748, June 19, 1934; Cenl. 1934, II 2900; C.A. 28, 5080 (1934). (18) Ott, Langenohl, Zerweck, Ber. 70, 2360-2362 (1932). (19) Davies, Perkin, J. Chem. Soc. 121, 2213 (1922). (20) Luthy, Thomas (to Monsanto Chem. Works), U.S. 1,906,761, May 2, 1933; C.A. 27, 3484 (1933); Brit. 397,775, Sept. 21, 1933; Cenl. 1933, II 3194.

(21) Scheiber, Ber. 46, 2366-2370 (1913). (22) Zal'kind, Belikova, Russ. 35,188, Mar. 31, 1934; Cent. 1935, II 1090; C.A. 30, 3443 (1936). (23) Hessert, Ber. 10, 1445-1447 (1877). (24) Hessert, Ber. 11, 238-239 (1878). (25) Bacyer, Ber. 10, 123-124 (1877). (26) Hessert, Ber. 12, 646-648 (1879). (27) Pearl, Evans, Dehn, J. Am. Chem. Soc. 60, 2479 (1938). (28) Gasopoulos, Praktika Akad. Athenon. 6, 347-353; Cent. 1932, I 3172. (29) Dann, Davies, Hambly, Paul, Semmens, J. Chem. Soc. 1933, 17. (30) Davies, Hambly, Semmens, J. Chem. Soc. 1933, 1309-1315.

(31) Kyrides, J. Am. Chem. Soc. **55**, 1209–1212 (1933). (32) Kyrides, Dvornikoff, J. Am. Chem. Soc. **55**, 4630–4632 (1933). (33) Kyrides (to Monsanto Chem. Co.), U.S. 1,939,216, Dec. 12, 1933; Cent. **1934**, I 2040; C.A. **28**, 1361 (1934). (34) Carothers, Arvin, J. Am. Chem. Soc. **51**, 2560–2570 (1929). (35) Brit. 319,584, Nov. 20, 1929; Cent. **1930**, I 1377. (36) McKee, U.S. 1,614,037, Jan. 11, 1927, Brit. 271,725, June 23, 1927, Cent. **1927**, II 1085; C.A. **21**, 745 (1927). (37) Ott, Ber. **55**, 2108–2125 (1922). (38) Darapsky, Gaudian, J. prakt. Chem. (2) **147**, 47–48 (1936). (39) Lindemann, Schultheis, Ann. **464**, 249–253 (1928). (40) Clar, St. John, Hawran, Ber. **62**, 940–950 (1929).

(41) Hoogewerff, van Dorp, Rec. trav. chim
11, 91-94 (1892)
(42) Scheiber, Knothe, Ber. 45, 2252-2255 (1912).
(43) von Braun, Kaiser, Ber. 55, 1307-1310 (1922).
(44) Maxim, Compt. rend. 184, 690 (1927).
(45) French 785,428, Aug. 9, 1935; Cent. 1935, II 3441; C.A. 30, 488 (1936).
(46) Evans, Dehn, J. Am. Chem. Soc. 51, 3652 (1929).

---- 2,3,5,6,6-HEXACHLOROCYCLOHEXEN-2-DIONE-1,4

 $C_6 C_2 C_1$ $C_1 C_2$ $C_1 C_2$

Beil. VII - 574 VII₁—

B.P. 275-285° dec.

M.P. 89°

See 3:2360. Division A: Solids.

B.P. 280-281° (1) $D_{22}^{22} = 1.607 (1)$

Oil which below 0° solidifies to colorless cryst.

[For prepn. of \tilde{C} from 2,4,5-trichlorotoluene (3:2100) at b.p. with Cl₂ see (1); for formn. of \tilde{C} from toluene in AcOH/HCl on electrolysis in dark see (6).]

 \bar{C} on hydrolysis with fumg. H₂SO₄ (2), warm conc. H₂SO₄ (3), or with aq. in s.t. at 260° (4) (1) gives 2,4,5-trichlorobenzaldehyde (3:3375).

[For use of \bar{C} in prepn. of dyestuffs see (5).]

3:6910 (1) Beilstein, Kuhlberg, Ann. 150, 299 (1869). (2) Seelig, Ann. 237, 148-149 (1887). (3) Fischer, Ger. 25,827; June 23, 1883, Friedländer 1, 42 (1877-87). (4) Beilstein, Kuhlberg, Ann. 152, 238-239 (1869). (5) Schmidlin (to Cassella and Co.), Ger. 363,290, Nov. 6, 1922; Cent. 1923, II 482; not in C.A. (6) Fichter, Glantzstein, Ber. 49, 2484 (1916).

--- 2,6-DICHLORONAPHTHALENE

Beil. V - 544 $C_{10}H_6Cl_2$ V1--- V_2 -(446)

B.P. 285° u.c.

M.P. 136°

See 3:4040. Division A: Solids.

 1,7-DICHLORONAPHTHALENE (2,8-Dichloronaphthalene)

 $C_{10}H_6Cl_2$ Beil. V - 543 V1-(263) V₂-(446)

B.P. 286° u.c.

M.P. 63.5-64.5°

See 3:1385. Division A: Solids.

---- 1.4-DICHLORONAPHTHALENE

 $C_{10}H_6Cl_2$ Beil. V - 542 CI V_{1} -(262) V_{2} -(445)

B.P. 286-287° at 740 mm. M.P. 68°

See 3:1655. Division A: Solids.

---- 1,3-DICHLORONAPHTHALENE

 $C_{10}H_6Cl_2$ Beil. V - 542 V_{1} -(262) V_{2} -(445)

B.P. 291° cor. at 775 mm. See 3:1310. Division A: Solids.

— 1,2-DICHLORONAPHTHALENE Beil. V - 542 $C_{10}H_6Cl_2$ V_{1} -(262) V_{2} -(445)

M.P. 61-62°

B.P. 295-298°

M.P. 34-35°

See 3:0320. Division A: Solids.

3:6930 a-NAPHTHOYL CHLORIDE

C₁₁H₇OCl Beil. IX - 648 IX_{1} -(275)

B.P. M.P. 26° (7) 297.5° (1) 182-183° at 14 mm. (2) 22° (5) 20° (3) (9) 172-173° at 15 mm. (3) (4) 167-168° at 15 mm. (11) 158° at 12 mm. (5) 168° at 10 mm. (6)

163° at 10 mm. (7) (8) [For prepn. of \tilde{C} from α -naphthoic acid (1:0785) with PCl₅ (yield: 100% (4) (8)) (6) (1) (11) in CCl₄ (10) or with SOCl₂ (12) (13) (14) (7) see indic. refs.]

 \tilde{C} + anhyd. Na₂CO₃ + pyridine treated with a few drops of aq. (14), or \tilde{C} with various RMgX or other organometallic epds. (15), or \tilde{C} htd. with Ca α -naphthoate (1), gives (80% yield (14)) α -naphthoic acid anhydride, pr. from C₆H₆, m.p. 145-146° (1) (14) (15).

[C on cat. hydrogenation gives (33% yield (5)) α-naphthaldehyde [Beil. VII-400, VII₁-

(212)], b.p. 173-174° at 35 mm. (p-nitrophenylhydrazone, m.p. 233-235° (5)).]

[\bar{C} with AlCl₃ + hydrocarbons give corresp. α -naphthyl ketones: e.g., with C₆H₆ (6), biphenyl (8), α -methylnaphthalene (16), β -methylnaphthalene (17) (18), with 2,3- (19), 2,6- and 2,7- (20) dimethyl-naphthalenes, with various subst. perylenes (21) (22), see indic. refs.; \bar{C} with RMgX cpds. also yields corresp. α -naphthyl ketones: e.g., with α -naphthyl MgBr (14) or α -tetralyl MgBr (23), see indic. refs.]

 \bar{C} with aq. hydrolyzes very slowly (9) yielding α -naphthoic acid (1.0785) m.p. 161–162°. — For the amide, anilide, and other derivs. corresp. to \bar{C} see α -naphthoic acid (1.0785);

in addition to these see below.

 \bigoplus α -Naphthoic β -naphthalide: cryst. from alc., m.p. 200° (13). [From $\bar{C} + \beta$ -naphthylamine in C_6H_6 (13).]

3:6930 (1) Hofmann, Ber. 1, 41-42 (1868). (2) Bergmann, Schuchardt, Ann. 487, 253 (1931). (3) Linnell, Roushdi, Quart. J. Pharm. Pharmacol. 14, 270-280 (1941). (4) von Braun, Ber. 38, 180 (1905). (5) Shoesmith, Guthrie, J. Chem. Soc. 1928, 2332 (6) Reddelen, Ber. 46, 2722, Note 2 (1913). (7) Bell, J. Chem. Soc. 1930, 1984-1985. (8) Schmidlin, Garcia-Banus, Ber. 45, 3183 (1912) (9) Pope, Winmill, J. Chem. Soc. 101, 2316 (1912). (10) West, J. Am. Chem. Soc. 42, 1662 (1920).

Szperl, Herszaft, Roczniki Chem. 14, 1238-1242 (1934), Cent. 1935, I 2530. (12) Stollé,
 J. prakt. Chem. (2) 74, 19 (1906). (13) Bockmann, Luesche, Correns, Ber. 56, 354 (1923). (14)
 Blicke, J. Am. Chem. Soc. 49, 2847-2848 (1927). (15) Bruce, J. Am. Chem. Soc. 60, 2277 (1938).
 Cook, Robinson, J. Chem. Soc. 1938, 510. (17) Clar, Ber. 62, 355-356 (1929). (18) French
 Gl4,959, Dec. 27, 1926; Cent. 1929, II 796. (19) Cook, J. Chem. Soc. 1933, 1596. (20) Cook,
 J. Chem. Soc. 1932, 492.

(21) Zinke, Funke, Ber. 58, 2222-2227 (1925).
 (22) French 589,643, June 2, 1925; Cent. 1926,
 I 1053.
 (23) Fieser, Seligman, J. Am. Chem. Soc. 58, 478-480 (1936).

---- 2,5-DICHLOROBENZOIC ACID

 $C_7H_4O_2Cl_2$ Beil. IX - 342 IX₁-(141)

B.P. 301°

M.P. 155°

See 3:4340. Division A: Solids.

---- 2,3,4,5,6-PENTACHLOROTOLUENE

 $\begin{array}{cccc} {\rm CH_3} & {\rm C_7H_3Cl_5} & & {\rm Beil.} \ {\rm V} - {\bf 303} \\ {\rm Cl} & & {\rm V_{1-}(153)} \\ {\rm Cl} & & {\rm V_{2-}(234)} \end{array}$

B.P. 301°

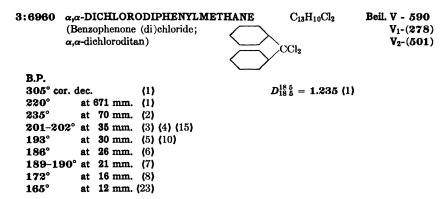
M.P. 224-225°

See 3:4937. Division A: Solids.

B.P. 304-306°

M.P. 51°

See 3:0900. Division A: Solids.



Colorless oil showing bluish fluorescence and having only faint odor (3).

[For prepn. of \bar{C} from benzophenone (1:5150) with PCl₅ (yield: 90% (3), 85% (7), 68% (9)) (1) (10) (11) (12) (15); with PCl₅ in C_6H_6 (92% yield (13)), or with oxalyl dichloride (3:5060) in s.t. at 130-140° (14) see indic. refs.; from C_6H_6 + AlCl₃ + excess CCl₄ (yield: 90-95% (16), 80-90% (18)) (17) see indic. refs.; for formn. of \bar{C} from diphenylmethane (1:7120) with PCl₅ in s.t. at 170° see (13), from bis-(triphenylmethyl) peroxide with PCl₅ (19) or with Cl₂ in CCl₄ in pres. of I₂ (19), from diphenyldiazomethane with SOCl₂ or SO₂Cl₂ in pet. ether (100% yield (20)), or from benzotriehloride (3:6540) htd. with uranium metal at 115-128° (4) see indic. refs.]

[For use of \bar{C} in prepn. of acid anhydrides by htg. at 110–120° with salts of aliph. or arom. acids see (21).]

 \bar{C} hydrolyzes slowly with cold but rapidly with hot aq. yielding (1) benzophenone (1:5150) and HCl (for study of rate of hydrol, of ether soln, on shaking with aq. see (22)); \bar{C} dis. in conc. H₂SO₄ with yel, color (which grad, disappears) and on pouring onto ice yields (6) benzophenone (1:5150); \bar{C} in dry ether shaken 2 hrs. with silver oxide gives (78% yield (23)) benzophenone (1:5150); \bar{C} with alc. NH₃ yields (33) benzophenone.

 \ddot{C} with MeOH alone (6), with dry MeOH + Mg (24), with dry MeOH in dry pyridine at 0° (25), with NaOMe in MeOH (3) (26), or with NaN₃ in dry MeOH (27) gives (yields: 86% (6) (24), 81% (3)) α,α -dimethoxy-diphenylmethane (benzophenone dimethylacetal) [Beil. VII-415], cryst. from MeOH, m.p. 107-108° (25), 107.5° cor. (24), 106.5-107° (3) (for application to higher alcs. see (3) (26)).

Č htd. with Ag (11) (5), or stood overnight with Ag or Zn in dry EtOAc (28) cf. (29), or refluxed in CS₂ with 3-4 moles Hg (28) (less Hg gives different result), or with 2 moles NaI in boilg. acetone (30) (1 mole NaI gives different result), or with excess cyclohexyl-MgBr (31) (less reagent gives different result), or with Na in liq. NH₃ (90% yield (32)) or htd. 8 hrs. with diphenylmethane (1:7120) (88% yield (12)) gives tetraphenylethylene [Beil. V-743, V₁-(376)], m.p. 227° cor., 222° u.c. (31), 221° (11). — [Č does not react with

Mg in dry ether even in pres. of I_2 (28).] — [\check{C} refluxed in CS_2 with less than 3 moles Hg (28), or \check{C} with 1 mole NaI in acetone in cold (30), or \check{C} with 1 mole cyclohexyl MgBr (31), gives tetraphenylethylene dichloride [Beil. V_1 -(371)], cryst. from ether, m.p. 186° cor. dec. (31).]

[Č with 2 moles Ag azide in ether gives (88% yield (34)) benzophenone diazide, m.p. 42°; Č treated as directed (15) with alc. NaSH gives 42–50% yield thiobenzophenone [Beil. VII-429, VII₁-(232)], cryst. from pet. ether, m.p. 53–54° (15) (note that an excess of Č must always be present to prevent reduction of the thiobenzophenone to dibenzohydryl disulfide [Beil. VI-681], ndls. from alc., m.p. 152°, and that the latter is obtd. in 70% yield (15) if Č is added to the alc. NaSH instead of the reverse); for reactn. of Č with diethyl sodio-malonate (2) (9) or with ethyl sodioacetoacetate (8) see indic. refs.; for reaction of Č with SbF₃ yielding α,α -difluorodiphenylmethane, b.p. 260° dec., 125° at 10 mm., m.p. -1.8° , $D_{4}^{20} = 1.1614$, $n_{D}^{20} = 1.53786$, see (35).]

 \bar{C} with 4 moles aniline in cold gives (36) benzophenone anil [Beil. XII-201, XII₁-(174)] + aniline hydrochloride; the former is sol. in ether, the latter in aq.; sepn. of the layers and addition of alc. to the ether ppts. benzophenone anil, pale yel. lfts. from abs. alc., m.p. 109° u.c. (36) 113°.

3:6960 (1) Kekulé, Franchimont, Ber. 5, 908-909 (1872). (2) Phalnikar, Nargund, J. Univ. Bombay 5, Part 2, 105-108 (1936); Cent. 1938, I 61, C.A. 31, 3036 (1937). (3) Mackenzie, J. Chem. Soc. 69, 987-991 (1896). (4) Lal, Dutt, J. Indian Chem. Soc. 12, 390 (1935). (5) Anschütz, Ann. 235, 221-222 (1886). (6) Straus, Ecker, Ber 39, 3005 (1906). (7) Hsu, Ingold, Wilson, J. Chem. Soc. 1935, 1782. (8) Klages, Fanto, Ber. 32, 1433 (1899). (9) Adickes, J. prakt. Chem. (2) 145, 239 (1936). (10) Gattermann, Schulze, Ber. 29, 2944-2945 (1896). (11) Behr, Ber. 3, 752 (1870). (12) Norris, Thomas, Brown, Ber. 43, 2958-2959 (1910). (13)

(11) Behr, Ber. 3, 752 (1870).
 (12) Norris, Thomas, Brown, Ber. 43, 2958-2959 (1910).
 (13) Cone, Robinson, Ber. 40, 2161-2162 (1907).
 (14) Staudinger, Ber. 42, 3976 (1909).
 (15) Staudinger, Freudenberger, Org. Syntheses, Coll. Vol. 2 (1st ed.), 573-574 (1943); 11, 94-95 (1931).
 (16) Gomberg, Jickling, J. Am. Chem. Soc. 37, 2577-2578 (1915).
 (17) Riddell, Noller, J. Am. Chem. Soc. 54, 292 (1932).
 (18) Boeseken, Rec. trav. chim. 23, 101-102 (1904), 24, 1-3 (1905).
 (19) Gomberg, Cone, Ber. 37, 3544 (1904).
 (20) Staudinger, Anthes, Pfenninger, Ber. 49, 1941 (1916).

(21) Evlampiev, Russ. 52,811, March 31, 1938; Cent. 1939, I 1449, C.A 34, 5468 (1940). (22) Straus, Hussey, Ber. 42, 2171 (1909). (23) Straus, Caspari, Ber. 40, 2709 (1907). (24) Zechmeister, Rom, Ann. 468, 127 (1928). (25) Papadakis, J. Am. Chem. Soc. 58, 666 (1936). (26) Mackenzie, J. Chem. Soc. 121, 1095-1096 (1922). (27) Schroeter, Ber. 42, 2340-2342 (1909). (28) Ref. 12, pp. 2946-2947. (29) Staudinger, Clar, Czako, Ber. 44, 1644 (1911). (30) Finkelstein, Ber. 43, 1532-1533 (1910).

(31) Schmidlin, von Escher, Ber. 45, 894-895 (1912); 43, 1157, 1159 (1910). (32) Dean, Berchet, J. Am. Chem. Soc. 52, 2825 (1930). (33) Pauly, Ann. 187, 217-220 (1877). (34) Götzky, Ber. 64, 1558 (1931). (35) Henne, Leicester, J. Am. Chem. Soc. 60, 864-865 (1938). (36) Ref. 33, pp. 199-202.

[For prepn. of \bar{C} from 2,3,4,6-tetrachlorotoluene (3:2480) or from 2,3,5,6-tetrachlorotoluene (3:2575) at their b.p.'s with Cl₂ (1) or with Cl₂ at 100-130° (especially in light from Hg-vapor lamp) (2) see indic. refs.]

Č with strong H₂SO₄ at 90° is hydrolyzed (2) to 2,3,4,6-(or 2,3,5,6-)-tetrachlorobenzalde-hyde (3:2700).

3:6980 (1) Beilstein, Kuhlberg, Ann. **150**, 303-304 (1869). (2) Cassella and Co., Ger. 290, 209, Feb. 8, 1916; Cent. **1916**, I 396-397; not in C.A.

---- PENTACHLOROPHENOL

B.P. 309-310° at 754 mm.

M.P. 190°

See 3:4850. Division A: Solids.

---- 4,5-DICHLOROPHTHALIC ANHYDRIDE

TORIDE C₈H₂O₃Cl₂ Beil. XVII - 483 XVII₁-(254)

B.P. 313°

M.P. 187-188°

See 3:4830. Division A: Solids.

--- 4,4'-DICHLOROBIPHENYL

B.P. 315°

M.P. 148°

See 3:4300. Division A: Solids.

---- 3.3'-DICHLOROBIPHENYL

B.P. 326°

M.P. 29°

See 3:0180. Division A: Solids.

---- HEXACHLOROBENZENE

B.P. 326°

M.P. 229°

See 3:4939. Division A: Solids.

3:6980

3,6-DICHLOROPHTHALIC ANHYDRIDE

 $C_8H_2O_3Cl_2$

Beil. XVII - 483 XVII₁-(254)

Beil. VII - 420 VII₁-(228)

B.P. 339°

M.P. 194°

See 3:4860. Division A: Solids.

---- 4,4'-DICHLOROBENZOPHENONE

Clash & OCl2

B.P. 353° at 757 mm.

M.P. 145°

See 3:4270. Division A: Solids.

- OCTACHLORONAPHTHALENE

B.P. 440-442°

M.P. 203°

See 3:4893. Division A: Solids.

CHAPTER XVI

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 2. D_4^{20} less than 1.1500

(3:7000-3:7499)

3:7000	CHLOROACETYLENE (Chloroethyne)	HC≡C—Cl	C₂HCl	Beil. I - 244 I ₁ -(106) I ₂ -(221)
B.P	29.6° (1) 32 to -30° (2)			-2 ()

[See also dichloroacetylene (3:5010).]

C is a gas with extremely nauseating odor reminiscent both of yellow phosphorus and of carbylamines; its inhalation even in traces produces very unpleasant symptoms. It is also treacherously explosive and may detonate during manipulation (2). — C ignites spontaneously in air (6) (3).

[For prepn. of C from cis-1,2-dichloroethylene (3.5042) via treatment in dil. alc. with aq. alk. Hg(CN)₂ to yield Hg(C=CCl)₂ (see below) which is then warmed (under N₂) with alk. NaCN soln. see (1) (2) (3) (4)] cf. (7).

[For formn. of C during reaction of 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) with solid KOH see (5); from 1,2-dichloroethylene with alc. KOH see (3) (4); from \$,\$-dichloroacrylic acid (3:1875) with Ba(OH)₂ see (6).]

C with NH₄OH/CuCl gives (3) (6) an explosive ppt. — C with NH₄OH/AgNO₃ gives (2) (3) a ppt. of silver salt, which is extremely explosive, detonating with great violence not only in dry state but also when moist and even under water, quantities as small as 0.1 g. causing considerable damage (2).

C with aq. alk. Hg(CN)₂ yields (3) (4) (1) (2) a mercury salt, Hg(C=CCl)₂, cryst. from CHCl₃ (1) (2) (3) (4), m.p. 185° (1) (4), 186° (2); explodes at 195° with flame and deposition of soot (3) (4). [This prod. with alk. KCN evolves C (use in prepn. of C as above).]

Č with Br₂/aq. yields (6) 1-chloro-1,1,2,2-tetrabromoethane [Beil. I-95], m.p. 33-34° (6). [For other reactns, see (2) (7); for study of oxidation of \bar{C} see (1).]

3:7000 (1) Bashford, Emeléus, Briscoe, J. Chem. Soc. 1938, 1358-1364. (2) Ingold, J. Chem. Soc. 125, 1535-1536 (1924). (3) Hofmann, Kirmreuther, Ber. 42, 4232-4238 (1909). (4) Hofmann, Kirmreuther, Ber. 41, 314-317 (1908). (5) Sastry, J. Soc. Chem. Ind. 35, 450-452 (6) Wallach, Ann. 203, 87-94 (1880). (7) Ott, Dittus, Weissenburger, Ber. 76, 87-88 (1916).(1943).

3:7005	CHLOROMETHANE (Methyl chloride)	CH₃.Cl	CH ₃ Cl	Beil. I - 59 I ₁ -(8) I ₂ -(11)
	2° at 760 mm. (1) ° at 760 mm. (3) (4)	M.P. -97.72° (1) -96.65° (2)	$n_{ m D}^{-42}$.5 = 1.3830 (3)

930

Colorless gas with ethereal faintly sweet non-irritating odor. — Important comml. fluid for refrigerating systems; for extensive reviews of properties, uses, handling, toxicity, hazards, etc., see (4) (5) (6). — For b.p. at various pressures from 26-761 mm. together with extensive thermodynamic data see (1) (4). — Solubility of \bar{C} (in cc.) in 100 cc. solvent at 20°C and 760 mm.: water, 303; EtOH, 3740; AcOH, 3679; CCl₄, 3756; C₆H₆, 4723 (4); for extensive data on solubility of \bar{C} in other solvents see (7) (8) (9).

[For prepn. of \bar{C} from MeOH (1:6120) with conc. H₂SO₄ + NaCl (10); with conc. HCl + ZnCl₂ (yield: 79% (11), (12)); with HCl gas + various catalysts (13) (14) (15); with PCl₃ + ZnCl₂ (68% yield (11)); with PCl₅ + ZnCl₂ (72% yield (11)); with SOCl₂ + pyridine (80% yield (11)); with AlCl₃ (100% yield (16)); with FeCl₃ (17) (20) see indic. refs.; for prepn. of \bar{C} from Me₂SO₄ with strong HCl (or NaCl) (90% yield (18)) or with AlCl₃ (100% yield (19)) see indic. refs.] [For study of mechanism of formn. of \bar{C} from MeOH + HCl see (24).] [For formn. (53% yield) from NH₄Cl with diazomethane in ether see (36).]

[For study of drying of \bar{C} see (21); for detn. of aq. in \bar{C} see (22); for study of pyrolysis see (23); for behavior with Na see (25).]

 \tilde{C} on warming with NaI in MeOH or EtOH gives (26) methyl iodide, b.p. 42°. [Use in detection and detn. of \tilde{C} (26).]

 \ddot{C} is inflammable in air within range 8.1-17.2% by vol. (4) (28) cf. (35). — [For study of detn. of \ddot{C} via combustion see (27) (29) (31) (32).] — \ddot{C} on burning in presence of copper gives strong Beilstein test; [use in detection and detn. of \ddot{C} in air and foods (29); for testing device see (30)].

[For detn. of \bar{C} by absorption in AcOH see (27); for detn. of small amts. of \bar{C} in air (31) (37) or in mixts. with other gases (32) see indic. refs.]

- Acetanilide: m.p. 112-113° u.c. (33). [From C via conversion to CH₃MgCl and reaction with phenyl isocyanate (33): note that C with Mg in dry ether + trace I₂ gives in 4 hrs. (99.7% yield) MeMgCl (38).]
- —— N-Methyl-3-nitrophthalimide: ndls. from CS₂, m.p. 112-113° (34). [Not recorded directly from C but from MeI by reactn. with K 3-nitrophthalimide; probably therefore from C + NaI + K 3-nitrophthalimide in MeOH.]
- 3:7005 (1) Messerly, Aston, J. Am. Chem. Soc. 62, 886-890 (1940). (2) Booth, Martin, J. Am. Chem. Soc. 64, 2201 (1942). (3) Grosse, J. Am. Chem. Soc. 59, 2739-2741 (1937). (4) Willson, Walker, Rinelli, Mars, Chem. Eng. News, 21, 1254-1261 (1943). (5) McGovern, Refrig. Eng. 34, 29-38 (1937). (6) Churchill, Ind. Eng. Chem. 24, 623-626 (1932). (7) Zellhoefer, Ind. Eng. Chem. 29, 548-551 (1937). (8) Zellhoefer, Copley, Marvel, J. Am. Chem. Soc. 60, 1338 (1938) (9) Kaplan, Romanchuk, J. Gen. Chem. (U.S.S.R.) 6, 950-954 (1936), Cent 1937, II 1771; C.A. 31, 594 (1937). (10) L. I. Smith, Org. Syntheses, Coll. Vol. 2 (1st ed.), 251-252, Note 3 (1943).
- (11) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929). (12) Norris, Taylor, J. Am. Chem. Soc. 46, 756 (1924). (13) McKee, Burke, U.S. 1,738,193, Dec. 3, 1929; Cent. 1930, 13829. (14) Carlisle (to Roessler & Hasslacher Chem. Co.), U.S. 1,834,089, Dec. 1, 1931; Cent. 1932, I 1438. (15) Daudt (to du Pont), U.S. 2,016,075, Oct. 1,1935; Cent. 1936, I 2206. (16) Norris, Sturgis, J. Am. Chem. Soc. 61, 1415 (1939). (17) Harding (to Roessler & Hasslacher Chem. Co.), U.S. 1,816,845, Aug. 4, 1931; Cent. 1931, II 3392. (18) Boulin, Simon, Compt. rend. 170, 595-597 (1920); C.A. 14, 2623 (1920). (19) Shamshurin, J. Gen. Chem. (U.S.S.R.) 9, 2207-2208 (1939); C.A. 34, 4052 (1940). (20) Dangyan, J. Gen. Chem. (U.S.S.R.) 9, 1907-1910 (1939); C.A. 34, 4052 (1940).
- (21) McGovern, Power 79, 579-580 (1935); C.A. 30, 654 (1936). (22) Walker, Rinelli (to Ansul Chem. Co.), U.S. 2,145,203, Jan. 24, 1939; Cent. 1939, I 3778. (23) Wiesler, Chem. Ztg. 52, 182-183 (1928). (24) Hinshelwood, J. Chem. Soc. 1935, 599-601. (25) Morton, LeFevre, Hechenbleikner, J. Am. Chem. Soc. 58, 757 (1936). (26) Roka, Fuchs, Z. anal. Chem. 71, 381-386 (1927). (27) Allison, Meighan, Ind. Eng. Chem. 11, 943-946 (1919). (28) Jones, Ind. Eng. Chem. 20, 367-370 (1928). (29) Martinek, Marti, Ind. Eng. Chem., Anal. Ed. 3, 408-410 (1931). (30) Lamb, U.S. 1,864,544, June 28, 1932; C.A. 26, 4214 (1932).

(31) Patty, Schrenk, Yant, Ind. Eng. Chem., Anal. Ed. 4, 259-262 (1932). (32) McKee, Burke, Ind. Eng. Chem. 15, 578-579 (1923). (33) Underwood, Gale, J. Am. Chem. Soc. 56, 2119 (1934). (34) Sah, Ma, Ber. 65, 1632 (1932). (35) Willson, Walker, Ind. Eng. Chem. 36, 466-468 (1944). (36) Frankel, Katchalski, J. Am. Chem. Soc. 66, 764-765 (1944). (37) Franklin, Gunn, Martin, Ind. Eng. Chem., Anal. Ed. 18, 314-317 (1946). (38) Houben, Boedler, Fischer, Ber. 69, 1768, 1774-1775 (1936).

3:7010 CHLOROETHENE CH₂=CHCl C₂H₃Cl Beil. I - 186 (Vinyl chloride) I_1 -(77) I_2 -(157)

B.P. -13.9° at 760 mm. (1) F.P. -159.7° (1)

Colorless gas easily liquefied by cooling. — For b.p.'s at various pressures from 39.5—760.3 mm. see (1). — Readily polymerizes in light or in dark if catalysts are present. The literature on polymerization of \bar{C} and on its polymers and copolymers is extremely extensive and cannot be treated here.

[For prepn. of \bar{C} from 1,2-dichloroethane (ethylene dichloride) (3:5130) by action of alc. KOH (85% yield (2)) see (2) (3); for prepn. of \bar{C} from acetylene by addn. of HCl see (4) (5) (14) (15) + Beil.; for purification of \bar{C} with conc. H₂SO₄ see (8).]

Č as liq. + SO₂ as liq. in 95% alc. + catalyst gives ppt. (6) of insol. pdr. of vinyl chloride polysulfone [(CH₂=CHCl)₂.SO₂]_n, darkens 135-140°, melts 250-275° (6); on hydrolysis with 20% aq. NaOH this polymer gives (7) acetaldehyde (1:0100) q.v.

 $\ddot{\mathbf{C}}$ adds HBr to give according to conditions (9) (10) either 100% 1-chloro-1-bromoethane (ethylidene chlorobromide), b.p. 82.7° at 760 mm. (11), b.p. 80.5-81.5° at 735 mm. (9), $n_D^{20} = 1.4660$ (9), or 1-chloro-2-bromoethane (ethylene chlorobromide), b.p. 106.7° at 760 mm. (12), b.p. $104-105^\circ$ at 735 mm. (9), $n_D^{20} = 1.4908$ (9). [Note: the ethylidene chlorobromide may be further identified by htg. with moist silver oxide in a s.t. for 5 hrs. at 100° giving acetaldehyde (1:0100) q.v.; the ethylene chlorobromide may be further identified by refluxing with aniline to yield N,N'-diphenylethylenediamine, m.p. $63.5-64^\circ$ (9).]

Č with HI yields only (9) 1-chloro-1-iodoethane (ethylidene chloroiodide), b.p. 117-119° (13), 114-115° (9).

Č adds Br₂ yielding (16) (17) 1-chloro-1,2-dibromoethane, b.p. 159-160° (16); 163° at 760 mm., 48° at 12 mm.; $D_{-i}^{19} = 2.248$; $n_{-}^{19} = 1.554$ (17); for study of this photochem. reaction see (18).

3:7010 (1) Dana, Burdick, Jenkins, J. Am. Chem. Soc. 49, 2802-2805 (1927). (2) Ostromysslenski, J. Russ. Phys.-Chem. Soc. 48, 1132-1151 (1916); Cent. 1923, IV 606. (3) Brous (to B. F. Goodrich Co.), U.S. 2,041,814, May 26, 1936; Cent. 1936, II 4048. (4) Wibaut, van Dalfsen, Rec. trav. chim. 51, 636-640 (1932). (5) van Dalfsen, Wibaut, Rec. trav. chim. 53, 489-496 (1934). (6) Marvel, Glavis, J. Am. Chem. Soc. 60, 2622-2628 (1938). (7) Marvel, Dunlap, J. Am. Chem. Soc. 61, 2709-2710 (1939). (8) Dosser, Arnold (to Dow Chem. Co.), U.S. 2,266,177, Dec. 16, 1941; C.A. 36, 2271 (1942). (9) Kharasch, Hannum, J. Am. Chem. Soc. 56, 712-714 (1934). (10) Kharasch, Haefele, Mayo, J. Am. Chem. Soc. 62, 2049 (1940).

(11) Städel, Denzel, Ber. 15, 2563 (1882). (12) Timmermans, Bull. soc. chim. Belg. 25, 300-327 (1911); Cent. 1911, II 1015. (13) Simpson, Bull. soc. chim. (2) 31, 411 (1879). (14) Toussaint (to Carbide and Carbon Chem. Corp.), U.S. 1,926,638, Sept. 12, 1933; C.A. 27, 5756 (1933). (15) Perkins (to Carbide and Carbon Chem. Corp.), U.S. 1,934,824, Nov. 7, 1933; C.A. 28, 488 (1934). (16) Földi, Ber. 60, 659 (1927). (17) Kirrmann, Bull. soc. chim. (5) 6, 846 (1939). (18) Schmitz, Schumacher, Z. physik. Chem. B-52, 80-89 (1942).

3: 7015 ETHYL CHLORIDE (Chloroethane) CH₈CH₂Cl C₂H₅Cl Beil. I - 82 I₁-(23) I₂-(50)

B.P. F.P. +13.1° at 760 mm. (1) (2) -142.5° (15) [
$$D_4^{15} = 0.90280$$
 (11)] 12.6° (3) -141.6° (16) $n_D^0 = 1.3790$ (10) [12.5-12.6° at 725 mm. (4)] -140° (17) $D_{12}^{12} = 0.8510$ (19) 12.52° (5) -139.4° (18) $n_D^{-20} = 1.3913$ (2) 12.50° (6) -138.7° (1) $D_8^8 = 0.9176$ (12) 12.5° (7) (8) (9) -136.4° (11) $n_D^{-50} = 1.4085$ (2) 12.4° (10) $D_0^0 = 0.92138$ (20) 12.18° at 760 mm. (12) 12-12.5° (13) (14)

Colorless mobile liq. with pungent ethereal odor and sweetish taste. — $\bar{\mathbf{C}}$ is inflammable (see also below) and burns with smoky green-edged flame producing fumes of HCl.

SELECTED PHYSICAL PROPERTIES

Vapor pressure. [For vapor-press. data over various temp. ranges, e.g., from -30 to $+40^{\circ}$ (5), -30° to 100° (21), $12-187^{\circ}$ (4) (22), see indic. refs.]

Solubility relations. \bar{C} is very spar. sol. aq., e.g., 100 g. aq. at 0° dis. 0.447 g. \bar{C} (23), 0.570 wt. % (24), although even this is somewhat more than its homologs (24).

 \bar{C} is miscible with EtOH although forced out of soln. by addn. of aq. (25); for use of mixt. of EtOH (50-80%) + aq. (50-20%) as selective solv. for \bar{C} in sepn. from butane see (26). — \bar{C} is also miscible with ether. — [For study of rate of volatilization of \bar{C} from solns. in ether or oils see (32).]

[For soly. of \bar{C} in CCl₄ (3:5100) or in ethylene dichloride (3:5130) at -10° and 20° and at 100-760 mm. press. see (27); for soly. of \bar{C} in various high-boilg. ethers and esters of interest to refrigeration industry see (28) (29); for solubility, density, b.p., vapor/liq. equil., etc., of system \bar{C} + kerosene see (30); for sepn. of \bar{C} from butane by azeotropic distn. with SO₂ see (31).]

[For soly. in \bar{C} of anhydrous FeCl₃ (33) (34) or anhydrous AlCl₃ (35) (36) see indic. refs.] Adsorption of \bar{C} . [For studies on adsorption of vapors of \bar{C} by activated carbon at -15° (37), 0° (37) (38), 20° (37), 25° (39), or 50° (40) see indic. refs. and also (41); for sepn. of \bar{C} from ethylene + HCl gas by adsorption on carbon see (42). — For adsorption of vapors of \bar{C} by dehydrated chabasite see (43).]

Inflammability of \bar{C} or its mixtures. \bar{C} is readily inflammable; in mixts. with air explosive range conts. 4.00–14.18 vol. % \bar{C} with minimum ignition temp. 517°C. (44) cf. (47) (48); in mixts. with O₂ explosive range conts. 4.05–67.2 vol. % \bar{C} (44) (45) with min. ignition temp. 468°C.; in mixts. with N₂O explosive range conts. 2.1–32.8 vol. % \bar{C} (45) cf. (46); for study of explosion range of \bar{C} + C₂Cl₂F₂ ("Freon") + air or \bar{C} + butane + air see (49). — See also below under use of \bar{C} as anesthetic.

Other miscellaneous physical props. [For study of thermal conductivity of \bar{C} see (50).] Binary systems contg. \bar{C} . [For f.p./compn. data and diagram of system \bar{C} + methylene (di)chloride (3:5020), eutectic, f.p. -149.7° , contg. 68.3 wt. % \bar{C} , see (18); for f.p./compn. data and diag. of system \bar{C} + EtBr (note no eutectic is formed) see (18); for system \bar{C} + solid CO₂ see (8).]

TOXICITY AND PHYSIOLOGICAL ACTION OF C

Full treatment of this topic is beyond the scope of this work; however, for lead references on its pharmacology (51), toxicity (52) (53) (54) (55), or anthelmintic props. (56) see indicrefs. — For use as narcotic and anesthetic see below.

USES OF C

Use for anesthesia and narcosis. [For general reviews on use of \bar{C} as anesthetic see (57) (58) (59) (60); for use of \bar{C} as dental anesthetic see (61) (62) (63); for short narcosis see (64) (65). — For data on mortality from use of \bar{C} as anesthetic see (66). — For studies of explosion hazards with \bar{C} or \bar{C} + ether (67) especially in presence of X-ray apparatus (68) see indic. refs. (see also above under inflammability of \bar{C}).]

Use as a refrigerant. \tilde{C} either alone or mixed with other cpds. is often used in refrigerating systems: e.g., for general survey of this aspect see (21); for examples of patents on use in refrigerating systems of \tilde{C} (70), of \tilde{C} (96%) + MeCl (4%) (3:7005) (71), of \tilde{C} (25%) + methylene (di)chloride (3:5020) (75%) (72), of \tilde{C} (40%) + EtBr (60%) (72), of \tilde{C} + an alc. + a hydrocarbon lubricant (74) see indic. refs. — For study of use of \tilde{C} with other suitable liq. in low-temp. cryostats see (18).

Use as solvent for extraction of oils. For use of \bar{C} as extremely volatile solvent for extraction of oils, fats, resins, perfumes, etc., see (75) (76) (77).

Miscellaneous uses of $\tilde{\mathbf{C}}$. $\tilde{\mathbf{C}}$ is now an important raw material in the prepn. of tetraethyllead for use as an anti-knock agent in gasoline; for further details see below under chem. behavior of $\tilde{\mathbf{C}}$ toward metals.

[For use of C in purification of metallic mercury see (78).]

Because of its inertness toward ozone, its availability, and its low b.p., Č is often used as solvent for ozonolysis.

DETERMINATION OF C

For detn. of \bar{C} by pyrolytic dissociation at 900° into ethylene and HCl, followed by detn. of chloride ion with stand. AgNO₃ (42) (80) cf. (81) or by combustion with O₂ in an explosion pipet to yield H₂O, CO₂ + HCl (47), see indic. refs. — For detn. of \bar{C} by hydrolysis with excess std. N/2 alc. KOH in s.t. at 120° for 15 min. and back titration with N/2 HCl see (79).

For detn. of \tilde{C} in CHCl₃ (3:5050) see (82); for detection of \tilde{C} in perfumes see (83). For further aspects of identification of \tilde{C} see below under \mathfrak{D} .

PREPARATION OF C

Č can be prepared from various sources and by many methods (see amplification below); however, for quick laboratory methods the most convenient are those from EtOH by htg. with AlCl₃ (1 mole) at 150° (97.6% yield (13)) and from diethyl sulfate with aq. CaCl₂ (63% yield (84)).

From ethyl alcohol (1:6130).

With hydrogen chloride or hydrochloric acid. [For prepn. of \bar{C} from EtOH by reactn. with HCl in absence of cat. under reflux (85) (86) or at 125° and 16 atm. (87), or 140° and 24 atm. (88), see indic. refs.; for use of EtOH + liq. HCl see (89).]

For prepn. of C from EtOH with conc. HCl in pres. of ZnCl₂ (60% yield (7) (91)) see articles represented by (90) (7) (91) (92) (93) [for patents (often including also other metal salt cat. such as BiCl₃, etc.) see (94)-(102), incl.].

[For prepn. of \tilde{C} from EtOH + HCl in pres. of H₃PO₄ (103) (104) (105) or H₂SO₄ (106) or EtHSO₄ (107) see indic. refs.]

By use of metal salts. For prepn. of \tilde{C} from EtOH by use of AlCl₃ at 150° (97.6% yield (13)) or of aq. FeCl₃ at 80° (108), or by reflux with subl. FeCl₃ for $1\frac{1}{2}$ hrs. (86% yield (112)), see indic. refs.

By use of inorganic acid chlorides. For prepn. of \bar{C} from EtOH by use of PCl₃ (43% yield (109)), PCl₃ + ZnCl₂ (62% yield (91)), PCl₅ + ZnCl₂ (70% yield (91)), SOCl₂ + pyridine (75% yield (91)), or SO₂Cl₂ + pyridine (110) see indic. refs.

By use of organic acid chlorides. [For prepn. of \bar{C} from EtOH with benzotrichloride (3:6540) + FeCl₃ see (111).]

From diethyl ether (1:6110).

By cleavage with HCl + a catalyst. [For prepn. of \tilde{C} from diethyl ether with $HCl + ZnCl_2$ (113) at 80–280° under press. (114) or at 300–370° under press. (115), or with $HCl + AlCl_3/NaCl/FeCl_3$ at 200–325° (116), or with HCl + a nitrogen heterocycle (117) see indic. refs.]

By cleavage with acid chlorides + a catalyst. [For prepn. of \tilde{C} from diethyl ether with SOCl₂ or S₂Cl₂ in pres. of SnCl₄ or TiCl₄ (118); or with SOCl₂ + ZnCl₂ (119); or with benzoyl chloride (3:6240) in pres. of Zn (120) cf. (121), ZnCl₂ at 150° (78% yield (122)) cf. (123) (124), MeZnI (125) or AlCl₃ (126); or with phthalyl (di)chloride (3:6900) in pres. of ZnCl₂ at 170° (80% yield (122)); or with acetyl chloride (3:7065) in pres. of ZnCl₂ (127) or AlCl₃ (126) see indic. refs.]

[For form. of \bar{C} from diethyl ether + CHCl₃ (3:5050) + cat. at 290° and 25 atm. see (128).]

From various ethyl esters of inorganic and organic acids. [For prepn. of \bar{C} from diethyl sulfate with aq. CaCl₂ as lab. method (63% yield (84)) or as manufacturing process (129); from diethyl sulfate with conc. IICl at 140° and 24 atm. (130); from ethyl chlorosulfonate with fumg. HCl at 100° (91% yield (131)) (132) cf. (189), pyridine (133), or di-n-butylamine at 100° (53% yield (134)) see indic. refs]

[For prepn. of \bar{C} from ethyl formate (1:3000) with AlCl₃ (1 mole) at 110° (82% yield (135)); from ethyl chloroformate (3:7295) on htg. at 250° (for study of this reaction see (136) (137)), with dimethylaniline at 150° (138), with pyridine (139), with quinoline at 100° (139) or even 59° (140) (141), or with AlCl₃ at room temp. (142), or with EtHSO₄ (143) see indic. refs.]

[For prepn. of C from ethyl acetate (1:3015) with subl. FeCl₃ on 1½ hrs. reflux (73% yield (112)), or with SiCl₄ (144), from ethyl benzoate (1:3721) with subl. FeCl₃ on 1½ hrs. reflux (74% yield (112)); or from diethyl phthalate (1:4331) with phthalyl (di)chloride (3:6900) + trace ZnCl₂ at 130° (145) see indic. refs.]

From vinyl chloride (3:7010). [For prepn. of C from vinyl chloride by cat. hydrogenation at elev. temp. and press. see (146).]

From ethane. [For prepn. of \bar{C} from ethane with Cl_2 above 290° in pres. of ethylene or PbEt₄ as cat. (yields 67.8–71.4% (147)) (148) see indic. refs. — For examples of other patents on prepn. of \bar{C} from ethane with Cl_2 in pres. of various cat. (149) (150) (151) (152) (153) see indic. refs.]

From ethylene. The preparation of \bar{C} from ethylene by catalytic addn. of hydrogen chloride has been extensively studied both in the scientific and in technical literature. At very low temperatures, the catalyzed reaction is quantitative, but as the temperature is increased the reverse reaction (dissociation of \bar{C} into ethylene and HCl) is favored.

[For studies on the prepn. of \tilde{C} from ethylene with HCl in pres. of AlCl₃ or BiCl₃ at -78° (100% yield (3) (155)), or as high as -12° (95% yield (154) (155)) or 130° (37% yield (42)), see indic. refs.; for studies on equilibrium at 114° and 124° (156), at 170°, 200°, and 230° (157) or for calcn. of entropy of system (158) see indic. refs.; for study of various cat. see (159).]

[The patent literature on prepn. of C from ethylene + HCl is extensive and overlapping, but illustrative examples may be cited. For patents involving use of AlCl₃ (160) (161) under pressure (162) (163) (164) (165) in the pres. of a solvent (often C itself) (162) (166) (167) (168) (190) see indic. refs. — For use of ethylene + mixt. of HCl (90%) + Cl₂ (10%) + AlCl₃ (169) (170) or for prepn. (171) or revivification (172) of AlCl₃ cat. see indic. refs.]

[For patents on prepn. of \bar{C} from C_2H_4 + HCl with various cat., e.g., with BiCl₃ (173) (174) (175), with anhydrous EtHSO₄ (176), with SnCl₄ on activated carbon at 150° (177), with bauxite cat. (178), with iron oxide cat. at 50° and ord. or increased press. (179), with BaCl₂ at 250° (180), with FeCl₃ in \bar{C} or AlCl₃ in nitrobenzene (181), with ZnCl₂ on activated carbon, silica gel, etc., (182) (183), with various surface agts. (184) (185), with SO₂ (186), with 90% H₂SO₄ + NaCl (188), or in liq. ethyl chlorosulfonate + BiCl₃ (189) see indic. refs.]

[For purification of C obtd. from techn. gases by HCl method see (187).]

From miscellaneous sources. [For formn. of \bar{C} from EtBr with CHCl₃ (3:5050) in pres. of AlCl₃ at 50° (191), from EtMgBr during reaction with S₂Cl₂ (192) or with 1,2-dichloroethylene (3:5030) (193), from EtI with Hg₂Cl₂ in s.t. at 140° (12), from ethyl α,β -dichlorovinyl ether (3:5540) with Cl₂ at ord. temp. followed by warms. or stdg. in absence of aq. (194), or from dichloroacetaldehyde diethylacetal (3:6110) with ZnEt₂ (195) see indic. refs.]

[For formn. of C from succinic acid (1:0530) with aq. FeCl₃ in sunlight (196) or from MeCl (3:7005) + aq. by disproportionation over cat. at 200-275° (197) see indic. refs.]

CHEMICAL BEHAVIOR OF C

Pyrolysis of C

 \tilde{C} passed through plain tube at 410° is largely unchanged, but \tilde{C} passed at 550° through tube contg. pumice (198) cf. (42) or other cat. (199) dissociates completely into ethylene + HCl (use in detn. of \tilde{C} (42)).

BEHAVIOR OF C WITH INORGANIC REACTANTS

Chlorination. [\bar{C} with liq. Cl₂ (1 mole) in u.v. light and cooling yields (200) mainly 1,1-dichloroethane (3:5035) accompanied by some 1,2-dichloroethane (3:5130) and higher chlorination prods.; the two dichloroethanes are also obtd. from \bar{C} with Cl₂ + aq. (201). — For very impt. study of behavior of \bar{C} with Cl₂ at 202-380° see (202) (147).]

[\bar{C} with SbCl₅ in s.t. at 100° (203) or \bar{C} with NCl₃ (204) yields 1,2-dichloroethane (ethylene dichloride) (3:5130).]

Bromination. [For behavior of C with Br₂ see (207) (208).]

Fluorination. [C at 900° with F₂ in pres. of Cu yields (205) CF₄, CF₃Cl, CF₃.CF₂Cl, CHF₂.CH₂Cl, CF₂—CCl₂, and other prods.]

Hydrogenation. [For behavior of C with atomic hydrogen see (206).]

Hydrolysis. [C over suitable partially dehydrated Al(OH)₃ at room temp. (209), or C + aq. vapor over cat. at 300-500° at ord. press. (210) (211) (212), or C with aq. NaOH above 150° under press. (213), or C with alc. NaOH (214), alc. Na₂CO₃, MgO, or CaOe (215) is saponified yielding EtOH (1:6130). — The reaction of C with EtOH/KOH is bimolecular (216); furthermore during hydrol. of C with alk. some diethyl ether is always formed cf. (213) (214) and the reaction may be adapted to its prepn. (217).]

Amination. [C with alc. NH3 in s.t. at 100° (218) or C with liq. NH3 at 220° and 220 atm. press. (219) gives salts of ethylamine, diethylamine, triethylamine, and other prods.—

 \tilde{C} with NaNH₂ in liq. NH₃ at 0° and 20 atm. gives ethylamine (30% yield (220)) and ethylene.

Behavior of \tilde{C} with inorganic acids. [\tilde{C} passed through boilg. H_2SO_4 gives $C_2H_4 + SO_2 + HCl$; \tilde{C} is absorbed by SO_3 giving a liq. which probably comprises a mixture of ethyl chlorosulfonate, β -chloroethanesulfonic acid, and β -hydroxyethanesulfonyl chloride (221).]

Behavior of C with inorganic salts. [For study of rate of reaction of C with KI in acetone at 50° and 60° see (222). — C with AlBr₃ under suitable cond. yields (223) ethyl bromide.]

Behavior of $\tilde{\mathbb{C}}$ with metals. With sodium. The most important reaction of $\tilde{\mathbb{C}}$ with metals is that involved in the manufacture of tetraethyllead for use as an anti-knock agent in motor fuels. Tetraethyllead is prepared for $\tilde{\mathbb{C}}$ either by direct reaction with Na/Pb alloys, or by reaction with Mg and subsequent conversion of the EtMgCl by means of PbCl₂. For a general survey (without references) on the manufacture of tetraethyllead see (224).

For patents involving the prepn. of Et₄Pb from \bar{C} by reactn. with Na/Pb alloys under various circumstances see (225)-(244) incl.; for patents involving the use of EtMgCl see (245)-(248) incl.

[For behavior of \bar{C} with Na in lgr. followed by CO₂ (249) or with amyl-sodium or octyl-sodium (250) see indic. refs. — \bar{C} with K/Na alloy in xylene gives (251) ethane (32%) and ethylene (5.5%). — \bar{C} with Tl/Na yields (252) TlEt₃.]

With magnesium. [\bar{C} with Mg in s.t. at 260° for 4 hrs. gives (253) gas (consisting of 45% butane + 20% olefins + 22% H₂) and a white solid which with aq. gives a gas contg. 86% H₂ + 13% ethane.]

 \bar{C} with Mg in dry ether in absence of air and in pres. of trace of I₂ gives (99.7% yield in 4 hrs. (254)) EtMgCl; this reagt. is actually an equil. mixt. contg. 25% EtMgCl + 42.5% MgCt₂ + 42.5% MgCl₂ (255). — For study of competitive reaction with Mg in ether of an equimolar mixt. of \bar{C} + EtI yielding 27% EtMgCl + 73% EtMgI see (256). — [For reactn. of EtMgCl with NH₄Cl or triethylamine.HCl (254), with NH₂Cl (257), or with NCl₃ (258) see indic. refs.; for study of electrolysis of EtMgCl in ether see (259). — For reactn. of EtMgCl with PbCl₂ yielding PbEt₄ see (245)–(248) incl.; with C₆H₅NCO yielding propionanilide see below under \bar{D} 's.]

BEHAVIOR OF C WITH ORGANIC REAGENTS

[\bar{C} with C_6H_6+Al/Hg gives (76% yield (260)) ethylbenzenc (1:7410); \bar{C} + hexane + AlCl₃ gives (261) octane.]

[\bar{C} with CO + AlCl₃ at 40-50° and 120 atm. followed by treatment with H₂O gives (43% yield (262)) (263) propionic acid (1:1025).]

[Č with ethylene oxide $(1:6105) + AlCl_3$ gives (264) a mixt. contg. 4-chlorobutanol-1 (3:9170) + ethylene chlorohydrin (3:5552).]

[C may be used for the ethylation of OH groups or NH₂ groups: e.g., for reaction of C with sodium phenolate yielding (265) ethyl phenyl ether (1:7485) or for use of C in ethylation of cellulose (266) (267) see indic. refs.; for use of C in ethylation of metanilic acid (268) (214) (215), o-toluidine (269), or m-aminophenol (268) see indic. refs.]

[For condens. of C with hexamethylenetetramine see (270).]

[C (2 moles) with ethylene (di)bromide (1 mole) + 3% AlCl₈ in steel bomb at 25° for 14 days undergoes a redistribution reactn. yielding (271) a mixt. consisting of 5 cpds., viz., C (35 mole %) + EtBr (30 mole %) + ethylene chlorobromide (17 mole %) + ethylene (di)bromide (11 mole %) + ethylene dichloride (3:5130) (7 mole %).]

[C (1 mole) with quinoline (1 mole) in s.t. in direct sunlight reacts only very slowly (incomplete in 1 year) but grad. separates ethylquinolium chloride, cryst. from abs. EtOH by addn. of dry ether, m.p. 122° (290).]

- **Propionanilide:** m.p. 104.0-104.5° u.c. (272). (See also under propionic acid (1:1025).) [From \bar{C} by conversion to EtMgCl (see above) and reactn. in dry ether with phenyl isocyanate (272).]
- —— Propion-p-toluidide: m.p. 123°. [Presumably obtainable (272) from C via conversion to EtMgCl (see above) and reaction in dry ether with p-tolyl isocyanate.]
- Propion- α -naphthalide: m.p. 126° u.c. (273). [Presumably obtainable (272) from $\bar{\mathbf{C}}$ via conversion to EtMgCl (see above) and reaction in dry ether with α -naphthyl isocyanate; the analogous process for EtBr has been reported (273).]
- Ethyl mercuric chloride: m.p. 193.5° cor. (274), 192.5° (275), 192° (276). [Prepd. indirectly (276); but should be preparable from EtMgCl with HgCl₂ since corresp. EtHgBr has been reported (276) from EtMgBr + HgBr₂. Note that m.p. of EtHgCl is almost identical with that (193.5°) of EtHgBr cf. (276).]
- ---- N-Ethylphthalimide: [Beil. XXI-461, XXI₁-(363)], ndls. from alc., m.p. 79° (279), 78° (280). [Prepd. indirectly (280), also from EtI with potassium phthalimide in s.t. at 150° (279).]
- —— N-Ethyl-3-nitrophthalimide: pl. from CS₂, m.p. 105-106° (281) (282); for photographs of crystals see (282). [Not reported from C itself, but obtd. from EtBr with K phthalimide on protracted reflux. (281).]
- N-Ethyltetrachlorophthalimide: pl. from CHCl₃ on pouring into 2 vols. EtOH, m.p. 192-193° (283). [Not reported from C but obtd. from EtBr or EtI with K tetrachlorophthalimide in s.t. at 200° for 6 hrs. (283).]
- —— N-Ethylsaccharin: cryst. from dil. alc., m.p. 94° (284). [This prod. cannot be obtd. from C itself (284) but is obtd. from either EtBr or EtI with sodium saccharin in aq. butylcarbitol (1:6517) contg. KI on refluxing for 30 min. (284).]
- ---- N-Ethyl-N-(p-bromobenzenesulfonyl)-p-anisidide: m.p. 113.5° u.c. (285). [Not reported from \(\bar{\chi}\) but obtained from EtBr with N-(p-bromobenzenesulfonyl)-p-anisidide (285).]
- —— p-Ethoxybenzoic acid: m.p. 195° (286) cf. (287).
- ---- Ethyl 2.4.6-triiodophenyl ether: m.p. 83.5° cor. (288).
- Ethyl α-naphthyl ether: oil, b.p. 280.5° cor., f.p. below -10° (289). (Corresp. picrate, m.p. 118.5-119.5° cor.; Neut. Eq. 401 (289).)
- Ethyl β-naphthyl ether: m.p. 35.5-36.0° cor., b.p. 282° cor. (289). (Corresp. picrate, m.p. 101.0-101.5° cor., Neut. Eq. 401 (289).)
- Timmermans, Bull. soc. chim. Belg. 27, 334 (1914), Cent. 1914, I 618. (2) Grosse, J. Am. Chem. Soc. 59, 2739-2741 (1937). (3) Tulleners, Tuyn, Waterman, Rec. trav. chim. 53, 544-554 (1934). (4) Berthoud, J. chim. phys. 15, 13 (1917). (5) Jenkin, Trans. Faraday Soc. 18, 197-199 (1922). (6) Regnault, Ann. chim. (4) 24, 380 (1871). (7) Norris, Taylor, J. Am. Chem. Soc. 45, 757 (1924). (8) Thiel, Schulte, Z. physik. Chem. 96, 331-333 (1920). (9) Beckmann, Z. anorg. allgem. Chem. 55, 379 (1907). (10) Fuchs, Z. Physik 63, 837 (1930).
- (11) Timmermans, Hennaut-Roland, J. chim. phys. 34, 699-700 (1937). (12) Linnemann, Ann. 160, 214 (1871). (13) Norris, Sturgis, J. Am. Chem. Soc. 61, 1415 (1939). (14) Paul, Schantz, Arch. Pharm. 257, 110-111, 127 (1919). (15) Schneider, Z. physik. Chem. 22, 235 (1897). (16) Gutmann, J. Chem. Soc. 87, 1040 (1905). (17) Awberry, Phil. Mag. (7) 31, 252 (1941). (18) Kanolt, Sci. Papers U.S. Bur. Standards No. 520; 20, 619-633 (1924-6). (19) Ramsay, J. Chem. Soc. 35, 470 (1879). (20) Pierre, Compt. rend. 27, 213 (1845/9).
- (21) Henning, J. Soc. Chem. Ind. 39, 1-8T (1920). (22) "International Critical Tables" III-231. (23) van Arkel, Vles, Rec. trav. chim. 55, 410 (1936). (24) Fühner, Ber. 57, 514 (1924).

(25) Genelen, Z. physik. chem. Unterricht 33, 147 (1920).
(26) Kimberlin (to Standard Oil Development Co.), U.S. 2,275,151, March 3, 1942; C.A. 36, 4137 (1942): Brit. 545,729, June 10, 1942; [C.A. 37, 2018 (1943)].
(27) Kaplan, Romanchuk, J. Gen. Chem. (U.S.S.R.) 6, 950-954 (1936); Cent. 1937, II 1771; C.A. 31, 594 (1937).
(28) Zellhoefer, Copley, Marvel, J. Am. Chem. Soc. 60, 1338 (1938).
(29) Zellhoefer, Ind. Eng. Chem. 29, 548 (1937).
(30) Kaplan, Monakhova, Reformatskaya, Bessanova, J. Applied Chem. (U.S.S.R.) 10, 2022-2027 (1937); Cent. 1939, I 2160; C.A. 32, 5281 (1938).

(31) Kimberlin (to du Pont Co.), U.S. 2,352,268, June 27, 1944; C.A. 38, 5508 (1944). (32) Baskerville, Hirsh, J. Ind. Eng. Chem. 13, 322-323 (1921). (33) Wertyporoch, Ber. 66, 1232-1238 (1933). (34) Wertyporoch, Kowalski, Z. physik. Chem. A-166, 205-213, 217 (1933). (35) Wertyporoch, Firla, Z. physik. Chem. A-162, 398-414 (1933). (36) Wertyporock, Firla, Ann. 500, 287-295 (1933). (37) Goldmann, Polyani, Z. physik. Chem. 132, 321-370 (1928). (38) Lamb, Coolidge, J. Am. Chem. Soc. 42, 1153 (1920). (39) Pearce, McKinley, J. Phys. Chem. 32, 370 (1928). (40) Pearce, Reed, J. Phys. Chem. 39, 294 (1935).

Gregg, J. Chem. Soc. 1943, 351-355. (42) Berl, Bitter, Ber. 57, 95-99 (1924). (43)
 Lamb, Ohl, J. Am. Chem. Soc. 57, 2154-2161 (1935). (44) Jones, U.S. Bur. Mines, Rept. Invest. 3745 (1949). (45) Huff, U.S. Bur. Mines, Rept. Invest. 3745 (1944). (46) Huff, U.S. Bur. Mines, Rept. Invest. 3745 (1944). (46) Huff, U.S. Bur. Mines, Rept. Invest. 3745 (1949). (47) Jones, Ind. Eng. Chem. 20, 367-370 (1928). (48) Deiss, Z. Elektrochem. 29, 586-587 (1923). (49) van Deventer, Rec. trav. chim. 57, 95-107 (1938).
 (50) Schafer, Foz Gazulla, Z. physik. Chem. B-52, 299-314 (1942); Anales fis quim. 38, 316-346

(1942); C.A. 37, 4943 (1943).

(51) Embley, Proc. Roy. Soc. (London) 78B, 391-413 (1906). (52) von Oettingen, J. Ind. Hyg. Toxcool. 19, 388-393 (1937). (53) Smyth, N.Y. State Med. J. 42, 1072-1079 (1942); C.A. 36, 4626 (1942). (54) Lehmann, Schmidt-Kehl, Arch. Hyg. Bakt. 116, 131-268 (1936); C.A. 31, 477 (1937). (55) Lazarev, Arch. exptl. Pathol. Pharmakol. 141, 19-24 (1928); Cent. 1929, II 451; not in C.A. (56) Faust, J. Am. Med. Assoc. 108, 386-392 (1937); C.A. 31, 3565 (1937). (57) Baskerville, Hamor, J. Ind. Eng. Chem. 5, 828-831 (1913). (58) Stewart, Anesthesiology 2, 635-640 (1941); C.A. 36, 865 (1942). (59) Efskind, Beitr. Klin. Chir. 167, 251-306 (1938); C.A. 32, 8558 (1938). (60) Schaefer, Schmerz, Narkose-Anesthesie 3, 330-340 (1930); Cent. 1931, 11 81; not in C.A.

(61) Lincoln, Anesthesia and Analgesia 20, 328-332 (1941); C.A. 36, 1094 (1942). (62) Miller, Bull. Am. Assoc. Nurse Anesthetists 8, 18-22 (1940); C.A. 34, 2137 (1940) (63) Marston, Brit. Dental J. 63, 569-575 (1937); Cent. 1938, I 3234. (64) Shields, Can. Med. Assoc. J. 24, 250-254 (1931); Cent. 1931, II 2351; not in C.A. (65) Davidson, J. Pharmacol. 26, 37-42 (1925); Cent. 1926, I 165; C.A. 19, 3123 (1925). (66) Committee on Anesthetic Deaths, S. African Dental J., March 1937; C.A. 32, 4220 (1938). (67) Coste, Chaplin, Brit. J. Anesthesia 14, 115-129 (1937); C.A. 31, 5165 (1937). (68) Greene, Ann. J. Roentgenol. Radium Therapy 45, 737-743 (1941); C.A. 35, 5703 (1941). (69) Greene, Anisthesiology 2, 144-160 (1941); C.A. 35, 4954 (1941). (70) Schwarzer, Ger. 326,407, Sept. 25, 1920, Cent. 1921, II 14; not in C.A.

(71) Henning, U.S. 1,356,765, Oct. 26, 1920; Cent. 1921, II 103; C.A. 15, 284 (1921). (72) Davenport (to Cheago Pneumatic Tool Co.), U.S. 1,986,959, Jan. 8, 1935; Cent. 1936, II 147; C.A. 29, 1294 (1935). (73) Sorenson, U.S. 1,845,355, Feb. 16, 1932; Cent. 1932, II 101; C.A. 26, 2257 (1932). (74) Davenport (to Cheago Pneumatic Tool Co.), U.S. 1,803,098, April 28, 1931; Cent. 1932, I 1935; [C.A. 25, 3746 (1931)]. (75) Henning, Ger. 354,609, June 9, 1922; Cent. 1922, IV 359; not in C.A.: Brit. 158,494, March 3, 1921; Cent. 1921, IV 274; C.A. 15, 1954 (1921). (76) Henning, Brit. 152,550. Nov. 11, 1920, Cent. 1921, II 323; C.A. 15, 737 (1921). (77) Solv. Extn. Refrig. Co., French 563,443, Dec. 5, 1923; Cent. 1924, II 2214; not in C.A. (78) DeRemer, (to Savage-DeRemer Corpn.), U.S. 1,707,471, April 2, 1929; Cent. 1929, II 85; C.A. 23, 2539 (1929). (79) Thorsell, Svensk Farm. Tid. 45, 341-344 (1941); C.A. 35, 6898 (1941). (80) Dement'eva, Serebryakova, Materials on Cracking and Chem. Treat. of Products Obtd., Khimteoret (Leningrad) No. 2, 144-146 (1935); C.A. 29, 6033 (1935); not in Cent.

(81) Martinek, Marti, Ind. Eng. Chem., Anal. Ed. 3, 408-410 (1931). (82) Newcomb, Analyst 51, 19-30 (1926). (83) Sudendorf, Penndorf, Pharm. Zentralhalle, 68, 226-228 (1927); Cent. 1927, II 754; C.A. 21, 2048 (1927). (84) Koten, J. Chem. Education 17, 461 (1940). (85) Buc, Gleason (Standard Oil Development Co), U.S. 2,153,170, April 4, 1939; Cent. 1939, II 2712; C.A. 33, 3005 (1939). (86) Ernst, Berndt (to I.G.), Ger. 467,185, Oct. 17, 1928; Cent. 1929, I 1045; C.A. 23, 1137 (1929); cf. Ernst, Berndt (to I.G.), Ger. 444,799, May 27, 1927; Cent. 1927, II 500; not in C.A. (87) I.G., Brtt. 375,199, July 14, 1932; Cent. 1932, II 2237; not in C.A. (88) I.G., French 716,217, Dec. 17, 1932; Cent. 1932, I 3345; C.A. 26, 2197 (1932). (89) Alckelin (to General Aniline Works), U.S. 2,007,322, July 9, 1935; Cent. 1935, II 3829; C.A. 29, 5862 (1935). (90) Eberhart, Z. physik. chem. Unterricht 50, 66 (1937).

(91) Clark, Streight, Trans. Roy. Soc. Can. (3) 29, III 77-89 (1929). (92) Groves, J. Chem.

Soc. 27, 636 (1874). (93) Krüger, J. prakt. Chem. (2) 14, 195-196 (1876). (94) Holt, Daudt (to du Pont Co.), U.S. 2,091,986, Sept. 7, 1937; Cent. 1937, II 4238; C.A. 31, 7445 (1937). (95) Daudt (to du Pont Co.), U.S. 2,016,075, Oct. 1, 1935; Cent. 1936, I 2206; C.A. 29, 8004 (1935): Brit. 450,843, Aug. 20, 1936; Cent. 1936, II 4048; [C.A. 31, 114 (1937)]. (96) Holt, Daudt (to du Pont Co.), U.S. 1,983,542, Dec. 11, 1934; Cent. 1935, I 3198; C.A. 29, 817 (1935). (97) Daudt (to du Pont Co.), U.S. 1,920,246, Aug. 1, 1933; Cent. 1933, II 2454; C.A. 27, 4818 (1933). (98) Frei (to du Pont Co.), U.S. 1,784,423, Dec. 9, 1930; Cent. 1931, I 2672; C.A. 25, 303 (1931); French 692,790, Nov. 10, 1930; Cent. 1931, I 2112; C.A. 25, 1537 (1931). (99) Backhaus (to U.S. Ind. Alc. Co.), U.S. 1,509,463, Sept. 23, 1924; Cent. 1925, I 573; C.A. 19, 78 (1925). (100) Willkie (to U.S. Ind. Alc. Co.), U.S. 1,478,498; Dec. 25, 1923; C.A. 18, 840 (1924); not in Cent. (101) Douane, Vila, French 529,558, Dec. 1, 1921; Cent. 1922, IV 940; not in C.A. (102) A.G.F.A., Ger. 280,740, Nov. 26, 1914; Cent. 1915, I 104; C.A. 9, 1829 (1915). (103) Ernst (to A. Wacker Soc. Electrochem. Ind.), Ger. 583,477, Sept. 4, 1933; Cent. 1933, II 2893; C.A. 28, 1052 (1934). (104) Ernst (to A. Wacker Soc. Electrochem. Ind.), U.S. 1,937,269, Nov. 28, 1933; [C.A. 28, 1052 (1934)]; Ger. 541,566, Aug. 10, 1929; C.A. 26, 2468 (1932); French 687,855, Aug. 14, 1930; Cent. 1930, II 3637; C.A. 25, 709 (1931). (105) Dachlauer, Eggert (to I.G.), Ger. 441,-747, March 10, 1927; Cent. 1927, I 2945; not in C.A. (106) I.G., Brit. 486,453, June 30, 1938; Cent. 1938, II 3157; C.A. 32, 8439 (1938). (107) Teupel (to I.G.), U.S. 1,950,827, March 13, 1934; C.A. 28, 3424 (1934); not in Cent.: French 716,217, Dec. 17, 1932; Cent. 1932, I 3345; C.A. 26, 2197 (1932). (108) Harding (to Roessler & Hasslacher Chem. Co.), U.S. 1,816,845, Aug. 4, 1931; Cent. 1931, II 3392; C.A. 25, 5433 (1931): Ger. 529,627, July 16, 1931; Cent. 1931, II 2386, C.A. 25, 5176 (1931). (109) Walker, Johnson, J. Chem. Soc. 87, 1592-1597 (1905).

(110) Baumgarten, Ber. 60, 1177 (1927).

(111) Verein chem. Metalurg. Prod., Ger. 472,422, Feb. 28, 1929; Cent. 1929, I 2823; C.A. 23, 2448 (1929). (112) Dangyan, J. Gen. Chem. (U.S.S.R.) 8, 1780-1783 (1938); C.A. 33, 4957 (1939); not in Cent. (113) Brooks (to Standard Alc. Co.), U.S. 2,015,706, Oct. 1, 1935; Cent. 1936, I 2206; C.A. 29, 8004 (1935). (114) Spurlin (to Hercules Powder Co.), U.S. 2,084,710, June 22, 1937; Cent. 1937, II 2900; C.A. 31, 5816 (1937). (115) du Pont Co., Brit. 390,209, April 27, 1933; Cent. 1933, II 604; C.A. 27, 4543 (1933). (116) Amos (to Dow Chem. Co.), U.S. 2,140,500, Dec. 20, 1938; Cent. 1939, I 3625; C.A. 33, 2540 (1939). (117) Leuchs (to I.G.), Ger. 659,927, May 13, 1938; Cent. 1938, II 2840; C.A. 32, 6666 (1938). (118) Goldfarb, Smorgonski, Ber. 69, 1036-1039 (1936). (119) Goldfarb, Smorgonski, Russ. 48,284, Aug. 31, 1936; Cent. 1937, II 139. (120) Varvoglis, Ber. 79, 2393 (1937).

(121) Kaufman, Fuchs, Arch. Pharm. 262, 119-125 (1924). (122) Kyrides, J. Am. Chem. Soc. 55, 1209-1212 (1933). (123) Underwood, Wakeman, J. Am. Chem. Soc. 52, 387-391 (1930). (124) Underwood, Toone, J. Am. Chem. Soc. 52, 391-394 (1930). (125) Blaisé, Bull. soc. chm. (4) 9, V (1911). (126) Kozlov, Bogdanovskava, Sologub, J. Gen. Chem. (U.S.S.R.) 6, 315-317 (1936); Cent. 1936, II 1896; C.A. 30, 4813 (1936). (127) Descudé, Compt. rend. 132, 1129 (1901). (128) Andrussow (to I.G.), Ger. 634,549, Aug. 29, 1936; Cent. 1936, II 4048; C.A. 31, 419 (1937): French 799,582, June 15, 1936; Cent. 1936, II 4048; C.A. 30, 7585 (1936). (129) Wilson (to Carbide and Carbon Chem. Corp.), U.S. 2,263,666, Nov. 25, 1941; C.A. 36, 1335 (1942). (130) Teupel (to I.G.), Ger. 574,833, April 24, 1933; Cent. 1933, II 131; C.A. 27, 4543 (1933).

(131) Traube, Z. angew. Chem. 38, 444 (1925). (132) Traube, Ger. 362,741, Oct. 31, 1922; Cent. 1923, II 741; not in C.A.; U.S. 1,470,656, Oct. 16, 1923; C.A. 18, 87 (1924). (133) Baumgarten, Ber. 59, 1166, 1169 (1926). (134) Binkley, Degering, Proc. Indiana Acad. Sci. 49, 117 (1939); C.A. 35, 5458 (1941). (135) Norris, Arthur, J. Am. Chem. Soc. 62, 875 (1940). (136) Choppin, Frediani, Kirby, J. Am. Chem. Soc. 61, 3176-3180 (1939). (137) Choppin, Kirby, J. Am. Chem. Soc. 62, 1592-1594 (1940). (138) Rivier, Richard, Helv. Chem. Acta 8, 492, 495 (1925). (139) Hopkins, J. Chem. Soc. 117, 278-282 (1920). (140) Carré, Passedouet, Compt. rend. 200, 1767-1769 (1935).

(141) Carré, Bull. soc. chim. (5) 3, 1069, 1072 (1936). (142) Rennie, J. Chem. Soc. 41, 33 (1882). (143) Kraft, Lyutina, J. Gen. Chem. (U.S.S.R.), 1, 190-192 (1931); Cent. 1931, II 3197; C.A. 26, 2167 (1932). (144) Vol'nov, J. Gen. Chem. (U.S.S.R.), 2, 2269-2282 (1939); C.A. 34, 5048 (1940). (145) Kyrides (to Monsanto Chem. Co.), U.S. 1,939,216, Dec. 12, 1933; Cent. 1934, I 2040; C.A. 28, 1361 (1934). (146) Baumann, Hirschbeck (to I.G.), U.S. 2,118,662, May 24, 1938; [C.A. 32, 5413 (1938)]: Brit. 470,817, Sept. 16, 1937; Cent. 1938, I 180; C.A. 32, 956 (1938). (Ger. 651,610, Oct. 23, 1937; Cent. 1938, I 180; C.A. 32, 596 (1938). (147) Vaughan, Rust, J. Org. Chem. 5, 449-471 (1940). (148) Vaughan, Rust (to Shell Development Co.), U.S. 2,299,441, Oct. 20, 1942; C.A. 37, 1722 (1943): U.S. 2,284,482, May 26, 1942; C.A. 36, 6546 (1942): U.S. 2,246,082, June 17, 1941; C.A. 35, 5911 (1941). (149) Flemming, Dachlauer, Schnitzler (to I.G.), U.S. 2,162,532, June 13, 1939; [C.A. 33, 7822 (1939)]: Brit. 483,051, May 5, 1938; Cent. 1938, II 2031; C.A. 32, 7057 (1938): French 826,808, April 11, 1938; Cent. 1938, II 2031; [C.A. 33, 2031]

7926 (1938)]. (150) Reilly (to Dow Chem. Co.), U.S. 2,140,547, Dec. 20, 1938; Cent. 1839, I 3625; C.A. 33, 2540 (1938).

(151) Lacy, U.S. 1,242,208, Oct. 9, 1917; C.A. 12, 155 (1918). (152) Gremli, Austrian 108,421. 108,424, Dec. 27, 1927; Cent. 1928, I 1229; not in C.A. (153) Müller, Conradi (to I.G.), Ger, 436,999, Nov. 11, 1926; Cent. 1927, I 354; not in C.A. (154) Rudkovskii, Aleksandrov, Pazhitnov, Ivanovskii, Goloushin, Org. Chem. Ind. (U.S.S.R.) 4, 499-502 (1937); C.A. 32, 4939 (1938); not in Cent. (155) Rudakovski, Trifel, Trans. Expt. Research Lab. "Khemgas," Materials on Cracking and Chem. Treatment of Cracking Products (U.S.S.R.) 3, 202-208 (1936); C.A. 31, 5319 (1937); not in Cent. (156) Wibaut, Z. Elektrochem. 35, 602-605 (1929). (157) Rudkovskii, Trifel. Frost, Ukrain. Khem. Zhur. 10, Sci. pt., 277-282 (1935); Cent. 1936, I 3667; C.A. 30, 2082 (1936), (158) Linnett, Trans. Faraday Soc. 36, 527-533 (1940). (159) Wibaut, Dickmann, Rutgers, Rec. trav. chim. 47, 477-495 (1928). (160) Hjerpe, Gruse (to Gulf Oil Co.), U.S. 2,099,480, Nov. 16, 1937; Cent. 1938, I 3418; [C.A. 32, 195 (1938)]; U.S. 1,944,839, Jan. 23, 1934; Cent. 1934,

I 2696; C.A. 28, 2174 (1934).

(161) Webb (to Carbide and Carbon Chem. Corp.), U.S. 1,560,625, Nov. 10, 1925; Cent. 1926. (162) Chem. Fabrik Weiler-ter-Meer, Brit. 235,521, July 9, 1925, I 1713; C.A. 20, 51 (1926). Cent. 1926, I 2240; C.A. 20, 918 (1926); Suida (to I.G.), Ger. 478,082, June 19, 1929; [Cent. 1929, II 1071]; C.A. 23, 4231 (1929). (163) Suida (to I.G.), Brit. 229,298, April 16, 1925; Cent. 1925. II 2090; C.A. 19, 3092 (1925): Ger. 485,434, Oct. 31, 1929; Cent. 1930, I 3829; C.A. 24, 866 (1930): French 591.753, July 17, 1925; Cent. 1925, II 2090; not in C.A. (164) Suida (to Chem. Fabrik Weiler-ter-Meer), Ger. 420,441, Oct. 24, 1925; Cent. 1926, I 2241; C.A. 20, 918 (1926). (165) Curme (to Carbide and Carbon Chem. Corp.), U.S. 1,518,182, Dec. 9, 1924; Cent. 1925, I 1129; C.A. 19, 523 (1925). (166) Tulleners, Tuyn, Waterman, Dutch 36,489, Oct. 15, 1935; Cent. 1936, I 1500; not in C.A. (167) Chamberlain, Williams, Blue (to Dow Chem. Co.), U.S. 2,140,507, Dec. 20, 1938; Chamberlain, Amos, Williams (to Dow Chem. Co.), U.S. 2,140,508, Dec. 20, 1938; Cent. 1939, I 3625; C.A. 33, 2540 (1939). (168) Pierce (to Dow Chem. Co.), U.S. 2,140,927, Dec. 20, 1938; Cent. 1939, I 3625; C.A. 33, 2540 (1939). (169) Hemminger (to Std. Oil. Dev. Co.), U.S. 2,353,563, July 11, 1944; C.A. 38, 5844 (1944). (170) Chem. Fabrik. Weiler-ter-Meer, Ger. 417,170, Aug. 8, 1925; Cent. 1925, II 2089; not in C.A.

(171) Blue (to Dow Chem. Co.), U.S. 2,180,345, Nov. 21, 1939; C.A. 34, 1688 (1940). Keyl, Blue (to Dow Chem. Co.), U.S. 2,209,981, Aug. 6, 1940; C.A. 35, 139 (1941). (173) Slotterbeck, Rosen (to Std. Oil Dev. Co.), U.S. 2,174,278, Sept. 26, 1939; C.A. 34, 778 (1940). (174) N. V. de Bataafsche Petroleum Maatschappij, French 830,602, Aug. 4, 1938; Cent. 1938, II 3460; C.A. 33, 1346 (1939). (175) Wibaut, U.S. 1,591,151, July 6, 1926; C.A. 20, 3170 (1926); not in Cent.: Brit. 209,722, March 5, 1924; Cent. 1925, 1 895; C.A. 18, 1673 (1924): Ger. 445,981. June 21, 1927; [Cent. 1927, II 863]; not in C.A.: French 574,800, July 18, 1924; Cent. 1925, I 895; not in C.A. (176) Chamberlain, Williams (to Dow Chem. Co.), U.S. 2,125,284, Aug. 2, 1938; Cent. 1939, I 531; C.A. 32, 7480 (1938). (177) Winkler, Ger. 574,802, March 30, 1933; Cent. 1933, I 3497; C.A. 27, 4543 (1933). (178) Strange, Kane, Brit. 500,880, March 16, 1939; Cent. 1839. II 226; C.A. 33, 5867 (1939). (179) Roush, Morrell (to Dow Chem. Co.), U.S. 2,110,141, March 8, 1938; Cent. 1938, I 4533; C.A. 32, 3421 (1938). (180) Balandin, Livanova, Uchenye Zapiski (Moscow State Univ.) 2, 237-239 (1934); Cent. 1935, II 1528; C.A. 30, 6321 (1936).

(181) I.G., French 780,057, April 18, 1935; Cent. 1935, II 1445; C.A. 29, 5862 (1935). (182) Arnold, Lessig (to du Pont Co.), U.S. 2,097,750, Nov. 2, 1937; Cent. 1938, I 1217; C.A. 32, 194 (1938). (183) Flemming (to I.G.), U.S. 2,094,064, Sept. 28, 1937; [C.A. 31, 7893 (1937)]; not in Cent., Brit. 448,269, July 2, 1936; Cent. 1936, II 2446; C.A. 30, 7127 (1936): Ger. 646,478, June 15, 1937; C.A. 31, 6260 (1937); not in Cent.: French 793,744, Jan. 30, 1936; Cent. 1936, I 4074; C.A. 30, 4515 (1936). (184) Bayer and Co., Ger. 361,041, Oct. 9, 1922; Cent. 1923, II 475; not in C.A. (185) Suida (to Chem. Fabrik Weiler-ter-Meer), Ger. 369,702, Feb. 22, 1923; Cent. 1923, II 906; not in C.A. (186) M.L.B., Brit. 216,368, June 19, 1924; Cent. 1925, I 1240; C.A. 19, 78 (1925): French 566,041, Feb. 8, 1924; Cent. 1925, I 1240; not in C.A. (187) Robinson (to Dow Chem. Co.), U.S. 2,286,379, June 16, 1942; C.A. 36, 7032 (1942). (188) Calcott, Daudt (to du Pont Co.), U.S. 2,016,072, Oct. 1, 1935; Cent. 1936, I 2206; C.A. 29, 8004 (1935). (189) Reilly (to Dow Chem. Co.), U.S. 2,031,228, Feb. 18, 1936; Cent. 1936, II 864; C.A. 30, 2205 (1936). (190) du Pont Co., Brit. 466,134, June 17, 1937; Cent. 1937, II 2431; C.A. 31, 7445 (1937).

(191) Dougherty, J. Am. Chem. Soc. 51, 579 (1929). (192) Ferrario, Bull. soc. chim. (4) 7. 525 (1910). (193) Binaghi, Gazz. chim. ital. 57, 672-673 (1927). (194) Crompton, Triffitt, J. Chem. Soc. 119, 1874 (1921). (195) Paterno, Gazz. chim. ital. 49, II 330 (1919). (196) Benrath, J. prakt. Chem. (2) 86, 337 (1912). (197) M.L.B., Brit. 196,272, June 6, 1923; Cent. 1925, I 1240; C.A. 17, 3879 (1923); French 564,641, Jan. 7, 1924; Cent. 1925, I 1240; not in C.A. (198) Nef, Ann. 318, 13-19 (1901). (199) Sabatier, Mailhe, Compt. rend. 141, 238 (1905). (200) D'Ans,

Kautzsch, J. prakt. Chem. (2) 89, 305-314 (1909).

(201) Aschan, Cent. 1919, I 221; C.A. 13, 2868 (1919). (202) Rust, Vaughan, J. Org. Chem. 6, 479-487 (1941). (203) Meyer, Muller, Ber. 24, 4249 (1891); J. prakt. Chem. (2) 46, 173-174 (1892). (204) Coleman, Noyes, J. Am. Chem. Soc. 43, 2214-2215 (1921). (205) Calfee, Fukuhara, Young, Bigelow, J. Am. Chem. Soc. 62, 267-269 (1939) (206) Chadwell, Titani, J. Am. Chem. Soc. 55, 1363-1375 (1933). (207) Denzel, Ann. 195, 189-205 (1879). (208) Meyer, Petrenko-Kritschenko, Ber. 25, 3306-3307 (1892). (209) Gurvich, J. Russ. Phys.-Chem. Soc. 48, 837-856 (1916); Cent. 1923, I 1531; C.A. 11, 1781 (1917); Z. physik. Chem. 107, 241 (1923). (210) Criqueboef, Gillet, French 528,344, Nov. 10, 1922, Cent. 1922, IV 946; not in C.A.

(211) Medvedev, Abkin, J. Phys. Chem. (U.S.S.R.) 4, 731-739 (1933); Cent. 1935, I 2520; not in C.A. (212) Abkin, Medvedev, Russ. 34,551, Feb. 28, 1934, CA. 29, 2973 (1935). (213) Hale (to Dow Chem. Co.), U.S. 1,938,453, Dec. 5, 1933, Cent. 1934, I 1709; C.A. 28, 1047 (1934). (214) Izmail'skii, Popov, Bull. soc. chim. (5) 3, 2028-2037 (1936). (215) Izmail'skii, Popov, J. Gen. Chem. (U.S.S.R.) 8, 695-697 (1938); Cent. 1939, I 2746; C.A. 33, 1263 (1939). (216) Grant, Hinshelwood, J. Chem. Soc. 1933, 260. (217) Carter, Coxe (to Karpen Bros.), U.S. 1,459,177, June 19, 1923; Cent. 1925, II 1224; C.A. 17, 2886 (1923). (218) Groves, J. Chem. Soc. 13, 331-333 (1861). (219) Stahler, Ber. 47, 910-911 (1914). (220) Picon, Bull. soc. chim. (4) 35, 979-981 (1924).

(221) Purgold, Ber. 6, 502-506 (1873). (222) Conant, Hussey, J. Am. Chem. Soc. 47, 477, 484 (1925). (223) Harlow, Ross (to Dow Chem. Co.), U.S. 1,891,415, Dec. 20, 1935; Cent. 1933, I 1683; C.A. 27, 1890 (1933). (224) Edgar, Ind. Eng. Chem. 31, 1439-1446 (1939). (225) Peck (to Std. Oil Dev. Co.), U.S. 2,293,214, Aug. 18, 1942. C.A. 37, 888 (1943). (226) Daudt (to du Pont Co.), U.S. 2,091,114, Aug. 24, 1937; Cent. 1937, II 3075; C.A. 31, 7446 (1937). (227) Amick, Parmelee, Stecher (to du Pont Co.), U.S. 2,091,112, Aug. 24, 1937; Cent. 1937, II 3075; C.A. 31, 7446 (1937). (228) Downing, Parmelee, Pedersen, Stecher (to du Pont Co.), U.S. 2,004,160, June 11, 1935; Cent. 1935, II 3702; C.A. 29, 4775 (1935). (229) Downing, Bake (to du Pont Co.), U.S. 2,000,069, May 7, 1935, Cent. 1935, II 3702; C.A. 29, 4026 (1935). (230) Calcott, Parmelee, Stecher (to du Pont Co), U.S. 1,983,535, Dec. 11, 1934; Cent. 1935, I 2599; C.A. 29, 817 (1935): Brit. 453,271, Sept. 1, 1936, C.A. 31, 1043 (1937), not in Cent.

(231) Downing, Bake (to du Pont Co.), U.S. 1,979,254, Nov. 6, 1934, Cent. 1935, II 1955: C.A. 29, 111 (1935). (232) Calcott, Parmelee, Meschter (to du Pont Co.), U.S. 1,962,173, June 12, 1934; Cent. 1934 II 3842; C.A. 28, 4847 (1934). (233) Calcott, Parmelee, Meschter (to du Pont Co.), U.S. 1,944,167, Jan. 23, 1934; Cent. 1934, I 2654; C.A. 28, 1982 (1934). Daudt (to du Pont Co.), U.S. 1,749,567, March 4, 1930; Cent. 1930, I 3354, C.A. 24, 2138 (1930). (235) Daudt, Parmelce (to du Pont Co.), U.S. 1,717,961, June 18, 1929; Cent. 1929, II 2101; C.A. 23, 3931 (1929). (236) Kraus, Callis (to Std. Oil Dev. Co.), U.S. 1,697,245, Jan. 1, 1929; Cent. 1929. I 2468; C.A. 23, 1262 (1929). (237) Calcott, Daudt (to du Pont), U.S. 1,692,926. Nov. 27, 1928; Cent. 1929, I 1741; C.A. 23, 608 (1929). (238) Calcott, Parmelee, Lorriman, U.S. 1,664,021, March 27, 1928; Cent. 1928, I 2989; C.A. 22, 1677 (1928). Brit. 280,169, Dec. 30, 1927; Cent. 1928, I 1459; [C.A. 22, 3042 (1928)]. Ger. 504,827, Aug. 14, 1930; [Cent. 1930, I 2440]; C.A. 25, 525 (1931): French 638,103, July 22, 1927; [C.A. 23, 275 (1929)], not in Cent. (239) Monroe (to du Pont Co.), U.S. 1,661,809, March 6, 1928; Cent. 1928, I 2304; C.A. 22, 1367 (1928). (240) Youtz (to Genl. Motors Corp.), U.S. 1,658,544, Feb. 7, 1928, Cent. 1928, I 1913, C.A. 22, 1164 (1928).

(241) Calcott, English (to du Pont Co.), U.S. 1,652,812, Dec. 13, 1927; Cent. 1928, I 1459; C.A. 22, 865 (1928). (242) Daudt, Parmelee, Calcott (to du Pont Co.), U.S. 1,645,375, Oct. 11, 1927; Cent. 1928, I 1328; C.A. 21, 3907 (1927). (243) Calingaert (to Genl. Motors Corp.), U.S. 1,622,233, March 22, 1927; Cent. 1928, I 1709; C A. 21, 1546 (1927). (244) Kraus, Callis (to Std. Oil Dev. Co.), U.S. 1,612,131, Dec. 28, 1926; Cent 1927, II 2111; C.A. 21, 593 (1927): Brit. 290,444, June 14, 1928; Cent. 1929, II 1214; C.A. 23, 848 (1929); Brit. 214,221, June 4, 1924; Cent. 1926, I 491; C.A. 18, 2524 (1924): French 578,858, Oct. 6, 1924, Cent. 1926, I 491; not in C.A. (245) Britton (to Dow Chem. Co.), U.S. 1,805,756, May 19, 1931; Cent. 1931, II 1192; C.A. 25, 3667 (1931). (246) Daudt (to du Pont Co.), U.S. 1,705,723, March 19, 1929; Cent. 1929, II 650; C.A. 23, 2192 (1929): Brit. 283,913, March 14, 1928, Cent. 1929, I 696; C.A. 22, 4134 (1928): Ger. 533,779, Oct. 13, 1927; C.A. 26, 738 (1932); not in Cent.: French 642,120, Aug. 22, 1928; Cent. 1929, I 696; C.A. 23, 1143 (1929). (247) Kraus, Callis (to Std. Oil Dev. Co.), U.S. 1,690,075, Oct. 30, 1928; Cent. 1929, I 696; C.A. 23, 245 (1929). (248) Daudt (to du Pont Co.), Brit. 297,106, Dec. 14, 1927; Cent. 1928, II 2404; C.A. 22, 2836 (1928). (249) Morton, LeFevre, Hechenbleikner, J. Am. Chem. Soc. 58, 757 (1936). (250) Morton, Davidson Hakan, J. Am. Chem. Soc. 64, 2243 (1942).

(251) Hückel, Kraemer, Thiele, J. prakt. Chem. (2) 42, 207-217 (1935). (252) Groll, J. Am. Chem. Soc. 52, 3000 (1930). (253) Spencer, Crewdson, J. Chem. Soc. 93, 1825 (1908). (254) Houben, Boedler, Fischer. Ber. 69, 1766-1788 (1936). (255) Schlenk, Ber. 64, 734-736 (1931). (256) Rudd, Turner, J. Chem. Soc. 1928, 686-691. (257) Coleman, Hermanson, Johnson, J. Am. Chem. Soc. 59, 1896 (1937). (258) Coleman, Buchanan, Paxson, J. Am. Chem. Soc. 55, 3670 (1933). (259) Evans, Lee, J. Am. Chem. Soc. 56, 654-657 (1934). (260) Diuguid, J. Am. Chem. Soc. 63, 3527-3529 (1941).

(261) I.G., French 669,739, Nov. 29, 1929; Cent. 1930, I 3237; C.A. 24, 1866 (1930). (262) Hopff, Ber. 64, 2478 (1931). (263) I.G., Brit. 310,438, May 23, 1929; Cent. 1929, II 1214; C.A. 24, 2137 (1930). (264) I.G., Brit. 354,992, Sept. 10, 1931; Cent. 1931, II 3545; C.A. 26, 5574 (1932). (265) Semon, Yohe (to B. F. Goodrich Co.), U.S. 2,070,848, Feb. 16, 1937; Cent. 1937, II 858; [C.A. 31, 2229 (1937)]. (266) Nikitin, Rudneva, J. Applied Chem. (U.S.S.R.) 6, 45-59 (1933); Cent. 1934, I 1415, C.A. 27, 5964 (1933). (267) Nikitin, Rudneva, J. Applied Chem. (U.S.S.R.) 12, 716-720 (1933); Cent. 1934, II 537; C.A. 28, 3891 (1934). (268) Ismail'skii, Popov, J. Applied Chem. (U.S.S.R.) 12, 776-785, 786-789 (1939); C.A. 34, 3246 (1940). (269) Tolmachev, Trans. Lenngrad Chem.-Tech. Inst. 1, 119-124 (1934); C.A. 29, 2930 (1935); not in Cent. (270) Sheppard, Adams (to Naugatuck Chem. Co.), U.S. 1,471,213, Oct. 16, 1923; Cent. 1926, II 2500; C.A. 18, 155 (1924): Brit. 207,499, Jan. 23, 1924; Cent. 1926, II 2500; C.A. 18, 150 (1924).

(271) Calingaert, Soroos, Hnizda, Shapiro, J. Am. Chem. Soc. 62, 1545-1547 (1940). (272)
Underwood, Gale, J. Am. Chem. Soc. 56, 2117-2120 (1934). (273) Gilman, Furry, J. Am. Chem. Soc. 59, 1214-1216 (1928). (274) Marvel, Gauerke, Hill, J. Am. Chem. Soc. 47, 3009-3011 (1925). (275) Crymble, J. Chem. Soc. 105, 668 (1914). (276) Slotta, Jacobi, J. prakt. Chem. (2) 120, 274 (1928). (277) Brown, Campbell, J. Chem. Soc. 1937, 1700. (278) Levy, Campbell, J. Chem. Soc. 1939, 1443. (279) Graebe, Pictet, Ann. 247, 302-303 (1888). (280) Wanag, Veinbergs, Ber. 75, 1569 (1942).

(281) Sah, Ma, Ber 65, 1630-1633 (1932). (282) Sah, Ma, Sci. Repts. Natl. Tsing Hua Univ.
2, 147-149 (1933). (283) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934). (284)
Morritt, Levey, Cutter, J. Am. Chem. Soc. 61, 15-16 (1939). (285) Gillespie, J. Am. Chem. Soc. 56, 2740-2741 (1934). (286) Bennett, Jones, J. Chem. Soc. 1939, 421. (287) Lauer, Sanders, Leekley, Ungnade, J. Am. Chem. Soc. 61, 3050 (1939). (288) Drew, Sturtevant, J. Am. Chem. Soc. 61, 2666 (1939). (289) V. H. Dermer, O. H. Dermer, J. Ory Chem. 3, 291 (1938). (290) Dehn, Cope, J. Am. Chem. Soc. 48, 2636-2637 (1926).

3:7020 2-CHLOROPROPENE-1 Cl
$$C_3H_5Cl$$
 Beil. I - 198 (Isopropenyl chloride α -methylyinyl chloride) CH_2 -C=CH₂ I_{1-} (169)

B.P. F.P. 22.65° at 760 mm. (1)
$$-138.6$$
° (2) $D_9^9 = 0.918$ (5) $n_D^{20} = 1.3949$ (4) 22.6° at 760 mm. (2) -137.4 ° (1) 22.5-23.5° at 760 mm. (3) 21.7-21.8° at 743 mm. (4)

[For prepn. of \bar{C} (45%) together with 2,2-dichloropropane, b.p. 70° (3:7140) (55%), from acetone (1:5400) + PCl₅ see (6) (7) (9); from 2,2-dichloropropane (3:7140) + alc. KOH (3) or KOAm in AmOH (10); for prepn. of \bar{C} (together with 1-chloropropene-1 (3:7030)) from 1,2-dichloropropane (3:5200) + alc. KOH see (11) (12) (13); for prepn. of \bar{C} together with cyclopropane (b.p. -34°) from a mixt. of 1,3-dichloropropane (3:5450) + 1,2,2-trichloropropane (3:5475) on treatment with Zn see (14).]

 \bar{C} with MeOH forms a const.-boilg. mixt., b.p. 22.0°, contg. 97% \bar{C} + 3% MeOH (15). \bar{C} treated with conc. H₂SO₄ and (after evoln. of HCl has ceased) poured into much aq. and steam-distd. (16) or \bar{C} htd. with 10 vols. aq. in s.t. at 140–180° (17) yields acetone (1:5400) q.v.

 \bar{C} adds Br_2 yielding (8) (12) 2-chloro-1,2-dibromopropane [Beil. I-111], b.p. 169–170° cor. (12).

 $\bar{\rm C}$ adds HBr fairly readily; in the presence of air or of antioxidants in vacuo, the product is pure 2-chloro-2-bromopropane, b.p. $91.0-92.0^{\circ}$ at 740 mm., $34.6-34.8^{\circ}$ at 100 mm., $n_{\rm D}^{20}=1.4575$ (4); in the presence of organic peroxides the major reactn. prod. is 2-chloro-1-bromopropane, b.p. $117.6-118.0^{\circ}$ at 740 mm., $52.2-52.8^{\circ}$ at 75 mm., $n_{\rm D}^{20}=1.4778$ (4).

3:7020 (1) Timmermans, Bull. soc. chim. Belg. 27, 334-343 (1913); Cent. 1914, I 618. (2) Timmermans, Bull. soc. chim. Belg. 36, 504 (1927). (3) Kahovec, Kohlrausch, Z. physik. Chem. B-46, 178 (1940). (4) Kharasch, Engelmann, Mayo, J. Org. Chem. 2, 288-302 (1938). (5) Linnemann, Ann. 138, 125 (1866). (6) Henne, Renoll, J. Am. Chem. Soc. 59, 2435 (1937). (7) Stewart, Weidenbaum, J. Am. Chem. Soc. 58, 98 (1936). (8) Friedel, Ann. 112, 236-238 (1859). Friedel, Ann. 134, 265 (1865). (10) West, Farnsworth, Trans. Faraday Soc. 27, 147 (1931).

(11) Goudet, Schenker, Helv. Chim. Acta 10, 136-137 (1927). (12) Reboul, Ann. chim. (5) 14, 462-464 (1878). (13) Young (to Carbide and Carbide Corp.), U.S. 1,752,049, March 25, 1930; Cent. 1930, II 1280. (14) Hass, Hinds (to Purdue Research Foundation), U.S. 2,235,762, March 18, 1941; C.A. 35, 4042 (1941). (15) Lecat, Rec. trav. chim. 46, 242 (1927). (16) Oppenheim, Ann. Suppl. 6, 364-366 (1868). (17) Linnemann, Ann. 161, 66 (1872).

3: 7022 ETHYL HYPOCHLORITE

CH₃.CH₂OCl

C₂H₅OCl

Beil. I - 324 I_{1} -(164)

 I_{2} -(325)

B.P. 36° at 758 mm. (1) 36° at 752 mm. (2) $D^{-6} = 1.013 (1)$

[See also ter-butyl hypochlorite (3:7165).]

Colorless oil (rapidly turning yellow in light) with odor like hypochlorous acid. — Č explodes on superhtg, its vapor or even in cold upon addn, of Cu powder or in bright sunlight — C gradually decomposes on stdg. in diffuse light with forms. of ethyl acetate and other prods. (3) (4) (10). [For study of stability of \bar{C} in aq. or in CCl₄ soln. see (4).] — Sol. ether, C₆H₆, CHCl₃; for distrib. of C between aq. and CCl₄ see (4).

[For prepn. of C from EtOH (1:6130) with Cl₂ in cold aq. alk. (2) (5) (1) (6) (7) (8) (9) or alk. earth (9) or with aq. HOCl in pres. of CCl4 (4) see indic. refs.; for formn. of C from EtOH (1:6130) with Cl_2 at -18° (8) or with dry $Ca(OCl)_2$ (15) or aq. HOCl (15) (16) see indic. refs.

Č is able according to prevailing circumstances to act as an oxidizing agent, chlorinating agent, or for addn. to unsaturated linkages: furthermore since in aq. C is extensively hydrolyzed (69% in sat. aq. soln. (4)) it may serve as source of HOCl; examples of these reactions are given below.

 $\bar{\mathbf{C}}$ with inorganic reactants. $\bar{\mathbf{C}}$ with KI + AcOH liberates I₂ quant, according to the equation $C_2H_5OCl + 2HI \rightarrow C_2H_5OH + HCl + I_2$ (use in quant. detn. of \bar{C} (2) (4) (7)); C with dil. alk. Na₃AsO₃ gives (11) (12) EtCl (3:7015) + Na₃AsO₄; C in dil. alk. KSH/ KCN mixt. gives (12) KSCN + KCl + EtOH.

[C adds to dry SO₂ yielding (5) ethyl chlorosulfonate [Beil. I-327, I₂-(327)], b.p. 151-154° $\operatorname{dec.}, n_{\mathbf{D}}^{18} = 1.4174.$

 \sqrt{C} (1 mole) with KCN (2 moles) in 7 pts. aq. at -5° gives (30% yield (13)) ethyl cyanoiminoformate [Beil. II-549, II₁-(238), II₂-(511)], oil, b.p. 133° dec., accompanied by a little diethyl di-imino-oxalate [Beil. II-547, II₁-(238)], m.p. 38°, b.p. 172° strong dec.; in aq. alc., however, the same components give (13) diethyl iminocarbonate [Beil. III-37, III₁-(18), III₂-(31)], oil, b.p. 141° cor., accompanied by diethyl di-iminooxalate (see above),

C with organic reactants. [C with EtOH (1:6130) yields (8) acetaldehyde (1:0100). acetaldehyde diethylacetal (1:0156), and paraldehyde (1:0170). — \tilde{C} with acetaldehyde (1:0100) at 0° followed by distn. of the mixture with anhyd. oxalic acid yields (3) chloroacetaldehyde (3:7212).]

IC with acetone (1:5400) yields (3) chloroacetone (3:5425); C with methyl phenyl ketone (acetophenone) (1:5515) yields (3) ω-chloroacetophenone (phenacyl chloride) (3:1212); Č with benzaldehyde (1:0195) yields (3) benzoyl chloride (3:6240),]

[C with phenol in CCl4 yields (3) both o-chlorophenol (3:5980) and p-chlorophenol

(3:0475); Č with hydroquinone (1:1590) in ether gives (3) 2,3-dichlorohydroquinone (3:4220).

Č with phenyl MgBr in ether at 0° gives (60% yield (14)) (1) chlorobenzene (3:7903). [Č with phenylacetylene (1:7425) in CCl₄ yields (3) ω,ω-dichloroacetophenone (3:6835).] [Č with cyclohexene (1:8070) in CCl₄ yields (3) 2-chlorocyclohexanol-1 (3:0175); for reactn. of Č with indene (1:7522) or with 1.4-dihydronaphthalene see (3).

[\bar{C} with olefins adds to the unsatd. linkage to give chlorohydrin ethyl ethers (a process now generically designated as chloroalkoxylation): e.g., \bar{C} with ethylene yields (15) (17) β -chloroethyl ethyl ether (ethylene chlorohydrin ethyl ether) (3:7463); \bar{C} with amylene gives (3) a corresp. prod.; the rate of addn. of \bar{C} to olefins increases from ethylene to amylene (18). — For extensive studies on the prepn. of chlorohydrin ethers from olefins by use of alcs. + N,N-dichlorobenzenesulfonamide (which mixture appears to generate ROCl as the active addn. agent) see (18) (19) (20) (21).]

[\bar{C} has, however, but slight tendency to add to unsaturated acids: e.g., \bar{C} in CCl₄ has no actn. (22) on cinnamic acid (1:0735); \bar{C} in dry ether or CCl₄ with crotonic acid (1:0425) or sorbic acid gives only traces (23) of the expected prods. — \bar{C} in CCl₄ with hexen-3-oic acid-1 (hydrosorbic acid) [Beil. II-435, II₁-(193), II₂-(404)] gives addn. to extent of 92% in 3 days (23), but the prod. is not a chloro-ethoxy-hexanoic acid and consists entirely of a mixt. of two stereoisomeric β -chlorohexanoic lactones.]

3:7022 (1) Durand, Naves, Bull. soc. chim. (4) 37, 717-723 (1925). (2) Sandmeyer, Ber. 18, 1767-1769 (1885). (3) Goldschmidt, Endres, Dirsch, Ber. 58, 572-577 (1925). (4) Taylor, MacMullen, Gammal, J. Am. Chem. Soc. 47, 395-403 (1925). (5) Sandmeyer, Ber. 19, 857-861 (1886). (6) Schaefer, Z. physik. Chem. 93, 316 (1919). (7) Chattaway, Backeberg, J. Chem. Soc. 123, 2999-3003 (1923). (8) Chattaway, Backeberg, J. Chem. Soc. 125, 1097-1101 (1924). (9) Deanesly (to Shell Development Co.), U.S. 1,938,175, Dec. 5, 1933; Cent. 1934, I 1709; C.A. 28, 1053 (1934). (10) Durand, Naves, Bull. soc. chim. (4) 37, 1152-1154 (1925).

(11) Gutmann, Z. anal. Chem. 66, 232 (1925). (12) Gutmann, Ber. 50, 1717-1718 (1917). (13) Nef, Ann. 287, 274-275, 298-299 (1895). (14) LeFevre, Markham, J. Chem. Soc. 1834, 703-704. (15) Sukhnevich, Chilingaryan, J. Gen. Chem. (U.S.S.R.) 2, 783-789 (1932); Cent. 1933, II 1170; C.A. 27, 2670 (1933). (16) Schmitt, Goldberg, J. prakt. Chem. (2) 19, 393-396 (1879). (17) Sukhnevich, Chilingaryan, Ber. 68, 1210 (1935). (18) Sklyarov, J. Applied Chem. (U.S.S.R.) 12, 1835-1839 (1939); Cent. 1940, II 607-608; C.A. 34, 7843 (1940). (19) Sklyarov, J. Gen. Chem. (U.S.S.R.) 9, 2121-2125 (1939); Cent. 1940, II 199-200; C.A. 34, 4055 (1940). (20) Likhosherstov, Sklyarov, Acta Univ. Voronegiensis 8, No. 2, 47-53 (1935); Cent. 1936, II 2524; C.A. 32, 4524-4525 (1938).

(21) Likhosherstov, Alekseev, J. Gen. Chem. (U.S.S.R.) 4, 1279-1282 (1934); Cent. 1936, I
4287; C.A. 29, 3306 (1935). (22) Jackson, Pasiut, J. Am. Chem. Soc. 49, 2079 (1927). (23)
Bloomfield, Farmer, J. Chem. Soc. 1932, 2065, 2070-2071.

B.P.
$$F.P.$$
 -117.0° (8) $D_{4}^{25} = 0.84281$ (8) 36.5° at 760 mm. (2) (5) $D_{4}^{20} = 0.86168$ (8) $n_{D}^{20} = 1.377$ (17) $36.2-36.5^{\circ}$ u.c. (3) 0.8610 (7) 36.25° (4) $D_{4}^{15} = 0.86797$ (8) $n_{D}^{15} = 1.38110$ (8) 36.0° at 760 mm. (6) 35.5° at 757 mm. (7) 34.8 at 760 mm. (8) 34.5° at 740 mm. (43)

Colorless limpid liquid with not unpleasant odor. — Alm. insol. aq. [for precise data see (9) (10) (11).] — [For use as refrigerant see (12).]

 $\bar{\mathbf{C}}$ with MeOH, b.p. 64.7°, forms const.-boilg. mixt., b.p. 33.4°, contg. 94 wt. % $\bar{\mathbf{C}}$ (4); $\bar{\mathbf{C}}$ with EtOH, b.p. 78.3°, forms const.-boilg. mixt., b.p. 35.6°, contg. 97.2 wt. % $\bar{\mathbf{C}}$ (4) [for other azeotropes see Beil. I₂-(72).]

[For prepn. of \bar{C} from propanol-2 (1.6135) with conc. HCl + ZnCl₂ (yield: 70-76% (13)) (14) (15) (16) (17) (43); with PCl₃ + ZnCl₂ (74% yield (15)); with PCl₅ + ZnCl₂ (66% yield (15)); with SOCl₂ + pyridine (80% yield (15)); or with AlCl₃ (70% yield (18)) see indic. refs., for prepn. from propylene by addn. of HCl under various conditions see (19) (20) (21) (22) (23) (24) (25) (26) (27) (28) (29) (30).]

[For formn. of \bar{C} (together with other products) by actn. of Cl_2 on propane see (31), for further actn. of Cl_2 on \bar{C} see (3).] — [For isomerization of 1-chloropropane to \bar{C} in presence of metallic catalysts see 1-chloropropane (3:7040).] — [For purification of \bar{C} with conc. H_2SO_4 see (32).]

Č on hydrolysis yields propanol-2 (1:6135). [For study of this reactn. see (2); for use in mfg. of propanol-2 see (33).]

[For reactn. of C with KI in acctone see (1).]

C with Mg in dry ether gives (90% yield (17), 93.9% (44)) RMgCl (for reactions of this see below).

[For study of behavior of \bar{C} with C_6H_6 or toluene in pure HCl under press. see (45); for behavior with C_6H_6+Al/Hg see (46).]

- (36) Isobutyranilide: m.p. 105° (34); 104-105° (35); u.e. (36); 103° cor. (37). [From C (36) or from isopropyl bromide (37) via conversion to RMgX and reactn. with phenyl isocyanate.]
- —— Isobutyr-p-toluidide: m.p. 108.5-109.5° (38); 106-106.5° (39). [Presumably similarly obtainable via RMgCl + p-tolyl isocyanate but not actually so recorded.]
- ---- Isobutyr- α -naphthalide: unrecorded.
- —— S-(Isopropyl)isothiourea picrate: m.p. 196° (40). [From isopropyl bromide on htg. 3 hrs. in alc. with thiourea, then adding PkOH (40), but not recorded from C.]
- Isopropyl mercuric chloride (sec-PrHgCl): m.p. 97° (47). [Reported only by indirect means (47).]
- ---- N-(Isopropyl)phthalimide (2-(N-phthalimido)propane): m.p. 86° (48), 85° (49). [Not reported from \bar{C} but obtd. from isopropyl bromide with K phthalimide in s.t. at 160-170° for 7 hrs. (49), also indirectly (48) (50).]
- ---- N-(Isopropyl)-3-nitrophthalimide: unreported.
- ---- N-(Isopropyl)tetrachlorophthalimide: unreported.
- ---- N-(Isopropyl)-N-(p-bromobenzenesulfonyl)-p-anisidine: m.p. 107° u.c. (52). [Not reported from $\bar{\mathbf{C}}$ but obtd. from isopropyl bromide with N-(p-bromobenzenesulfonyl)-p-anisidine in alc. KOH (52).]
- ---- p-Isopropoxybenzoic acid: m.p. 160-163° (53). [From \tilde{C} (?) or from isopropyl bromide with ethyl p-hydroxybenzoate (1:1534) in abs. alc. NaOEt on refluxing 1 hr. (53).]
- —— Isopropyl 2,4,6-triiodophenyl ether: m.p. 43° cor. (41). [From isopropyl bromide on refluxing with 2,4,6-triiodophenol, m.p. 157-158°, in alc. NaOEt (41).]
- Isopropyl α -naphthyl ether: b.p. 282.5° cor. (42) [picrate: m.p. 104.5-105.5° cor. (42)].

—— Isopropyl β-naphthyl ether: b.p. 285° cor., m.p. 40.0° cor. (42) [picrate: m.p. 95.0-95.5° cor. (42)].

3:7025 (1) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925). (2) Hughes, Shapiro, J.Chem. Soc. 1937, 1177-1183. (3) Rust Vaughan, J. Org. Chem. 6, 479-488 (1941). (4) Lecat, Rec. trav. chim. 46, 242 (1927). (5) Zander, Ann. 214, 157-158 (1882). (6) Matthews, Fehland, J. Am. Chem. Soc. 53, 3216 (1931). (7) Groves, Sugden, J. Chem. Soc. 1937, 161. (8) Timmermans, Martin, J. chim. phys. 25, 422 (1927). (9) Fühner, Ber. 57, 514 (1924). (10) van Arkel, Vles, Rec. trav. chim. 55, 408 (1936)

(11) Rex, Z. physik. Chem. 55, 364 (1906). (12) Churchill, U.S. 1,996,538, April 2, 1935; Cent. 1936, II 1984. (13) Norris, Orp. Syntheses, Coll. Vol. 1 (1st ed.), 137-138 (1932). (14) Norris, Taylor, J. Am. Chem. Soc. 46, 757 (1924). (15) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929). (16) Linnemann, Ann. 136, 41-42 (1865). (17) Whitmore, Johnston, J. Am. Chem. Soc. 60, 2265 (1938). (18) Norris, Sturgis, J. Am. Chem. Soc. 61, 1415 (1939). (19) Maass, Sivertz, J. Am. Chem. Soc. 47, 2883-2891 (1925). (20) Sutherland, Mass, Trans.

Roy. Soc. Can. (3) 20, III 499-505 (1926); Cent. 1927, II 2174; C.A. 21, 2657 (1927).

(21) Thomas, Morris (to Monsanto Chem. Co.), U.S. 2,285,173, June 9, 1942; C.A. 36, 6546 (1942). (22) Ballard (to Shell Development Co.), U.S. 2,284,467, May 26, 1942; C.A. 36, 6546 (1942). (23) Arnold, Lessig (to du Pont), U.S. 2,097,750, Nov. 2, 1937, Cent. 1938, I 1217. (24) du Pont Co., Brit. 466,134, June 17, 1937; Cent. 1937, II 2431. (25) Daudt (to du Pont), U.S. 2,016,075, Oct. 1, 1935; Cent. 1936, I 2206. (26) Daudt, Stansfield (to du Pont), U.S. 2,016,072, Oct. 1, 1935; Cent. 1936, I 2206. (27) du Pont Co., Brit. 450,843, Aug. 20, 1936; Cent. 1936, II 4048. (28) Nutting, Petrie, Crooke, Huscher (to Dow Chem. Co., U.S. 1,985,457, Dec. 25, 1934; Cent. 1935, I 3597. (29) Brouwer, Wibaut, Rec. trav. chim. 53, 1001-1010 (1934). (30) Wibaut, Diekmann, Rutgers, Rec. trav. chim. 47, 477-495 (1928).

(31) Hass, McBee, Weber, Ind. Eng. Chem. 27, 1190-1195 (1935) (32) Norris (to Petroleum Chem. Corp), U.S. 1,825,814, Oct. 6, 1931; Cent. 1932, I 1438. (33) Britton, Coleman, Moore (to Dow Chem. Co.), U.S. 2,110,838, Mar. 8, 1938; Cent. 1938, I 4533. (34) Tingle, Blanck, J. Am. Chem. Soc. 30, 1408 (1908). (35) Fieser, Campbell, J. Am. Chem. Soc. 60, 168-169 (1938). (36) Underwood, Gale, J. Am. Chem. Soc. 56, 2119 (1934). (37) Schwartz, Johnson, J. Am. Chem. Soc. 53, 1065 (1931). (38) von Auwers, Ungemach, Ber. 67, 252 (1934). (39) Fieser, Hartwell, Seligman, J. Am. Chem. Soc. 58, 1226 (1936). (40) Levy, Campbell, J. Chem. Soc. 1939, 1443.

(41) Drew, Sturtevant, J. Am. Chem. Soc. 61, 2666 (1931). (42) V. H. Dermer, O. C. Dermer, J. Org. Chem. 3, 290-291 (1939). (43) Vogel, J. Chem. Soc. 1943, 638-639. (44) Houben, Boedler, Fischer, Ber. 69, 1769, 1781 (1936). (45) Simmons, Hart, J. Am. Chem. Soc. 66, 1310-1311 (1944). (46) Diuguid, J. Am. Chem. Soc. 63, 3527-3529 (1941). (47) Goret, Cent. 1922 III 1371. (48) Vanags, Acta Univ. Latrensis, Kım. Fakultat, Series 4, No. 8, 405-421 (1939); Cent. 1939 II 3816; C.A. 34, 1983 (1940). (49) Gabriel, Ber. 24, 3106-3107 (1891). (50) Sachs, Ber. 31, 1228 (1898).

(51) Merritt, Levey, Cutter, J. Am. Chem. Soc. **61**, 15-16 (1939). (52) Gillespie, J. Am. Chem. Soc. **56**, 2740-2741 (1934). (53) Lauer, Sanders, Leekley, Ugnade, J. Am. Chem. Soc. **61**, 3050 (1939).

3: 7030 1-CHLOROPROPENE-1 H
$$C_3H_5Cl$$
 Beil. I - 198 (Propenyl chloride, β -methylvinyl chloride) CH₃. CH= C C_1

trans form

B.P. F.P. 37.4° at 760 mm. (1)
$$-99^{\circ}$$
 (1) $n_{\rm D}^{20} = 1.4054$ (2) 36.7° at 747 mm. (2)

cis form

B.P. F.P.
$$n_{\rm D}^{20} = 1.4053$$
 (2) $n_{\rm D}^{20} = 1.4053$ (2) $n_{\rm D}^{20} = 1.4053$ (2)

Mobile colorless liq. lighter than water (3). $\ddot{\mathbf{C}}$ is stable toward hydrolysis; for use in anal. of mixts. of $\ddot{\mathbf{C}}$ with 3-chloropropene-1 (allyl chloride) (3:7035) see (7).

[For prepn. of \bar{C} from 1,1-dichloropropane (3:7230) + alc. KOH in s.t. at 100° (3) (4) or with alc. NaOEt (2) see indicated refs.; for formn. from 1,2-dichloropropane (propylene dichloride) (3:5200) + alc. KOH see (3) (5) (\bar{C} is principal product (5), but some 2-chloropropene-1 (3:7020) and propadiene are also formed); for formn. of cis isomer from α,β -dichloro-n-butyric acid of m.p. 62.5-63° by warming with Na₂CO₃ see (6).]

 \ddot{C} with Br₂ at -15° yields 1-chloro-1,2-dibromopropane, b.p. 177-177.5° cor. (3).

 $\bar{\mathbf{C}}$ in presence of air or added peroxides adds HBr rapidly to give exclusively (2) 1-chloro-2-bromopropane, b.p. 117.2-117.3° at 740 mm., 52.0° at 75 mm., $n_D^{20} = 1.4795$ (2).

[For study of molecular refraction and dipole moment of both cis and trans forms of C see (8).]

3:7030 (1) Timmermans, Bull. soc. chim. Belg. 36, 504 (1927). (2) Kharasch, Engelmann, Mayo, J. Org. Chem. 2, 288-302 (1938). (3) Reboul, Ann. chim. (5) 14, 462-464 (1878). (4) Goudet, Schenker, Helv. Chim. Acta 10, 132-133 (1927). (5) Klebanskii, Vol'kenshtein, J. Applied Chem. (U.S.S.R.) 8, 108-116 (1935); Cent. 1931, II 1255; C.A. 29, 6879 (1935). (6) Wislicenus, Ann. 248, 297-298 (1888). (7) McBee, Hass, Chao, Welch, Thomas, Ind. Eng. Chem. 33, 180-181 (1941). (8) Hannay, Smyth, J. Am. Chem. Soc. 68, 1005-1008 (1946).

3: 7035 3-CHLOROPROPENE-1 CH₂=CH.CH₂ C₃H₅Cl Beil. I - 198 (Allyl chloride) Cl
$$I_{1-}$$
 (82) I_{2-} (169)

B.P. F.P. 46.0-47.5° at 772.5 mm. (1) -134.5°, (7) $D_4^{25} = 0.93109$ (7) 46-47° at 758 mm. (2) -136.4° (10) 46.0-46.5° (3) $D_4^{20} = 0.9379$ (14) 45.7° at 760 mm. (5) 0.9374. (11) 0.9267 (9) 45.36° (6) $D_4^{15} = 0.94419$ (7) 45.1° at 760 mm. (7) 44.9° at 751 mm. (108) $D_4^{15} = 0.94419$ (7) 44.8° at 754 mm. (8) (61) 44.8° at 754 mm. (9) 44.6° at 760 mm. (10) 44.6° (11) (12) $D_4^{15} = 0.94419$ (7) 44.5-44.7° at 744 mm. (13) 44.4-44.6° (14)

Colorless oil, spar. sol. aq.; volatile with steam.

Č with EtOH (1:6130) forms a const.-boilg. mixt., b.p. 44° at 760 mm., contg. 95% Č (5); with formic acid (1:1005) forms a const.-boilg. mixt., b.p. 45.0° at 760 mm., contg. 92.5% Č (15).

C is one of most toxic of all halohydrocarbons (for study see (16)).

[For prepn. of Č from allyl alcohol (1:6145) on satn. at 0° with HCl gas and htg. in s.t. at 100° for 3 hrs. (17), with conc. HCl (2 moles) in s.t. 15 hrs. at 100° (78% yield (3)) cf. (1) (23) or 10 days at room temp. (55-65% yield (18)), on distn. with large excess (16 pts.) 6 N HCl (50% yield (19)), with ZnCl₂ + HCl gas at 75-82° (yield: 60% (20), 58% (21)), or dislvd. in cold conc. HCl and treated with Cu₂Cl₂ (small amt.) + conc. H₂SO₄ (yield 85-90% (2), 80% (22)) see indic. refs.; from allyl alcohol (1:6145) with SOCl₂ in CaH₈

(71% yield (21)), with PCl₃ (1) (24), with PCl₃ + ZnCl₂ in C_6H_6 at 0° (63% yield (21)), with PCl₅ + pyridine (73% yield (9)), with PCl₅ + ZnCl₂ in C_6H_6 (57% yield (21)) see indic. refs.]

[For prepn. of \bar{C} from allyl formate (1:3035) with conc. HCl + a little Cu₂Cl₂ + conc. H₂SO₄ (93–98% yield (22)), or with ZnCl₂ + HCl gas (80–90% yield (25)) (26) see indic. refs.; from allyl oxalate in alc. CaCl₂ in s.t. at 100° see (27); from allyl iodide with alc. HgCl₂ at ord. temp. see (27).]

[For comml. prepn. of $\bar{\rm C}$ from propylene with Cl₂ at elevated temps., e.g., 500° (yield 96% $\bar{\rm C}$ accompanied by 3% 2-chloropropene-1 (3:7020) + 1% mixed cis and trans isomers of 1-chloropropene-1 (3:7030) (11)) (28) (29), see indic. refs. (note also that the high-boiling material from distn. of comml. $\bar{\rm C}$ contains (110) approx. 60% 1,3-dichloropropene-1 (3:5280) + 30% 1,2-dichloropropene (3:5200)); for examples of patents covering this procedure see (30) (31) (32) (33) (34) (35); from propane (34) (36) or 1-chloropropane (3:7040) (36) with Cl₂ + cat. at 500-700° see indic. refs.; from 1,2-dichloropropane (3:5200) by suitable pyrolysis (yield: 55-70% $\bar{\rm C}$ + 30-40% of mixt. of cis and trans isomers of 1-chloropropene-1 (3:7030) + 5% 2-chloropropene-1 (3:7020) (11)) cf. (12) (13) (39); for examples of relevant patents see (37) (38) (40).]

Reactions involving the double bond of \bar{C} . [\bar{C} with Cl_2 adds and/or substitutes according to conditions (for study of relative proportions of these reactions see (29) (11)); \bar{C} with Cl_2 at ord. temp. (41) or \bar{C} with SO_2Cl_2 in CCl_4 in pres. of peroxides (42) gives (80–90% yield (42)) 1,2,3-trichloropropane (3:5840) (note that this comprises one step in one of the modern syntheses of glycerol from petroleum (43) (44)); \bar{C} with Cl_2 at high temp. yields (11) a mixt. of prods. of which the dichloropropene fraction comprises (11) 47% 1,3-dichloropropene-1 (high-boilg. isomer) (3:5280) + 42% 1,3-dichloropropene-1 (low-boilg. isomer) (3:5280) + 11% 1,1-dichloropropene-2 (3:5140) + trace of 1,2-dichloropropene-2 (3:5190).]

[\bar{C} with Br₂ adds 1 mole of halogen yielding (45) mainly 1,2-dibromo-3-chloropropane (γ -chloropropylene dibromide) [Beil. I-111], b.p. 195° (45); for study of rate of addn. of Br₂ under various conditions see (14) (9) (46) (105); for heat of reactn. see (47).]

[\bar{C} with conc. aq. HCl in s.t. at 100° for 18 hrs. (48), or \bar{C} with dry HCl in dark at 0° in absence of FeCl₃ (33% yield (49)) or at room temp. in pres. of FeCl₃ (85–89% yield (49)), gives 1,2-dichloropropane (propylene dichloride) (3:5200); note that addn. of HCl is not complicated by a peroxide effect but is very slow unless FeCl₃ (or less advantageously AlCl₃) is used as a cat. (49). — \bar{C} satd. with HBr gas at 0° or below (50), or with conc. aq. HBr at 0° (51), or with HBr gas in s.t. at 100° for 8 hrs. (48) cf. (52), or in presence of Fe (53) or other cat., e.g., BiCl₃ (54), as directed, gives (yields: 36–38% (53), 43% (52), 50% (51), 87% (50)) 1-bromo-3-chloropropane (γ -chloro-n-propyl bromide) (trimethylene chlorobromide) [Beil. I-109, I₁-(36), I₂-(75)], b.p. 142°; note that the above mode of addn. is favored by peroxides (49) (54) cf. (106). — \bar{C} with HI (10–20% excess at 0°) gives exclusively (90–100% yield (55)) 1-chloro-2-iodopropane, b.p. 66.2° at 50 mm., $n_D^{20} = 1.5472$ (55); note that in this reactn. formn. of 2-iodopropane (isopropyl iodide) has also been reported (56).]

 $[\bar{C}\ (1\ mole)\ with conc.\ H_2SO_4\ (2\ moles)\ at\ 0^\circ\ gives\ an\ oily\ addn.\ prod.\ (24)\ (presumably\ \beta$ -chloroisopropyl hydrogen sulfate) which upon dilution with aq. and subsequent distillation gives (50% yield (57) (61)) (24) (58) (59) (60) 1-chloropropanol-2 (3:7747); in pres. of CuSO_4 the yield rises to 66-70% (62). — \bar{C} adds HOCl yielding (63) (64) (65) (76) 2,3-dichloropropanol-1 (glycerol β -dichlorohydrin) (3:6060). — \bar{C} with ter-butyl hypochlorite (3:7165) in MeOH contg. a little p-toluenesulfonic acid gives at 40° (44% yield (66)) 1,3-dichloro-2-methoxypropane (β , β '-dichloroisopropyl methyl ether), b.p. 154-156° at 730 mm., $D_{-}^{20}=1.2235,\ n_{10}^{20}=1.4542$ (66).]

[\bar{C} with liq. SO₂ + trace of ascaridole + a few drops of aq. or alc. HCl, HBr, or H₂SO₄ gives (70–100% yield (67)) cf. (68) allyl chloride polysulfone, no def. m.p., dec. 210–235°, sol. CHCl₃ or acetone but insol. most other org. solvents; note, however, that this addn. of SO₂ is completely inhibited by the pres. of as little as 5 mole % of allyl bromide or cinnamyl bromide (67). — \bar{C} (2 moles) with S₂Cl₂ (1 mole) in s.t. at 100° for 6 hrs. deposits sulfur and yields (69) bis-(β , γ -dichloro-n-propyl) sulfide, pale yel. oil, b.p. 181–182° at 15 mm. (69); the same components maintained at room temp. for 10 days, however, deposit no sulfur and on distn. yield (69) bis-(β , γ -dichloro-n-propyl) disulfide, b.p. 190° at 11 mm. (69).]

[\bar{C} (2 moles) with cyclopentadiene (1 mole) (1:8030) in s.t. at 170–180° for 8 hrs. gives (74% yield on C_5H_6 (70)) by Diels-Alder addn. 2,5-endomethylene-1,2,5,6-tetrahydrobenzyl chloride (1-(chloromethyl)-2,5-endomethylenecyclohexene-3), b.p. 54–57° at 11 mm. (70). — For polymerization of \bar{C} see (71) (101).]

[\bar{C} with excess diazomethane in ether stood for 3 days yields a yel. very hygroscopic ppt. presumably 3-(chloromethyl)- Δ^2 -pyrazoline (72).]

[\bar{C} with C_6H_6 + conc. H_2SO_4 gives (73) by addn. to the ethylene linkage β-chloro-n-propylbenzene (2-chloro-1-phenylpropane) [Beil. V-391, V₁-(189), V₂-(304)], b.p. 85° at 13 mm., $D_{-}^{19} = 1.047$, $n_{D}^{19} = 1.5245$ (73); note, however, that \bar{C} with C_6H_6 in pres. of FeCl₃ at -20° gives (33.5% yield (74)) (73) the isomeric (β-chloroisopropyl)benzene (1-chloro-2-phenylpropane) [Beil. V₁-(191)], b.p. 79° at 10 mm., $D_4^{17} = 1.0367$, $n_D^{16} = 1.52129$ (74); \bar{C} with C_6H_6 + AlCl₃ (½ mole) gives none of the β-chloroisopropylbenzene since it apparently reacts with more C_6H_6 yielding (74) α-methylbibenzyl (1,2-diphenylpropane [Beil. V-613, V₁-(288), V₂-(517)].] [For analogous condensation of \bar{C} with fluorobenzene, chlorobenzene (3:7903), and bromobenzene see (118).]

[For oxidn. of \bar{C} in liq. phase at 75–250° by O_2 in pres. of $Cu(OAc)_2$ or peroxide catalysts and in an org. solv. such as AcOH to hydroxylated cpds. sec (75).]

Reactions involving the halogen atom of \bar{C} . $[\bar{C} + H_2 \text{ over activated charcoal at } 300-500^{\circ}$ gives (58% yield (77)) propylene; note that the double bond is *not* (77) hydrogenated.] $[\bar{C}$ passed over activated charcoal contg. 1-2% KOH is dehalogenated (78) at 375° to extent of 21%; at 400°, 58%.]

[C with aq. vapor at 550-850° + cat. (79) or under press. with alkali hydroxides (80) or with HCl/Cu₂Cl₂(108) yields (cf. (43) (44)) allyl alcohol (1:7145). — C with alc. KOH (81) (107) or alc. NaOH (12) yields allyl ethyl ether (1:7850) + alkali chloride; for use of this reactn. in detn. of C in pres. of cis-1-chloropropene-1 (3:7030) and trans-1-chloropropene-1 (3:7030) see (12); for study of rate of reactn. of C with NaOMe at 16-18° (82) or of C with NaOEt at 35° and 50° (83) see indic. refs.]

[$\ddot{\mathbf{C}}$ with alc. KSH gives mainly (84) di-allyl sulfide [Beil. I-441, I₁-(226), I₂-(478)], b.p. 138-139° (84).] — [For reactn. of $\ddot{\mathbf{C}}$ with alkali polysulfides in propn. of rubber-like prod. see (85).]

[For studies of rate of reactn. of \bar{C} with KI in acetone at 20° (83), 25° (86), or 60° (87) cf. (9) see indic. refs.; for reactn. of \bar{C} with Na₃AsO₃ yielding allylarsinic acid see (88); for reactn. of \bar{C} with CuCN giving (85% yield (22)) allyl cyanide (vinylacetonitrile) [Beil. II-408, II₁-(187), II₂-(389)], b.p. 117.8-118.2° at 757 mm. (22), see indic. refs.; for reactn. of \bar{C} with Mg + acetone, giving allyl-dimethyl-carbinol [Beil. I-445, I₂-(487)], b.p. 118-120°, $D_4^{17} = 0.83452$, $n_D^{17} = 1.4300$ see (89).]

[\tilde{C} with conc. aq. NH₄OH as directed (90) yields allylamine [Beil. IV-205, IV₁-(389), IV₂-(662)], b.p. 56°, misc. aq. — For study of rate of addn. of \tilde{C} to pyridine or reactn. with piperidine see (82) (91); for sepn. of \tilde{C} from other chloro-olefins, e.g., 1-chloropropene-1 (3:7030) or 2-chloropropene-1 (3:7020), by conv. of \tilde{C} to quaternary salt see (111).]

 \dot{C} with Mg in dry ether under carefully regulated conditions gives (84% yield (102))

cf. (109) (119) allyl MgCl; note that if this prod. reacts with phenyl isocyanate in a fashion analogous (103) to allyl MgBr the prod. obtd. should be crotonanilide, m.p. 113-114° cor. (103).

[\bar{C} with Mg in dry ether as directed gives (68% yield crude, 27% pure (92), 60% (93)) hexadienc-1,5 (1:8045). — \bar{C} with NaNH₂ in liq. NH₃ as directed gives (30% yield (94)) hexatriene-1,3,5 [Beil. I-263, I₂-(243)], b.p. 76-80°, $D_4^{20} = 0.7182$, $n_D^{20} = 1.4330$ (94); during the reactn. an intermediate chlorohexadiene (95), b.p. 115° at 748 sl. dec., 46-47.5° at 96 mm., $n_D^{20} = 1.4483$, appears to be formed, and the hexatriene is accompanied (94) (95) by variable amts. of its dimer, trimer, and tetramer. — For reaction of \bar{C} with monosodium acetylene in liq. NH₃ see (96).]

[Č with 1-chloro-2-methylpropene-2 (methallyl chloride) (3:7145) + Mg in ether gives (93) 47% 2-methylhexadiene-1,5 (b.p. 88.1° at 760 mm., $D_4^{20}=0.7198$, $n_D^{20}=1.4184$) + 30% 2,5-dimethylhexadiene-1,5 (b.p. 114.3° at 760 mm., $D_4^{20}=0.7423$, $n_D^{20}=1.4293$) + 12% hexadiene-1,5 (biallyl) (1:8045). — Č with crotyl chloride (the equil. mixt. of 1-chlorobutene-2 (3:7205) and 3-chlorobutene-1 (3:7090)) + Mg in ether gives 34% heptadiene-1,5 (b.p. 93.7° at 760 mm., $D_4^{20}=0.7186$, $n_D^{20}=1.4200$) + 21% 3-methylheptadiene-1,5 (b.p. 111.0° at 760 mm., $D_4^{20}=0.7291$, $n_D^{20}=1.4240$) + 10% hexadiene-1,5 (1:8045) + 10% 3-methylhexadiene-1,5 (b.p. 80.0° at 760 mm., $D_4^{20}=0.7103$, $n_D^{20}=1.4116$) + 1% octadiene-1,6 (b.p. 124.5° at 760 mm., $D_4^{20}=0.7441$, $n_D^{20}=1.4336$) (93).]

[Č reacts with RMgX cpds. in normal coupling; e.g., Č with EtMgBr gives (97) pentene-1 (1:8205); Č with n-PrMgBr gives (97) hexene-1 (1:8255); Č + n-C₅H₁₁MgCl gives (80% yield (93)) octene-1 (1:8375); Č with iso-AmMgCl gives (60% yield (93)) 6-methylheptene-1 (b.p. 113.2° at 760 mm., $D_4^{20} = 0.7119$, $n_D^{20} = 1.4068$); Č with o-tolyl MgBr gives (98) o-allyltoluene (b.p. 182–183° at 757 mm., $D_4^{20} = 0.9001$, $n_D^{20} = 1.5186$).]

Miscellaneous reactions of \bar{C} . $[\bar{C}$ with phenol (1:1420) + conc. H_2SO_4 stood at room temp. for 6 months gives (99) o-isopropenylphenol [Beil. VI-572, VI₁-(283)]; for analogous prods. from \bar{C} with o-cresol (1:1400), m-cresol (1:1730), and p-cresol (1:1410) see (99).]

- S-Allylisothiurea picrate: m.p. 155° (100). [From C thiourea in EtOH, refluxed for 5 min., treated with PkOH (100).]
- —— N-(Allyl)phthalimide [Beil. XXI-464, XXI₁-(364)]: m.p. 70°. [The direct prepn. of this epd. from C has not been reported; it has, however, been obtd. from allyl bromide with K phthalimide in s.t. at 150° for 2-3 hrs. (50% yield (104)) and has also been prepd. by numerous indirect means; with Cl₂ in CHCl₃ it yields N-(β,γ-dichloro-n-propyl)phthalimide, ndls. from alc., m.p. 93° (104); with Br₂ in CHCl₃ it yields N-(β,γ-dibromo-n-propyl)phthalimide, m.p. 113-114° (104).]
- —— N-(Allyl)-3-nitrophthalimide: pl. from CS₂, m.p. 100-101° (112). [Not reported from C but obtd. from allyl bromide with K 3-nitrophthalimide (112); for photographs of cryst. see (113).]
- ---- N-(Allyl)tetrachlorophthalimide: unreported.
- N-(Allyl)-o-sulfobenzoic imide (N-allylsaccharin): m.p. 58° (114). [From C with sodium saccharin in aq. butylcarbitol (1:6517) on refluxing 30 min. (114).]
- —— p-Allyloxybenzoic acid: m.p. 162–163° u.c. (116). [From \bar{C} (?) or from allyl bromide with ethyl p-hydroxybenzoate (1:1534) in abs. alc. NaOEt on refluxing 1 hr. (116); note, however, that m.p. of prod. is almost identical with corresp. deriv., m.p. 160–163°, from isopropyl halides.]

- —— Allyl α-naphthyl ether: m.p. -10° (117) (corresp. picrate, m.p. 100.5-101.0° cor. (117)).
- —— Allyl β -naphthyl ether: m.p. +16° (117) (corresp. picrate, m.p. 98.5–99.0° cor. (117).)
- Tollens, Ann. 186, 154-156 (1870). (2) Dewael, Bull. soc. chim. Belg. 39, 41-42 (1930). (3) Pilyugin, Ukrain. Chem. Zhur. 6, Tech.-Wiss. Teil 213-216 (1932); Cent. 1932, II 1608; C.A. 26, 4581 (1932). (4) Zander, Ann. 214, 142-144 (1882). (5) Lecat, Rec. trav. chim. 46, 242 (1927). (6) Thorpe, Rodger, Phil. Trans. Roy. Soc. A-185, 464 (1894). (7) Timmermans, Hennaut-Roland, J. chim. phys. 29, 536-537 (1932). (8) Schiff, Ann. 220, 98 (1883). (9) Juvala, Ber. 63, 1991, 2001, 2006 (1930). (10) Timmermans, Bull. soc. chim. Belg. 25, 300-327 (1911); Cent. 1911, II 1015.
- (11) Groll, Hearne, Ind. Eng. Chem. 31, 1530-1537 (1939). (12) McBee, Hass, Chao, Welch, Thomas, Ind. Eng. Chem. 33, 176-181 (1941). (13) Bruhl, Ann. 200, 179-180 (1879). (14) Nozaki, Ogg, J. Am. Chem. Soc. 64, 703, 704-708, 709-716 (1942). (15) Lecat, Ann. soc. sci. Bruxelles 49-B, 111 (1929). (16) Adams, Spencer, Irish, J. Ind. Hyg. Toxicol. 22, 79-86 (1940); C.A. 34, 2065 (1940). (17) Bruylants, Rec. trav. chim. 28, 247 (1909). (18) McCullough, Cortese, J. Am. Chem. Soc. 51, 226 (1929). (19) Norris, Watt, Thomas, J. Am. Chem. Soc. 38, 1075 (1916). (20) Coffey, Ward, J. Chem. Soc. 119, 1302, 1305 (1921).
- (21) Clark, Streight, Trans. Roy Soc. Can. (3) 23, III 77-89 (1929). (22) Breckpot, Bull. soc. chim. Belg. 39, 462-469 (1930). (23) Eltekow, J. Russ. Phys.-Chem. Soc. 14, 394 (1882). (24) Bancroft, J. Am. Chem. Soc. 41, 426-427 (1919). (25) Chem. Fabrik Schering, Ger. 268,340, Dec. 12, 1913; Cent. 1914, I 309. (26) Aschan, Cent. 1919, I 221. (27) Oppenheim, Ann. 140, 205-206 (1866). (28) Vaughan, Rust, J. Org. Chem. 5, 449-471 (1940). (29) Rust, Vaughan, J. Org. Chem. 5, 472-503 (1940). (30) Engs, Redmond (to Shell Development Co.1, 2,077,382, April 20, 1937; Cent. 1937, II 1660; C.A. 31, 3937 (1937).
- (31) Groll, Hearne, Burgin, LaFrance (to Shell Development Co.), U.S. 2,130,084, Sept. 13, 1938; Cent. 1939, I 1253; C.A. 32, 9096 (1938). (32) Engs, Wik (to Shell Development Co.), U.S. 2,321,472, June 8, 1943; C.A. 37, 6675 (1943). (33) I.G., Brit. 502,611, April 20, 1939; Cent. 1939, II 525; C.A. 33, 7318 (1939); French 844,015, July 18, 1939; C.A. 34, 6946 (1940). (34) Flemming, Stein (to I.G.), Ger. 720,545, April 9, 1942; C.A. 37, 2389 (1943). (35) N. V., de Bataafsche Petroleum Maatschappij, Brit. 468,016, July 22, 1937; French 810,112, March 15. 1937; Cent. 1937, II 4101. (36) I.G., Brit. 495,500, Dec. 22, 1938; Cent. 1939, I 1652. (37) Groll (to Shell Development Co.), U.S. 2,207,193, July 9, 1940; C.A. 34, 7934 (1940). (38) Essex, Ward (to du Pont Co.), U.S. 1,477,047, Dec. 11, 1923; Cent. 1925, I 895. (39) Klebanskii Vol'kenstein, J. Applied Chem. (U.S.S.R.) 8, 106-116 (1935); Cent. 1935, II 3298; C.A. 29, 6879 (1935). (40) N. V. de Bataafsche Petroleum Maatschappij, French 843,274, June 28, 1939; Cent. 1939, II 3192; C.A. 34, 6654 (1939).
- (41) Herzfelder, Ber. 28, 2435 (1893). (42) Kharasch, Brown, J. Am. Chem. Soc. 61, 3433 (1939). (43) Williams et al., Chem. Met. Eng. 47, 834-838 (1940); Williams, Trans. Am. Inst. Chem. Engrs. 35, 157-207 (1941). (44) Williams, Ind. Eng. Chem., News Ed. 16, 630-632 (Dec. 10, 1938). (45) Oppenheim, Ann. Suppl. 6, 372 (1868). (46) Bockemüller, Pfeuffer, Ann. 537, 182-183 (1939). (47) Louguinine, Kablukoff, J. chim. phys. 5, 186-202 (1907). (48) Reboul, Ann. chim. (5) 14, 461, 487 (1878). (49) Kharasch, Kleiger, Mayo, J. Org. Chem. 4, 430, 433 (1939). (50) Putochin, Ber. 55, 2748 (1922).
- (51) Dalle, Rec. trav. chim. 21, 125-126 (1902). (52) Bruylants, Rec. trav. chim. 28, 241-246 (1909). (53) Kharasch, Haefele, Mayo, J. Am. Chem. Soc. 52, 2049 (1940). (54) Windecker, Schormuller, U.S. 2,255,605, Sept. 9, 1941; C.A. 36, 100 (1942). (55) Kharasch, Norton, Mayo, J. Am. Chem. Soc. 62, 83-86 (1940). (56) Oppenheim, Ann. Suppl. 6, 359 (1868). (57) Henry, Rec. trav. chim. 22, 324-326 (1903). (58) Oppenheim, Ann. Suppl. 6, 367 (1868). (59) Michael, Ber. 39, 2787 (1906). (60) Michael, J. prakt. Chem. (2) 69, 455 (1899).
- (61) Smith, Z. physik. Chem. 93, 63-64 (1918/19).
 (62) Dewael, Bull. soc. chim. Belg. 39, 87 (1930).
 (63) Smith, Z. physik. Chem. 92, 739 (1918).
 (64) Henry, Ber. 7, 409-416 (1874); Ber. 8, 352 (1870).
 (65) Emling, Vogt, Hennion, J. Am. Chem. Soc. 63, 1624-1625 (1941).
 (67) Kharasch, Sternfeld, J. Am. Chem. Soc. 62, 2559-2560 (1940).
 (68) Marvel, Glavis, J. Am. Chem. Soc. 60, 2025 (1938).
 (69) Pope, Smith, J. Chem. Soc. 121, 1168-1169 (1922).
 (70) Alder, Windemuth, Ber. 71, 1941, 1951 (1938).
- (71) Bauer, Göts (to Röhm, Haas Co.), Ger. 706,510, April 24, 1941; C.A. 36, 1952 (1942).
 (72) Caronna, Gazz. chim. ital. 67, 618-619 (1937); Cent. 1938, I 2877; C.A. 32, 4578 (1938).
 (73) Truffault, Bull. soc. chim. (5) 6, 730-733 (1939); Compt. rend. 292, 1288-1289 (1938).
 (74) Nenitzescu, Isacescu, Ber. 66, 1100-1103 (1933).
 (75) Loder, McAlevy (to du Pont Co.), U.S.

2,316,604, April 13, 1943; C.A. 37, 5737 (1943).
(76) Essex, Ward (to du Pont Co.), U.S. 1,477, 113, Dec. 11, 1923; Cent. 1925, I 896; U.S. 1,594,879, Aug. 3, 1926; Cent. 1926, II 1688; U.S. 1,626,398, April 26, 1927; Cent. 1928, I 410.
(77) Balandin, Patrikeev, J. Gen. Chem. (U.S.S.R.)
11, 225-231 (1941); Cent. 1942, I 2233; C.A. 35, 7937 (1941).
(78) Balandin, Patrikeev, Acta Physicochim. U.R.S.S. 15, 281-292 (1941); C.A. 37, 4959 (1943).
(79) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994.
(80) Tamele, Groll (to Shell Development Co.), U.S. 2,072,015, 2,072,016, Feb. 23, 1937; Cent. 1937, II 472; C.A. 31, 2612 (1937).

(81) Oppenheim, Ann. 140, 206 (1866). (82) Tronow, Gerschewitsch, J. Russ. Phys.-Chem. Soc. 59, 735 (1927); Cent. 1928, I 2924. (83) Tamele, Ott, Marple, Hearne, Ind. Eng. Chem. 33, 119 (1941). (84) von Braun, Murjahn, Ber. 59, 1207 (1926). (85) Jacobi, Flemming, U.S. 2,259,470, Oct. 21, 1941; C.A. 36, 590 (1942); I.G., Brit. 509,796, July 21, 1939; C.A. 34, 4302 (1940). (86) Conant, Kirner, Hussey, J. Am. Chem. Soc. 47, 498 (1925). (87) Murray, J. Am. Chem. Soc. 60, 2663 (1938). (88) Hofmann-LaRoche Co., Brit. 167,157, Sept. 21, 1921; Cent. 1921, IV 1065. (89) Coffey, Rec. trav. chim. 41, 653 (1921). (90) Converse (to Shell

Development Co.), U.S. 2,216,548, Oct. 1, 1940; C.A. 35, 754 (1941).

(91) Tronow, J. Russ. Phys.-Chem. Soc. 58, 1278-1301 (1926); Cent. 1927, II 1145-1146.
(92) Cortese, J. Am. Chem. Soc. 51, 2266-2269 (1929).
(93) Henne, Chanan, Turk, J. Am. Chem. Soc. 63, 3474-3476 (1941).
(94) Kharasch, Sternfeld, J. Am. Chem. Soc. 61, 2318-2322 (1939).
(95) Kharasch, Nudenberg, Sternfeld, J. Am. Chem. Soc. 62, 2035 (1940).
(96) Lespieau, Journaud, Bull. soc. chim. (4) 49, 423-425 (1931).
(97) Mikhailov, Arbuzov, Compt. rend. acad. sci. U.R.S.S. 1936, III, 423-426; Cent. 1937, 1 2579.
(98) Levina, Grinberg, J. Gen. Chem. (U.S.S.R.) 7, 2306-2308 (1937); Cent. 1938, I 1770; C.A. 32, 510 (1938).
(99) Smith, Niederl, J. Am. Chem. Soc. 55, 4151-4153 (1933).
(100) Levy, Campbell, J. Chem. Soc. 1939, 1443.

(101) Staudinger, Fleitmann, Ann. 480, 92-108 (1930). (102) Young, Andrews, Cristol, J. Am. Chem. Soc. 65, 1657 (1943). (103) Schwartz, Johnson, J. Am. Chem. Soc. 53, 1063-1067 (1931). (104) Neumann, Ber. 23, 999-1000 (1890). (105) Sweddund, Robertson, J. Chem. Soc. 1945, 131-133. (106) Kharasch, Fuchs, J. Org. Chem. 10, 167-168 (1945). (107) Groll, Ott (to Shell Development Co.) U.S. 2,042,219, May 26, 1936; Cent. 1937, I 1013; [C.A. 30, 4871 (1936).] (108) Hatch, Estes, J. Am. Chem. Soc. 67, 1730-1733 (1945). (109) Houben, Boedler, Fischer, Ber. 69, 1783 (1936). (110) Hatch, Moore, J. Am. Chem. Soc. 66, 286 (1944).

(111) Pollack (to Pittsburgh Plate Glass Co.), U.S. 2,349,752, May 23, 1944; C.A. 39, 1416 (1945). (112) Sah, Ma, Ber. 65, 1630-1633 (1932). (113) Sah, Ma, Sci. Repts. Natl. Tsing Hua Univ. 2, 147-149 et. seq. (1933). (114) Merntt, Levey, Cutter, J. Am. Chem. Soc. 61, 15-16 (1939). (115) Gillespie, J. Am. Chem. Soc. 56, 2740-2741 (1934). (116) Lauer, Sanders, Leekley, Ungnade, J. Am. Chem. Soc. 61, 3050 (1939). (117) V. H. Dermer, O. C. Dermer, J. Org. Chem. 3, 290-291 (1939). (118) Patrick, McBee, Hass, J. Am Chem. Soc. 68, 1009-1011 (1946). (119) Kharasch, Fuchs, J. Org. Chem. 9, 364 (1944).

B.P.				F.P.		
46.60°	at	760 mm.	(1)	-122.8° (1) (7)	$D_4^{25} = 0.88611 (1)$	
46.6°	at	770.5 mm.	(2)		$D_4^{20} = 0.89229 (1)$	
46.3-46.7° ı	1.C.		(3)		0.8890 (52)	
46.4° cor.	at	760 mm.	(4) (5)		$D_4^{15} = 0.89486 (1)$	
46.0-46.5°	at	764 mm.	(52)		$n_{\rm D}^{20}=1.38856$	(8)
45.70-45.78	5° at	760 mm.	(6)		1.38838	(9)
44°	at	744 mm.	(8)		1.38800	(52)

Colorless limpid liquid with not unpleasant odor. — Almost insol. aq. [for precise data see (10) (11) (12)].

Č with MeOH, b.p. 64.7°, forms const.-boilg. mixt., b.p. 40.5°, contg. 90.5 wt. % Č (13); Č with EtOH, b.p. 78.3°, forms const.-boilg. mixt., b.p. 45.0°, contg. 94 wt. % Č (14); Č with isopropyl alc., b.p. 82.5°, forms const.-boilg. mixt., b.p. 46.4°, contg. 97.2 wt. % Č (14); Č with CS₂, b.p. 46.3°, forms const.-boilg. mixt., b.p. 42.05°, contg. 44.5 wt. % Č (14).—
[For f.p./compn. data on mixts. of Č with cyclohexyl chloride (3:8040) or with isopropyl bromide see (15).]

reactn. see (30).]

[For prepn. of \bar{C} from propanol-1 (1:6150) with conc. $HCl + ZnCl_2$ (yield: 92% (52); 70–72% (16), 65–70% (17), 61% (18) (19)); with PCl_3 (20) + $ZnCl_2$ (yield: 94% (21) (19)), with PCl_5 (5) + $ZnCl_2$ (76% yield (19)); with $SOCl_2$ + pyridine (84% yield (19)) see indic. refs.; for other misc. methods see Beil.]

[For formn. of \tilde{C} (together with other products) from propane by actn. of Cl_2 see (22) (23); for further actn. of Cl_2 on \tilde{C} see (3) (24) (25); for further chlorination with SO_2Cl_2 see (26).] [For isomerization of \tilde{C} to isopropyl chloride (3:7025) in pres. of metallic cat. see (27) (28); for isomerization of \tilde{C} accompanying alkylation see (29); for \tilde{C} in Friedel-Crafts

 \bar{C} on passing over various cat. espec. at elevated temps. loses HCl (30) (31) + Beil. I₂-(72).

[For study of behavior of \bar{C} with KI see (33); toward Na see (34) (35) (36); with Mg in dry ether see (37) (note that \bar{C} with Mg in dry ether contg. trace of I₂ gives in absence of air 98.2% yield (51) RMgCl).]

- n-Butyranilide: m.p. 96° (38); 97° (39); 92° cor. (40), u.c. (41). [From C (41) or n-propyl bromide (40) via conversion to RMgX and reactn. with phenyl isocyanate (41).]
- —— n-Butyr-p-toluidide: m.p. 75° (38); 74-75° (42); 73-74° (43). [Presumably similarly obtainable via RMgCl + p-tolyl isocyanate, but not actually so recorded.]
- n-Butyr-α-naphthalide: m.p. 120° (44); 121° (45). [From RMgBr via reactn. with α-naphthyl isocyanate (45).]
- ---- n-Propyl mercuric chloride: m.p. 140° (46).
- S-(n-Propyl)isothiourea picrate: m.p. 176° (47). [In small yield from C on htg. 5 hrs. with thiourea in alc., followed by addn. of PkOH (47).]
- —— n-Propyl 2,4,6-triiodophenyl ether: m.p. 82° cor. (48). [From n-propyl bromide on refluxing with 2,4,6-triiodophenol, m.p. 157-158°, in alc. NaOEt (48).] [Note that this ether depresses m.p. of corresp. Et 2,4,6-triiodophenyl ether, m.p. 82° cor. (48).]
- —— N-(n-Propyl)-3-nitrophthalimide: ndls. from CS₂, m.p. 84-85° (49). [From n-propyl bromide on refluxing with K 3-nitrophthalimide (49).]
- —— n-Propyl β-naphthyl ether: b.p. 297.0° cor., m.p. 39.5-40.0° cor. (50) [picrate: m.p. 80.5-81.5° cor. (50)].
- 3:7040 (1) Timmermans, Hennaut-Roland, J. chim. phys. 27, 407-408 (1930). (2) Karvonen, Ann. Acad. Sci. Fennaca A-3, No. 7, 1-103; Cent. 1912, II 1271. (3) Rust, Vaughan, J. Org. Chem. 6, 479-488 (1941). (4) Linnemann, Ann. 161, 38-39 (1872). (5) Pierre, Puchot, Ann. 163, 266-269 (1872). (6) Matthews, Fehland, J. Am. Chem. Soc. 53, 3216 (1931). (7) Timmermans, Bull. soc. chim. Belg. 27, 334-343 (1913); Cent. 1914, I 618. (8) Bruhl, Ann. 200, 179 (1879). (9) Karvonen, Ann. Acad. Sci. Fennaca A-5, No. 6, 121. (10) Rex, Z. physik. Chem. 55, 364 (1906).
- (11) Fühner, Ber. 57, 514 (1924). (12) van Arkel, Vles, Rec. trav. chim. 55, 408 (1936). (13) Lecat, Rec. trav. chim. 46, 242 (1927). (14) Lecat, Ann. soc. sci. Bruxelles 47, I 66 (1927). (15) van de Vloed, Bull. soc. chim. Belg. 48, 261 (1939). (16) Copenhaver, Whaley, J. Am. Chem. Soc. 60, 2497-2498 (1938) (17) Copenhaver, Whaley, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 143, Note 6 (1941). (18) Norris, Taylor, J. Am. Chem. Soc. 46, 756 (1924). (19) Clark, Streight, Trans. Roy. Soc. Can. (3) 29, III 77-89 (1929). (20) Walker, Johnson, J. Chem. Soc. 87, 1592-1597 (1905).
- (21) Dehn, Davis, J. Am. Chem. Soc. 29, 1328-1334 (1907). (22) Hass, McBee, Weber, Ind. Eng. Chem. 27, 1190-1195 (1935). (23) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,073, June 4, 1935; Cent. 1936, I 1500. (24) Hass, McBee (to Purdue Research Foundation), Can. 374,242, June 7, 1938; Cent. 1938, II 3005. (25) Hass, McBee (to Purdue Research Foundation), U.S. 2,147,577, Feb. 14, 1939; Cent. 1939, II 226. (26) Kharasch, Brown, J. Am. Chem. Soc. 61, 2142-2149 (1939). (27) N. V. de Bataafsche Petroleum Maatschappij. Brit. 535,435.

April 9, 1941; C.A. 36, 1614 (1942). (28) Nagai, J. Chem. Soc. Japan 61, 864-866 (1940); C.A. 34, 7841 (1940). (29) Ipatieff, Pines, Schmerling, J. Org. Chem. 5, 253-263 (1940). (30), Wertyporoch, Ann. 500, 287-295 (1933).

(31) Senderens, Bull. soc. chm. (4) 3, 828 (1908).
(32) Senderens, Compl. rend. 200, 612-615 (1935).
(33) Conant, Hussey, J. Am. Chem. Soc. 47, 484 (1925).
(34) Morton, LeFevre, Hechenbleikner, J. Am. Chem. Soc. 58, 754-757 (1936).
(35) Morton, Hechenbleikner, J. Am. Chem. Soc. 58, 1697-1701 (1936).
(36) Morton, Hechenbleikner, J. Am. Chem. Soc. 58, 2599-2605 (1936).
(37) Rudd, Turner, J. Chem. Soc. 1928, 686-691.
(38) Robertson, J. Chem. Soc. 115, 1220-1221 (1919).
(39) Fournier, Bull. soc. chm. (4) 7, 25-26 (1910).
(40) Schwartz, Johnson, J. Am. Chem. Soc. 53, 1065 (1931).

(41) Underwood, Gale, J. Am. Chem. Soc. 56, 2119 (1934).
(42) Davis, J. Chem. Soc. 95, 1398 (1909).
(43) Fichter, Rosenberger, J. prakt. Chem. (2) 74, 323 (1906).
(44) Robertson, J. Chem. Soc. 93, 1037 (1908).
(45) Gilman, Furry, J. Am. Chem. Soc. 50, 1214-1216 (1928).
(46) Marvel, Gauerke, Hill, J. Am. Chem. Soc. 47, 3010 (1925).
(47) Levy, Campbell, J. Chem. Soc. 1939, 1443.
(48) Drew, Sturtevant, J. Am. Chem. Soc. 61, 2666 (1939).
(49) Sah, Ma, Ber. 65, 1630-1633 (1932).
(50) V. H. Dermer, O. C. Dermer, J. Org. Chem. 3, 290-291 (1939).
(51) Houben, Boedler, Fischer, Ber. 69, 1768, 1776 (1936).
(52) Vogel, J. Chem. Soc. 1943, 638-639.

3: 7045 2-CHLORO-2-METHYLPROPANE CH₃ C₄H₉Cl Beil. I - 125 (ter-Butyl chloride; CH₃—C—CH₃ I₁-(40) I₂-(88)

					0.	•	
B.P.				F.P.			
52°			(1)	-24.6°	(12)	$D_4^{25} = 0.83537 (9)$	
51.52° cor.		(2)	(36)	-25.4°	(13)	$D_4^{20} = 0.8511 (20)$	
51.6°			(3)	-27.1°	(9) (19)	0.8457 (16)	
51.0-51.2°			(4)	-28.5°	(5)	0.84138 (9)	
51°			(5)			$D_4^{15} = 0.84739 (9)$	
50.9°	at	762 mm.	(6)				
50.9°			(7)				
50.8°	at	756 mm.	(8)			$n_{\rm D}^{20}=1.38786$	(13)
50.7°	at	760 mm.	(9)			1.3858	(8)
50.7°			(10)			1.38564	(16)
50.6-50.8°	at	766 mm.	(11)			1.3855	(17) (21)
50.60°			(12)	(18) (8)		1.3853	(8)
50.5°			(13)			1.38528	(10)
50.0°	at	749 mm.	(14)			1.38470	(12)
49.7°	at '	742.4 mm.	(15)			1.3839	(18)
49.5°	at	738 mm.	(16)			$n_{\rm D}^{18} = 1.3860$	(22)
49-50°			(17)			$n_{\rm D}^{178} = 1.38686$	(1)

[See also 1-chloro-2-methylpropane (3:7135).]

Binary systems of \tilde{C} with other org. cpds. — For f.p./compn. data of mixts. of \tilde{C} with CCl₄ (3:5100) (23) (13), with *n*-butyl chloride (3:7160) (19), with *n*-butyl bromide (19), or with isobutyl bromide (19) see indic. refs.

 $\ddot{\mathbf{C}}$ with MeOH (1:6120) forms a const.-boilg. mixt., b.p. 43.75°, contg. 90% $\ddot{\mathbf{C}}$ (24); $\ddot{\mathbf{C}}$ with formic acid (1:1005) forms a const.-boilg. mixt., b.p. 50.0°, contg. 88.8% $\ddot{\mathbf{C}}$ (3); $\ddot{\mathbf{C}}$ with CS₂ forms a const.-boilg. mixt., b.p. 43.3°, contg. 37% $\ddot{\mathbf{C}}$ (25). — Note that $\ddot{\mathbf{C}}$ gives no azeotrope with ter-BuOH (1:6140) (9).

Preparation of C. [For prepn. of C from ter-BuOH (1:6140) with conc. HCl (3 vols.) by shaking in cold (espec. in pres. of CaCl₂) (78-88% yield (26)) or by distillation (using

7-8 pts. by wt. conc. HCl) (94% yield (27)), or with dil. aq. HCl (18-20 Bé) in pres. of inorg. halide cat. (28) see indic. refs.]

[For prepn. of C from ter-BuOH (1:6140) with dry HCl gas in cold (1) (29), with HCl gas in pres. of pyridine at elevated temp. (some isobutyl chloride (3:7135) is also formed (30)); with PCl₃ (31), PCl₃ + ZnCl₂ (92% yield (32)), PCl₅ (33) (34), PCl₅ + ZnCl₂ (85% yield (32)), or excess AlCl₃ (35); with oxalyl (di)chloride (3:5060) (36) or with trichloromethyl chloroformate (diphosgene) (3:5515) (20) see indic. refs.]

 \bar{C} can also be obtained from various isobutyl cpds. (see following paragraphs), but it must be constantly kept in mind that reactns. of this type involve the equilibrium between \bar{C} , isobutylene, and isobutyl chloride, and the proportions of the two halides may vary widely according to particular conditions; for some types of utilization, however, such a mixture may serve just as well as pure \bar{C} .

[For prepn. of \tilde{C} from 2-methylpropane (isobutane) with Cl₂ see (37) (38) (39); from isobutylene with HCl gas (40) (41) (4) (18), with conc. aq. HCl (42) (43) (44), with HCl gas + AlCl₃ at -50° (45), with HCl gas + cat. (46), from tech. cracked gas (contg. isobutylene) with HCl (47) (48) (49) (57), with chloromethyl methyl ether (3:7085) + HgCl₂ (other prods. are also formed (50)), or even with Cl₂ (other prods. also formed) (51) (52) (53) see indic. refs.]

[For prepn. of \bar{C} from 1-chloro-2-methylpropane (isobutyl chloride) (3:7135) by htg. at 306° (8% \bar{C} (54)), or passing vapor over BaCl₂ at 380-400° (40% \bar{C} (55)), or over suitable cat. at 200° as directed (56); from isobutyl iodide with ICl (58); from isobutylamine with NOCl in xylene at -15° (59); from isobutyl alcohol (1:6165) with HCl gas (60) cf. (1), with HCl gas over Al₂O₃ at 420° (61), or with PCl₃ + ZnCl₂ (62) see indic. refs.]

[For formn. of \bar{C} from 2-chloro-2-methylbutane (ter-amyl chloride) (3:7220) by cleavage with AlCl₃ (35) or with anhydrous HF at 0° (10-17% yield (17)) see indic. refs.]

Pyrolysis of C. [C on suitable htg. dec. into isobutylene + HCl; this begins to occur at 300° even in absence of cat. (63) (for study of equilibria involved see (4) (18)); for study of reactn. over ThO₂ at 100° (64), over pumice at 400-500° (65), or over activated carbon contg. 1-2% KOH (dehalogenation is 19.8% at 375°, 51% at 400° (66)) see indic. refs. — Note that C passed over activated carbon at 400° in pres. of H₂ is 51% dehalogenated but the isobutylene is not reduced (67).]

Further halogenation of $\bar{\mathbf{C}}$. [$\bar{\mathbf{C}}$ in liq. phase with Cl₂ in light gives (68) a mixt. of chlorination prods. contg. approx. 37% 1,2,3-trichloro-2-methylpropane (3:5885) + 25% 1,1,2-trichloro-2-methylpropane (3:5710) + 21% 1,1,2,3-tetrachloro-2-methylpropane (3:6165) + 10% 1,2-dichloro-2-methylpropane (3:7430) + 6% 1,2,3-trichloro-2-(chloromethyl)-propane (3:6335) + a trace of 1,1,1,2-tetrachloro-2-methylpropane (3:4725). $-\bar{\mathbf{C}}$ in vapor phase under reduced press. with Cl₂ in u.v. light or in dark electric discharge (69) or $\bar{\mathbf{C}}$ with SbCl₅ (1 mole) with cooling (34) gives 1,2-dichloro-2-methylpropane (3:7430).]

 \bar{C} with Br₂ in pres. of Fe (70) or in liq. SO₂ at room temp. for 14 hrs. (100% yield (72)) evolves HCl and gives 1,2-dibromo-2-methylbutane (isobutylene dibromide) [Beil. I-127, I₁-(41), I₂-(90)], b.p. 149.0°.

Reactions of the halogen atom of \tilde{C} . The tertiary chlorine atom of \tilde{C} is very reactive and therefore readily hydrolyzed or alcoholized. — \tilde{C} on shaking with aq. for 24 hrs. at room temp. (6) or \tilde{C} on refluxing with 2 vols. aq. for 8 hrs. (71% hydrolysis (72)) yields ter-BuOH (1:6140); note rate of hydrolysis of \tilde{C} is greater in pure aq. than in 5% aq. Na₂CO₃ (72); for use of this facile hydrolysis in removal of \tilde{C} from isobutyl chloride (3:7135) see under latter). [For details of studies of kinetics of hydrol. of \tilde{C} under various circumstances, e.g., in aq. alc., see (73) (74) (75) (6) (11); in formic acid (14) (77) (78).] [For use in prepn. of ter-butyl alc. (1:6140) see (79).]

[\bar{C} (2 moles) in ether shaken with Ag₂CO₃ (1 mole) gives (35% yield {114}) di-ter-butyl ether, b.p. 106.5-107°, $D_4^{20} = 0.7658$, $n_D^{20} = 1.3949$ {114}.]

[C in the presence of small amts. AlCl₃ exchanges halogen with reactive H atoms of certain hydrocarbons; e.g., C with 2,3-dimethylbutane (1:8515) + AlCl₃ shaken for ½ min. at room temp. gives (23% yield (112)) 2-chloro-2,3-dimethylbutane (3:7600); C with 2,2,3-trimethylbutane (1:8544) + AlCl₃ shaken for 30-45 seconds gives (16% yield (112)) 3-chloro-2,2,3-trimethylbutane (3:4020); for other examples see (112).]

[C also undergoes alcoholysis: e.g., C shaken with equal vol. 50 mole % MeOH for several days (74) (11) seps. a non-aq. phase of ter-butyl methyl ether (1:7830), b.p. 55°; C with EtOH gives (11) ter-butyl ethyl ether (1:7860), b.p. 73°; for study of this equilibrium and detn. of these ethers see (11).]

[For rate of reactn. of \bar{C} with KI in acetone at 60° see (80); for reactn. of \bar{C} with Ca formate yielding (77) (78) ter-butyl formate (1:3033), b.p. 83°, see indic. refs.; for conv. of \bar{C} to esters by htg. with alkali salt of a suitable acid under press. at 125-225° in pres. of Cu and the use of this reactn. in sepn. of \bar{C} from less reactive chlorine cpds. see (81).

[$\bar{\mathbb{C}}$ readily condenses with arom. hydrocarbons and phenols: e.g., $\bar{\mathbb{C}}$ with Al/Hg + C₆H₆ gives (74.5% yield (109)) or $\bar{\mathbb{C}}$ with C₆H₆ + AlCl₃ gives (yields: 69% (82), 60% (83)) (62) (1) mainly ter-butylbenzene (1:7460), b.p. 168.8°, often accompanied by some p-(di-ter-butyl)benzene, cryst. from alc., m.p. 77° (82); this same condensation can also be effected in anhydrous HCl at 235° under press. (88% yield (84)) or in anhydrous HF (yield: 60% di- + 10% mono- (85)). $-\bar{\mathbb{C}}$ with toluene + AlCl₃ gives both p-ter-butyl-toluene and m-ter-butyltoluene (in ratio of 30–35/65–70, resp. (86)) but $\bar{\mathbb{C}}$ with toluene in anhyd. HCl or HF (85) (22) cf. (113) gives exclusively (84) p-ter-butyltoluene, b.p. 188–189°, n_D^{20} = 1.4930 (84). $-\bar{\mathbb{C}}$ For reactn. of $\bar{\mathbb{C}}$ with naphthalene + AlCl₃ (87) or Al/Hg (109) or $\bar{\mathbb{C}}$ with m-cymene + AlCl₃ (88) see indic. refs.]

[\bar{C} with phenol (1:1420) in anhyd. HF gives (85% yield (89)) p-ter-butylphenol (1:1510); \bar{C} with β -naphthol (1:1540) + AlCl₃ gives (90) 4-(ter-butyl)naphthol-2, m.p. 102° (90). — \bar{C} with anisole (1:7445) + ZnF₂ gives (30.6% yield (91)) p-ter-butylanisole, but \bar{C} does not react with anisole + AlF₃ or with furan + ZnF₂ (91).]

[\bar{C} with acetanilide + AlCl₃ in ethylene dichloride at —10° gives (93% yield) N-acetyl-p-ter-butylaniline (111).]

Č under proper conditions gives the corresponding RMgCl cpd.: e.g., Č with Mg in dry ether as directed gives (yields: 80% (92), 62% (93), 60% (95)) cf. (94) ter-BuMgCl; this RMgCl cpd. undergoes the usual reactions (see also below under ⊕'s) including the following: ter-BuMgCl with O₂ below 0° gives (80% yield (95)) ter-BuOH (1:6140) q.v.; with acetyl chloride (1 mole) in C₆H₆ gives (40-54% yield (92)) ter-butyl methyl ketone (pinacolone) (1:5425) (note, however, that ter-BuMgCl with excess acetyl chloride takes a different course (97) and that with various other acyl halides the reducing action of the ter-BuMgCl becomes conspicuous cf. (98) (99) (100)); Č with ethyl chloroformate (3:7295) or diethyl carbonate (1:3150) gives (56% yield (92)) ethyl trimethylacetate (ethyl pivalate) (1:3117); with Č itself to give (10% yield (96)) hexamethylethane (1:7090).

Č reacts with other RMgX cpds. in conventional fashion: e.g., Č with MeMgCl gives (42-50% yield (108)) tetramethylmethane (neopentane) (1:8499); Č with n-PrMgBr in ether + HgCl₂ gives (yield 21% (101), 20% (110)) 2,2-dimethylpentane (1:8543); the numerous other reactions of ter-BuMgCl cannot be reviewed here.

[For reactn. of C with Et₂Zn and numerous homologs see (102).]

- ① ter-Butyl alcohol (1:6140): m.p. 25.6°, b.p. 82.5°. [From Č by shaking with aq. for 24 hrs. at room temp. (6), or on refluxing with 2 vols. aq. for 8 hrs. (72), neutralizing with Na₂CO₃, salting out the alcohol with NaCl, drying over anhyd. Na₂CO₃, and distilling.]
- Trimethylacetic acid (pivalic acid) (1:0410): m.p. 35.5°, b.p. 163-164°. [From Č by

- conversion to ter-BuMgCl (see above) and reactn. of latter with dry CO₂ (yields based on C, 75% (92), 62% (93), 42.5% (17)) (94).]
- Trimethylacetic anilide (pivalanilide): m.p. 132-133° u.c. (103), 132.5-133° (17). [From C by conv. to ter-BuMgCl (see above) and reactn. of latter with phenyl isocvanate in dry ether (17) (103) (104).]
- Trimethylaceto-p-toluidide (pivalo-p-toluidide): m.p. 119-120° u.c. (103). [From $\bar{\mathbf{C}}$ by conversion to ter-BuMgCl (see above) and reactn. of latter with p-tolyl isocyanate in dry ether (103).
- **D** Trimethylaceto- α -naphthalide (pivalo- α -naphthalide): m.p. 146-147° u.c. (103). [From \bar{C} by conversion to ter-BuMgCl (see above) and reactn. of latter with α -naphthyl isocyanate in dry ether (103).]
- ter-Butyl mercuric chloride: long ndls. from aq. acetone as directed (105), m.p. 122-123° dec. (105). [From ter-BuMgCl with HgCl₂ (105).]
- S-ter-Butylisothiourea picrate: m.p. 160-161° (106). [From C with thiourea on htg. in alc. followed by conversion of the resultant hydrochloride to picrate (106); note, however, that, because of the lability of the ter-butyl radical, reactions carried out in MeOH or EtOH may give the corresp. S-methylisothiourea picrate, m.p. 224°, or S-ethylisothiourea picrate, m.p. 188°, and this definitely occurs (107) starting with ter-butyl iodide.]
 - --- N-(ter-Butvl)phthalimide: unreported.
 - ---- ter-Butyl 2,4,6-triiodophenyl ether: unreported.
 - ---- ter-Butyl α-naphthyl ether: unreported.
 - ---- ter-Butyl β-naphthyl ether: unreported.
- 3:7045 (1) Boedtker, Bull soc. chim. (3) 31, 965-971 (1904). (2) Perkin, J. prakt. Chem. (2) 31, 493 (1885). (3) Lecat, Ann. soc sci. Bruxelles 49-B, II 22 (1929). (4) Brearley, Kistiakowsky, Stauffer, J. Am. Chem. Soc. 58, 43-47 (1936). (5) Timmermans, Bull. soc. chim. Belg. 30, 66
- Stauffer, J. Am. Chem. Soc. 53, 43-41 (1930). (3) Himmermans, Butt. soc. carm. Bey. 50, 00 (1921). (6) Hughes, J. Chem. Soc. 1935, 255-258. (7) Lewis, Hammett, J. Am. Chem. Soc. 64, 1938-1940 (1942). (8) Wiswall, Smyth, J. Chem. Phys. 9, 357 (1941). (9) Timmermans, Delcourt, J. chem. phys. 31, 98-99 (1934). (10) Smyth, Dornte, J. Am. Chem. Soc. 53, 546 (1931). (11) Bateman, Hughes, Ingold, J. Chem. Soc. 1938, 876-887. (12) Baker, Smyth, J. Am. Chem. Soc. 61, 2798 (1939). (13) Turkevich, Smyth, J. Am. Chem. Soc. 62, 2473 (1940). (14) Bateman, Hughes, J. Chem. Soc. 1937, 1187-1192. (15) Koskoski, Thomas, Fowler, J. Am. Chem. Soc. 63, 2451 (1941). (16) Vogel, J. Chem. Soc. 1943, 638-639. (17) Simons, Fleming, Whitmare Rissinger, J. Am. Chem. Soc. 60, 2267-2269 (1938). (18) Kissingery J. Am. Chem. Soc. 1947, J. Am. Chem. Soc. 63, 2451 (1941). more, Bissinger, J. Am. Chem. Soc. **60**, 2267–2269 (1938). (18) Kistiakowsky, Stauffer, J. Am. Chem. Soc. **59**, 164–169 (1937). (19) Timmermans, Bull. soc. chim. Belg. **43**, 630 (1934). (20) Nekrassow, Melnikow, J. prakt. Chem. (2) **127**, 216 (1930).
- (21) Audsley, Joss, J. Chem. Soc. 1941, 873. (22) Sprauer, Simons, J. Am. Chem. Soc. 64 648-659 (1942). (23) Conner, Smyth, J. Am. Chem. Soc. 63, 3424-3428 (1941). (24) Lecat, Ann. soc. sci. Bruxelles, 47, II 112 (1927). (25) Lecat, Ann. soc. sci. Bruxelles 47, I 66 (1927). (26) Norris, Olmsted, Org Syntheses, Coll. Vol. 1 (2nd ed.), 144-145 (1941); (1st ed.), 138-139 (1932); 8, 50-51 (1928). (27) Norris, Am. Chem. J. 38, 642 (1907). (28) Wirth (to du Pont Co.), U.S. 2.013,722, Sept. 10, 1935; Cent. 1936, I 2826; C.A. 29, 6907 (1935). (29) Schramm, Monatsh. 9. 618-619 (1888). (30) Haack (to Chem. Fabrik von Heyden), Ger. 624,693, Jan. 30, 1936; Cent. 1936, I 3575; C.A. 30, 4876 (1936).
- (31) Jaroschenko, J. Russ. Phys.-Chem. Soc. 29, 223-227 (1879); Cent. 1897, II 334. (32) Clark, Streight, Trans. Roy. Soc. Canada (3) 23, III 77-89 (1929). (33) Butlerow, Jahresber. 1864, 497. (34) Meyer, Muller, J. prakt. Chem. (2) 46, 187-188 (1892). (35) Tzukervanik, J. Gen. Chem. (U.S.S.R.) 5, 117-120 (1935); Cent. 1936, II 2896; C.A. 29, 4746 (1935). (36) Adams, Weeks, J. Am. Chem. Soc. 38, 2518-2519 (1916). (37) Butlerow, Ann. 144, 15-18 (1867). (38) Hass, McBee, Weber, Ind. Eng. Chem. 27, 1190-1195 (1935). (39) Britton, Coleman, Hadler (to Dow Chem. Co.), U.S. 1,954,438, April 10, 1934; Cent. 1934, II 3180; C.A. 28, 3739 (1934); U.S. 2,018,345, Oct. 22, 1935; Cent. 1936, I 3907; C.A. 30, 106 (1936). (40) Coffin, Sutherland, Maas, Can. J. Research 2, 267–278 (1930); Cent. 1930, II 2250; C.A. 24, 3750 (1930).
- (41) Coffin, Maas, Can. J. Research 3, 526-539 (1930), Cent. 1931, I 2430; C.A. 25, 1146-1147 (1931). (42) Zalessky, Ber. 5, 480 (1872). (43) LeBel, Bull. soc. chim. (2) 28, 462 (1877). (44) Puchot, Ann. chim. (5) 28, 549-550 (1883). (45) Tulleners, Tuyn, Waterman, Dutch

- 36,489, Oct. 15, 1935; Cent. 1936, I 1500. (46) Strange, Kane, Brit. 435,858, Oct. 31, 1935; French 787,340, Sept. 20, 1935; Cent. 1936, I 2826 (47) Rudkovskii, Trans. Mendeleev Congr. Theor. Applied Chem. 6th Congr. 1932, 2, Part 1, 715-719 (1935); Cent. 1936, II 2269; C.A. 30, 2734 (1936). (48) Dobryanskii, Rudkovskii, Org. Chem. Ind. (U.S.S.R.) 1, 537-540 (1936); Cent. 1936, II 3865; C.A. 30, 6702 (1936). (49) Rudkovskii, Trifel, Org. Chem. Ind. (U.S.S.R.), 2, 203-205 (1936); Cent. 1937, I 3576; C.A. 31, 1004 (1937). (50) Straus, Thiel, Ann. 525, 174-175 (1936).
- (51) Pogorshelski, J. Russ. Phys.-Chem. Soc. 36, 1129-1184 (1904), Cent. 1905, I 667.
 (52) N. V. de Bataafsche Petroleum Mautschappij, French 761,614, March 23, 1934; Cent. 1934, II 1200.
 (53) D'yakonov, Tishchenko, J. Gen. Chem. (U.S.S.R.) 9, 1258-1264 (1939), C.A. 34, 710 (1940).
 (54) Michael, Zeidler, Ann. 393, 110-111 (1912).
 (55) Sabatier, Mailhe, Compt. rend. 156, 658 (1913).
 (56) Nutting, Britton, Huscher, Petrie (to Dow Chem. Co.), U.S. 1,993,719, March 5, 1935, Cent. 1935, II 2879-2880; C.A. 29, 2549 (1935).
 (57) Winkler, Ger. 574,802, March 30, 1933; Cent. 1933, I 3497.
 (58) Linnemann, Ann. 162, 18-19 (1872).
 (59) Ssolonina, J. Russ. Phys.-Chem. Soc. 30, 431-449 (1898); Cent. 1898, II 888.
 (60) Freund, J. prakt. Chem. (2) 12, 27-33 (1875).
- (61) Sabatier, Mailhe, Compt. rend. 169, 124 (1919). (62) Shoesmith, Mackie, J. Chem. Soc. 1928, 2336. (63) Senderens, Aboulenc, Compt. rend. 202, 104-106 (1936) (64) Senderens, Compt. rend. 200, 612-615 (1935). (65) Nef, Ann. 318, 24-28 (1901). (66) Balandin, Patrikeev, Acta Physicochim. U.R.S.S. 15, 281-292 (1941), C.A. 37, 4959 (1943). (67) Balandin, Patrikeev, J. Gen. Chem. (U.S. S.R.) 11, 225-231 (1941); C.A. 35, 7937-7938 (1941). (68) Rogers, Nelson, J. Am. Chem. Soc. 58, 1027-1029 (1936). (69) B.A.S.F., Ger. 259,192, April 4, 1913, Cent. 1913, I 1740-1741. (70) Herzfelder, Ber. 26, 1261 (1893).
- (71) Hughes, Ingold, Scott, J. Chem. Soc. 1937, 1276; Nature 138, 120-121 (1936).
 (72) Woodburn, Whitmore, J. Am Chem. Soc. 56, 1394-1395 (1934).
 (73) Brown, Kharasch, Chao, J. Am. Chem. Soc. 62, 3439 (1940).
 (74) Olson, Halford, J. Am. Chem. Soc. 59, 2644-2647 (1937).
 (75) Cooper, Hughes, Ingold, J. Chem. Soc. 1937, 1280-1283.
 (76) Straus, Ann. 370, 366-367 (1909).
 (77) Taylor, J. Chem. Soc. 1937, 1852-1853.
 (78) Bateman, Hughes, J. Chem. Soc. 1940, 935-940.
 (79) Britton, Coleman, Wairen (to Dow Chem. Co.), U.S. 1,984,725, Dec. 18, 1934, Cent. 1935, I 3199, C.A. 29, 819 (1935).
 (80) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925).
- (81) Coleman, Moore (to Dow Chem. Co), U.S. 2,207,611, July 9, 1940; C.A. 34, 7934 (1940).
 (82) Backer, Kramer, Rec trav. chrm. 53, 1103 (1934).
 (83) Schramm, Monatsh. 9, 618-619 (1888).
 (84) Simons, Hart, J. Am. Chem. Soc. 66, 1309-1312 (1944).
 (85) Simons, Archer, J. Am. Chem. Soc. 60, 986; 2953-2954 (1938).
 (86) Shoesmith, McGeethen, J. Chem. Soc. 1930, 2231-2236.
 (87) Gump, J. Am. Chem. Soc. 53, 380-381 (1931).
 (88) Barbier, Helv. Chrm. Acta 15, 592-596 (1932).
 (89) Simons, Archer, Passino, J. Am. Chem. Soc. 60, 2956-2957 (1938).
 (90) Königsberger (to Dehls and Stein), U.S. 1,788, 529, Jan. 13, 1931; Cent. 1931, II 1351.
- (91) Calloway, J. Am. Chem. Soc. 59, 1477 (1937)
 (92) Whitmore, Badertscher, J. Am. Chem. Soc. 55, 1561-1567 (1933).
 (93) Gilman, Zoellner, J. Am. Chem. Soc. 50, 425-428 (1928).
 (94) Gilman, Zoellner, Rec. trav chim. 47, 1058-1063 (1928).
 (95) Whitmore, Lux, J. Am. Chem. Soc. 54, 3454 (1932).
 (96) Flood, Calingaert, J. Am. Chem. Soc. 56, 1211 (1934).
 (97) Whitmore, Wheeler, J. Am. Chem. Soc. 60, 2899-2900 (1938).
 (98) Greenwood, Whitmore, Crooks, J. Am. Chem. Soc. 60, 2028-2030 (1938).
 (99) Whitmore, Heyd, J. Am. Chem. Soc. 60, 2030-2031 (1938).
 (100) Whitmore, Whitaker, Mosher, Brevik, Wheeler, Miner, Sutherland, Wagner, Clapper, Lewis, Lux, Popkin, J. Am. Chem. Soc. 63, 643-654 (1941)
- (101) Edgar, Calingaert, Mather, J. Am. Chem. Soc. 51, 1487 (1929).
 (102) Noller, J. Am. Chem. Soc. 51, 594-599 (1929).
 (103) Underwood, Gale, J. Am. Chem. Soc. 56, 2117-2119 (1934).
 (104) Schwartz, Johnson, J. Am. Chem. Soc. 53, 1065 (1931).
 (105) Whitmore, Bernstein, J. Am. Chem. Soc. 60, 2627 (1938).
 (106) Sprague, Johnson, J. Am. Chem. Soc. 59, 1839 (1937).
 (107) Levy, Campbell, J. Chem. Soc. 1939, 1442-1443.
 (108) Whitmore, Fleming, J. Am. Chem. Soc. 55, 3803-3806 (1933).
 (109) Diuguid, J. Am. Chem. Soc. 63, 3527-3529 (1941).
 (110) Soroos, Willis, J. Am. Chem. Soc. 63, 881 (1941).
- (111) U.S. Industrial Alc. Co., French 811,832, April 23, 1937; Cent. 1937, II 1267. (112)
 Bartlett, Condon, Schneider, J. Am. Chem. Soc. 66, 1531-1539 (1944). (113)
 Pearlson, Simons, J. Am. Chem. Soc. 67, 352-362 (1945). (114)
 Erickson, Ashton, J. Am. Chem. Soc. 63, 1769 (1941).

3:7065	ACETYL CHLORI (Ethanoyl chloride			$\mathrm{C_{2}H_{3}OCl}$	Beil. II - 173 II ₁ -(79) II ₂ -(175)	
B.P.			F.P.			
55°	at 760 mm.	(1)	-112.0° (6)	$D_4^{25} = 1.0983$	(5)	
51-52°	at 761 mm.	(2)	• •	1.0982	(11)	
52°	at 737 mm.	(3)				
51-52°		(12)		$D_4^{20.8} = 1.1037$	(12)	
51-52°	at 720 mm.	(4)				
51.8°		(5)		$D_4^{20} = 1.1044$	(8)	
51.0°	at 760 mm.	(6)		$n_{ m D}^{25}$	= 1.3878	(5)
50.92°	at 746 mm.	(7)				
50.6°	at 756 mm.	(8)		$n_{ m D}^{20.8}$	= 1.38831	(12)
50.2°		(9)				
50.08-	50.12° at 741 mm.	(10)		$n_{ m D}^{20}$	= 1.38976	(4)
50°	at 740 mm.	(13)			1.3887	(8)

Colorless mobile liq. with sharp and penetrating odor. — Note that ordinary samples of \bar{C} may (according to their method of preparation) contain more or less PCl₃ (b.p. 75.95° at 760 mm.), POCl₃ (b.p. 107.2° at 760 mm.), SOCl₂ (b.p. 78.8°), AcOH (b.p. 118.2°), Ac₂O (b.p. 140.0°), or various acetylated derivs. of phosphorous acid (if present in large amt. the last in part form a white ppt. on long stdg.), removal of which is difficult. the presence of these impurities doubtless accounts for various instances of abnormally high b.p.'s cf. (7). — \bar{C} may be freed from dissolved HCl and from AcOH by distn. with dimethylaniline (13) or by treatment with powdered basic oxides, hydroxides, carbonates, etc. (14).

PREPARATION OF C

 \bar{C} can be prepared from various sources with a wide variety of reagents; examples of the more important types of combinations are given below grouped under indicated subheadings. — It must also be recognized that many other processes (notably for manufacture of Ac₂O) involve the formation of \bar{C} but immediately utilize it without separate isolation; these cannot be included here.

Preparation of \tilde{C} from AcOH. [For preparation of \tilde{C} from AcOH with PCl₃ (79% yield (20)) (15) (16) (7) (17) under press. at 80° (yield 100% (18)) or in Ac₂O (85% yield (19)) see indic. refs. (note particularly the form. of Ac₂O and of AcO.P(OH)₂ discussed in (17)): with PCl₃ + ZnCl₂ (90% yield) see (20); with PCl₅ (80% yield (20)) (21) see indic. refs.; with POCl₃ (22) (23) see indic. refs.; with P₂O₅ + HCl gas at 0° see (24) (25); with P + Cl₂ in POCl₃ see (26).]

[For prepn. of \bar{C} from AcOH with SOCl₂ (46% yield (20)), with S₂Cl₂ + Cl₂ at -4° in pres. of Fe (95.5% yield (27)), with ClSO₃H (20-25% yield (28)); with sodium chlorosulfonate (29) in pres. of NaCl or Na₂S₂O₇ (30) (31), or with SiCl₄ in toluene (85% yield (32)), see indic. refs.]

[For prepn. of \bar{C} from AcOH with COCl₂ (3:5000) at 110–120° (33) in vapor phase at 160° over MgCl₂ on diatomaceous earth (34) cf. (35) (36); with an arylsulfochloride such as p-toluenesulfonyl chloride + NaCl (30); with another org. acid chloride such as chloroacetyl chloride (3:5235) (37), dichloroacetyl chloride (3:5290) (38), or benzoyl chloride (3:6240) (yield 85–88% (39), 70% (42)) (40) (41); with benzotrichloride (3:6540) (90% yield (42)) see indic. refs.]

Preparation of C from salts of acetic acid. [For prepn. of C from NaOAc (or other metallic acetates) with POCl₃ (43) (44); with SO₂Cl₂ (45) (46); with sodium chlorosulfonate

(29) cf. (30); with SiCl₄ (47) (48); with COCl₂ at 120° under press. (49); with p-toluene-sulfonyl chloride (50); with benzoyl chloride (3:6240) (40) see indic. refs.; from NaOAc/H₂SO₃ compd. with Cl₂ see (51).]

Preparation of \tilde{C} from acetic anhydride. [For prepn. of \tilde{C} from Ac₂O (1:1015) with Cl₂ (52); with dry HCl gas at 100° (52) or in continuous process at 85–90° (93% yield (53)) or under 18–42 atm. press. (100% yield (54)); with PCl₃ (15); with PCl₅ (21); with SOCl₂ at 20–25° (SO₂ being evolved) (55), or with sodium chlorosulfonate (29) see indic. refs.]

[For prepn. of \bar{C} from Ac₂O (1:1015) with phosgene (3:5000) + cat. (56); with benzoyl chloride (3:6240) (77% yield (42)) (41) (40); with oxalyl (di)chloride (3:5060) (80-95% yield (57)); with benzo-trichloride (3:6540) + ZnCl₂ (33% yield (58)); with benzyl chloride (3:8535) + cat. (59) see indic. refs.; for formn. of \bar{C} as by-prod. from reactn. of ethylene with Cl₂ in Ac₂O see (60).]

Preparation of C from methyl chloride. [For prepn. of C from CH₃Cl (3:7005) with CO at 700-800° over pumice contg. sodium metaphosphate (61) or with CO, COCl₂, or COS at 700-900° in pres. of metallic cat. (62) see indic. refs.]

Preparation of \bar{C} from miscellaneous sources. [For prepn. of \bar{C} from 1,1,1-trichloroethane (methylchloroform) (3:5085) by partial cat. hydrolysis (63) (64); from ketene + liq. HCl (65) or with HCl gas over activated carbon at 100° (100% yield (66)); from ethyl, isobutyl, isoamyl, benzyl, phenyl, or p-tolyl acetates with SiCl₄ (67); from α -chloroethyl acetate (3:7625) (68) (69) or α,β -dichloroethyl acetate (69) with ZnCl₂ (68) or over pumice at 250–300° (69); from β -bromo- α,β -dichlorovinyl ethyl ether with AcOH (70); from acetyl bromide with HCl gas at ord. temp. (71); from N,N-diacetylaniline (diacetanilide) with HCl gas at 150–170° (72); from diacetyl sulfite (see below) with SOCl₂ (73) see indic. refs.]

PYROLYSIS OF C

[C in absence of cat. is stable to heat up to at least 450° (74). — C passed at 700-850° over hot Pt wire gives ethylene + CO + HCl (75), but at 400° over Pt on pumice gives (74) 45% MeCl (3:7005) + 49% CO + 5% H₂. — C over Cu filings at 350° is partially decomposed yielding (74) MeCl (3:7005) + CO + CO₂ + H₂ + dehydroacetic acid (1:0700) + acetone. — C over ZnCl₂ on pumice at 400° gives (74) HCl + dehydroacetic acid (1:0700) + gas mixt. contg. 87% CO₂ + 4% CO + 2% H₂. — C over Ni at 420° gives (76) HCl + gas mixt. contg. 62% CO + 32% H₂. — For studies on pyrolysis of C over Al₂O₃, Cu₂Cl₂, CuO, Ni, etc., see (74).]

REACTIONS OF C WITH INORGANIC REAGENTS

Reaction of \tilde{C} with H_2O (hydrolysis). \tilde{C} reacts violently with aq. hydrolyzing to AcOH (1:1010) + HCl (for kinetic studies see (777)); for use of this reactn. in volumetric detn. of H_2O in org. liquids see (185) (78). — Because of its ease of reactn. with aq. \tilde{C} is widely used for condensations, ring closures, etc.

Reaction of C with NH₃ and similar cpds. C with cold conc. aq. NH₄OH (16) or C with liq. NH₃ (79) gives (yields: 77% (16), 88% (79)) acetamide, very sol. aq., m.p. 81.5°, b.p. 222° (best recrystd. from dry AcOEt by addn. of dry ether).

[The direct reaction of \bar{C} with NH₂OH (or its salts) seems to be unreported, but the presumable prod., viz., N-acetylhydroxylamine (acethydroxamic acid) [Beil. II-187, II₁-(85), II₂-(184)], very eas. sol. aq. or alc., insol. ether, cryst. from EtOAc, m.p. anhydrous 89°, contg. crystal aq. 57° , has been obtd. indirectly.]

[The direct reacts. of \tilde{C} with hydrazine hydrate, NH₂.NH₂.H₂O, seems to be unreported, but the presumable prod., viz., acethydrazide (acetylhydrazine) [Beil. II-191, II₁-(86), II₂-(185)], ndls. from alc., m.p. 67°, has been obtd. by indirect means.]

Reaction of \tilde{C} with halogens. [\tilde{C} with Cl_2 in CCl_4 in light (80) or in pres. of I_2 (82) gives mainly chloroacetyl chloride (3:5235); for study of mechanism of chlorination see (81); for influence of \tilde{C} on chlorination of AcOH or Ac₂O see (82), on bromination of AcOH see (83).]

[For studies of \overline{C} with Br₂ see (84) (85) (86).]

Reaction of \bar{C} with inorganic acids. [\bar{C} with dry HBr gas for 2 hrs. gives (80% yield (87)) acetyl bromide [Beil. II-174, II₁-(79), II₂-(176)], b.p. 76.7° at 760 mm., $D_4^{15.8} = 1.6625$, $n_D^{15.8} = 1.45370$; for details on this equilibrium see (88).]

[C with 3 pts. dry HI in the cold gives (70% yield (87)) (89) acetyl iodide [Beil. II-174, II₁-(80), II₂-(177)], b.p. 104-106° at 735 mm. (89) (for studies of use of AcI in splitting of aliphatic ethers (90) or in addn. to unsatd. hydrocarbons (91) see indic. refs.).]

[\bar{C} with cold conc. H_2SO_4 (1 mole) forms a mol. cpd. (88) (92) which can even be obtd. in cryst. form (92); this cpd. loses HCl only upon htg. (88) (92), and the residual acetyl hydrogen sulfate [Beil. II-170, II₁-(78), II₂-(174)] which might be expected is transformed into sulfoacetic acid and other prods. (92). — \bar{C} with nitrosylsulfuric acid in CCl₄ evolves NOCl and yields acetyl HSO₄ which rapidly changes to sulfoacetic acid (93).]

[C with ClSO₃H stood for several days (94) (95) evolves HCl and forms the transient acetyl sulfonyl chloride, CH₃.CO.O.SO₂Cl; above 45° this intermediate rearr. to sulfoacetyl chloride which with water hydrolyzes to sulfoacetic acid; C with ClCO₃H at 60–140°, however, also undergoes condensation involving 4 moles of C with evoln. of HCl and formn. of an acid chloride which on hydrolysis with aq. gives (3% yield (94)) a monobasic acid of compn. C₈H₈O₄ [Beil. XVIII-412], m.p. 99°, which is either 2,6-dimethylpyrone-4-carboxylic acid-3 or 2-methylpyrone-1,4-acetic acid-6 (96); note that this acid is isomeric with but distinct from dehydroacetic acid (1:0700), m.p. 109°. — Note also that C in AcOH boiled with conc. H₂SO₄ gives (97) traces of 2,6-dimethylpyrone.]

[C with solid H₂O₂ (0.6 mole) yields (98) about 60% acetyl hydrogen peroxide (peracetic acid) [Beil. II-169, II₁-(78), II₂-(174)] accompanied by some diacetyl peroxide [Beil. II-170, II₁-(78), II₂-(174)].— C with liq. H₂S yields (99) "dithioacetic acid anhydride," (CH₃.CS)₂S, white cryst., m.p. 225° (99); note that, although neither C nor Ac₂O separately treated with H₂S gas shows any appreciable reaction, yet Ac₂O contg. 2% C absorbs H₂S giving (70% yield (100)) thiolacetic acid [Beil. II-230, II₁-(101), II₂-(208)], CH₃.CO.SH, b.p. 93°. — C (4 moles) with H₂S₃ + ZnCl₂ yields (101) diacetyl trisulfide.]

Reaction of \bar{C} with salts of inorganic acids. $[\bar{C}$ with metal oxides in CHCl₃ at -60 to -20° yields (102) the corresp. metallic chlorides. $-\bar{C}$ with Sb₂S₃ at 300-350° (103) or with K₂S (104) gives diacetyl sulfide [Beil. II-232], b.p. 120°. $-\bar{C}$ with PbSO₃ gives (72) diacetyl sulfite which with SOCl₂ gives $\bar{C} + SO_2$ (72).

[\overline{C} (6 pts.) with KNO₃ (first fused, then powdered) (1 pt.) (105) or \overline{C} with Pb(NO₃)₂ (106) gives mainly (yields: 81-85% (105), 58% (106)) acetic anhydride (1:1015).]

[C with NaN₃ in di-isoamyl ether stood overnight {108} {109}, then warmed at 60-70°, evolves N₂ and gives (86% yield (107)) methyl isocyanate [Beil. IV-77, IV₁-(337), IV₂-(578)], b.p. 27.4-27.8°; note, however, that C with NaN₃ in AcOH evolves N₂ and gives (50-63% yield {110}) N-methylacetamide, m.p. 27-28°, b.p. 202-204° (presumably by cleavage of the CH₃NCO and acetylation of the MeNH₂).]

[\bar{C} with NaHF₂ in Ac₂O (111), with KF in AcOH (41) (42), AgF (112), ZnF₂ (112) (113), HgF₂ (114), C₆H₅HgF (115), SbF₃ (112) (116), or AsF₃ (112) gives (yields: 132% on \bar{C} or 66% on NaHF₂ (111), 76% (41) (42), 40% (113), 30.8% (116)) acetyl fluoride, b.p. 20.8° at 770 mm.]

[\bar{C} with AlCl₃ in CS₂ at -10° gives (117) a mol. cpd., \bar{C} .AlCl₃, as a pale yel. gummy mass; \bar{C} with AlCl₃.Et₂O gives EtOAc (70% yield (118)) + EtCl (3:7015) + AlCl₃. $-\bar{C}$ (1 mole) with AlCl₃ (6 moles) in CHCl₃ gives (124) (CH₃CO)₂.CH.CCl₂.O.AlCl₂ (125) which with

aq. yields (124) (125) acetylacetone (1:1700). — Note also that \bar{C} forms other analogous complexes: e.g., \bar{C} .BCl₃ (119), \bar{C} .BF₃ (119), \bar{C} .SbCl₅ (119) (for use of these in splitting of ethers see (119)).]

[\tilde{C} with 2 pts. sublimed FeCl₃ in CS₂ for 24 hrs. gives (small yield (120)) dehydroacetic acid (1:0700).]

[Č with CaI₂ in s.t. at 70–75° for 120 hrs. gives (121) acetyl iodide (see above under HI).] Reaction of Č with esters of inorganic acids. [Č with Me₂SO₄ (1 mole) + trace of ZnCl₂ at 140–150° evolves HCl and gives (20–25% yield (122)) dimethyl sulfoacetate, b.p. 155–165° at 20–22 mm. (122). — Č + di-n-propyl sulfite + trace ZnCl₂ at 170–200° gives (80% yield (123)) n-propyl acetate (1:3075).]

Reaction of \tilde{C} with metals. [\tilde{C} in excess with metallic Zn gives a solid of compn. $C_{16}H_{18}O_4$ (126), now (127) thought to be 3,8-diacetyl-5,6-dimethyldecatetraene-3,4,6,7-dione-2,9. — \tilde{C} with metallic Zn in dry ether yields (128) EtOAc (1:3015) and AcOH (1:1010). — \tilde{C} with metallic Zn in dry dioxane (1:6400) gives (85% yield (128)) (129) ethylene glycol diacetate (1:3511). — \tilde{C} with CuH evolves H_2 and gives (130) cf. (131) EtOAc (1:3015) + ethylidene diacetate (1:3383).]

REACTIONS OF C WITH ORGANIC REAGENTS

REACTIONS OF C WITH HYDROCARBONS

Reactions of $\tilde{\mathbb{C}}$ with alkanes. [$\tilde{\mathbb{C}}$ with n-butane (or isobutane) + AlCl₃ at 60° for 15 hrs. under press. gives (small yield (132)) isobutyl methyl ketone (1:5430). — $\tilde{\mathbb{C}}$ with n-pentane + AlCl₃ at 15° at ord. press. gives (10% yield (133)) (134) 2,3-dimethylpentanone-4 (unsym.-isopropyl-methyl-acetone) [Beil. 1-703, 1_{1^-} (360)], b.p. 135–136° (oxime, b.p. 101–105° at 20 mm., semicarbazone, m.p. 114° (133)) accompanied (134) by some 2,3-dimethylpenten-3-one-2 (unsym.-isopropylidene-methyl-acetone) [Beil. 1_{2^-} (796)] (corresp. semicarbazone, m.p. 192.5° (134)). — $\tilde{\mathbb{C}}$ with n-hexane + AlCl₃ in similar fashion gives (7% yield (135)) (134) 3-ethyl-2-methylpentanone-4 (unsym.-ethyl-isopropyl-acetone) [Beil. 1-707], b.p. 154–155° (semicarbazone, m.p. 120° (135)) accompanied by a little 3-ethyl-2-methylpenten-2-one-4 (unsym.-ethyl-isopropylidene-acetone), b.p. 177–178° (semicarbazone, m.p. 220° (135).]

Reactions of $\bar{\mathbf{C}}$ with alkenes. $[\bar{\mathbf{C}}$ in the pres. of suitable cat. can add to olefin linkages forming halogenated ketones: e.g., $\bar{\mathbf{C}}$ with ethylene + AlCl₃ at 0° (137) (138) or $\bar{\mathbf{C}}$ + ethylene over activated carbon at 100° and 50 atm. (139) gives (yields: 53% (136), 33% (137)) (138) cf. (60) β -chloroethyl methyl ketone (3:7640) (note that $\bar{\mathbf{C}}$ + ethylene + AlCl₃ in CS₂, latter subsequently replaced by C₆H₆, goes further yielding (140) benzylacetone [Beil. VII-314, VII₁-(167)], b.p. 235°). — For studies of analogous cat. addn. of $\bar{\mathbf{C}}$ to 2-methylbutene-2, 2,3-dimethylbutene-2, and 2-methylbexene-2 see (141).]

Reactions of \bar{C} with alkynes. $[\bar{C}$ in the pres. of suitable cat. can also add to a triple unsatd. linkage yielding olefinic chloroketones: e.g., \bar{C} with acetylene + AlCl₃ at 15° (142) (143) or other cat. (143) gives (25% yield (142)) β -chlorovinyl methyl ketone, b.p. 35–38° at 12 mm. (143). — \bar{C} with butyne-1 (ethylacetylene) + SnCl₄ gives (144) 4-chlorohexen-3-one-2, b.p. 46–53° at 10 mm., $D_4^{25} = 1.0973$, $n_D^{25} = 1.4906$ (144); for analogous reactions with pentyne-1, hexyne-1, hexyne-3, heptyne-1, octyne-4, decyne-5, and dodecyne-6 together with corresp. constants of prods. see (144).]

Reaction of \bar{C} with cycloparaffins (cycloalkanes). [\bar{C} in the pres. of AlCl₃ also condenses with cycloalkanes eliminating HCl; e.g., \bar{C} (1.9 moles) + cyclopentane (1:8400) (5.4 moles) + AlCl₃ (2.2 moles) at 0° gives (145) cyclopentyl methyl ketone (acetylcyclopentane), b.p. 159.5-160.5° at 760 mm., $D_{20}^{20} = 0.9172$, $n = \frac{20}{D} 1.44351$ (145) (semicarbazone, m.p. 142-143° (145)); \bar{C} + methylcyclopentane (1:8403) + AlCl₃ similarly gives (145) 1-

methylcyclopentyl-2 methyl ketone (1-acetyl-2-methylcyclopentane) accompanied by some 1-methylcyclopenten-1-yl-2 methyl ketone (1-acetyl-2-methylcyclopentene-1) (see below).

[\bar{C} in the pres. of AlCl₃ also condenses with cyclohexane, but here the reaction involves in addn. a change from a 6-membered to 5-membered ring: e.g., \bar{C} with cyclohexane (1:8405) + AlCl₃ gives (135) (146) (147) (148) 1-methylcyclopentyl-2 methyl ketone (1-acetyl-2-methylcyclopentane), b.p. 167-168° at 759 mm., $D_4^{20}=0.8976$, $n_D^{20}=1.4404$ (semicarbazone, m.p. 162.5-163° (148), 158° (146); p-nitrophenylhydrazone, m.p. 102.5° (148), accompanied under certain circumstances (135) by 1-methylcyclopenten-1-yl-2 methyl ketone (1-acetyl-2-methylcyclopentene-1), b.p. 185-187° (135) (oxime, m.p. 85-85.5° (148), p-nitrophenylhydrazone, m.p. 162° (148), semicarbazone, m.p. 221° (148), 220° (135)); note that various hydrocarbon by-products are also formed. — \bar{C} + methylcyclohexane (hexahydrotoluene) (1:8410) + AlCl₃ at room temp. similarly gives (149) 1-acetyl-2,3-dimethylcyclopentane, b.p. 182-184° at 754 mm., $D_{20}^{20}=0.8969$, $n_D^{22}=1.44551$ (semicarbazone, m.p. 152°) (149).]

Reaction of \bar{C} with cycloalkenes. [\bar{C} in the pres. of suitable cat. adds to unsatd. linkages of cycloalkenes: e.g., \bar{C} with cyclopentene (1:8037) + AlCl₃ (2 moles) in cyclohexane at -15° gives (50% yield (150)) cyclopentyl methyl ketone (1-acetylcyclopentane) (for constants see above under \bar{C} + cyclopentane); note, however, that \bar{C} + cyclopentene (1:8037) + AlCl₃ at -14° in CS₂ (the latter being subsequently replaced by benzene) gives (140) 1-acetyl-3-phenylcyclopentane (note rearr.).]

[Č with cyclohexene $(1:8070) + \text{AlCl}_3$ (2 moles) in cyclohexane gives $(53\% \text{ yield } \{150\})$ cyclohexyl methyl ketone (1-acetylcyclohexane) [Beil. VII-22, VII₁-(16)]. — Č with cyclohexene $(1:8070) + \text{AlCl}_3$ (1 mole) in CS₂ gives $(21\% \text{ yield } \{151\})$ (152) cyclohexen-1-yl-1 methyl ketone (1-acetylcyclohexene-1) (tetrahydroacetophenone) [Beil. VII-58, VII₁-(49)], b.p. $201-202^\circ$, $D_4^{20} = 0.9655$, $n_2^{20} = 1.4881$ (oxime, m.p. 99° , semicarbazone, m.p. $220-221^\circ$). — Č with cyclohexene $(1:8070) + \text{AlCl}_3$ in CS₂ at -15° gives by addn. a prod. supposed (153) to be 2-chlorocyclohexyl-1 methyl ketone (since it can be converted by loss of HCl to tetrahydroacetophenone (above)) but which when reacted with $C_6H_6 + \text{AlCl}_3$ gives (140) 4-phenylcyclohexyl-1 methyl ketone (1-acetyl-4-phenylcyclohexane); in just which phase rearr. occurs has not been established with certainty.]

Reaction of C with aromatic hydrocarbons. C with aromatic hydrocarbons in the presence of various cat. (notably AlCl₃) evolves HCl and yields aryl methyl ketones; examples are cited in the following paragraphs.

[\tilde{C} with C_6H_6 + AlCl₃ (154) in CS₂ (155) gives (70% yield (155)) methyl phenyl ketone (acetophenone) (1:5515) accompanied by a little 1,3-diphenylbuten-2-one-1 (dypnone) cf. (155); for study of relative reactivity in this sense of AcF, AcCl, AcBr, and AcI see (111); for study of influence of other cat., e.g., FeCl₃ (156) (157), TlCl₃ (158), ZrCl₄ (159), UCl₄ (160), BeCl₂ (161), Al powder (162) or Cr powder (163), or for study of effect of various solvents with AlCl₃ (164) see indic. refs.]

[\bar{C} with toluene + AlCl₃ gives (70% yield (165)) (166) methyl p-tolyl ketone (1:5530); for study of use of BeCl₂ (80% yield (161)) or of 39 other metallic chlorides (167) (168) see indic. refs. — For reactn. of \bar{C} + AlCl₃ with a long series of homologous monoalkylbenzenes see (169) (170), with p-cymene (1:7505) see (171); many other, similar cases cannot be included here.]

[$\bar{\mathbb{C}}$ with naphthalene (1:7200) + AlCl₃ in CS₂ gives a mixt. (75% yield {172}) comprising 50-60% 1-acetylnaphthalene (1:5600) + 15-20% 2-acetylnaphthalene (1:5153). — $\bar{\mathbb{C}}$ with 1-methylnaphthalene (1:7600) + AlCl₃ in nitrobenzene at -3° gives {173} cf. (174) 1-aceto-4-methylnaphthalene; $\bar{\mathbb{C}}$ with 2-methylnaphthalene (1:7605) + AlCl₃ in nitrobenzene gives a mixt. (64% yield {175}) comprising mainly 6-acetyl-2-methylnaphthalene accompanied by some 8-acetyl-2-methylnaphthalene.]

[$\bar{\mathbf{C}}$ with biphenyl (1:7175) + AlCl₃ in CS₂ (176) or C₆H₆ (177) gives (yields: 90% (176), 70% (177)) 4-acetylbiphenyl (p-phenylacetophenone) (1:5201); under appropriate conditions $\bar{\mathbf{C}}$ with biphenyl + AlCl₃ in CS₂ gives (yields: 45% (176), 43% (178)) 4,4'-diacetyl-biphenyl.]

[\tilde{C} with acenaphthene (1:7225) + AlCl₃ in nitrobenzene (179) or with liq. HF (180) gives (29% yield (180)) 1-acetoacenaphthene.]

[Friedel-Crafts condensation can also be carried out with $\bar{\mathbf{C}}$ and heterocyclic systems: e.g., $\bar{\mathbf{C}}$ with thiophene + SnCl₄ in C₆H₆ gives (79-83% yield (181)) 2-acetylthiophene (methyl 2-thienyl ketone); $\bar{\mathbf{C}}$ with thionaphthene + AlCl₃ in CS₂ gives (30% yield (182)) 3-acetylthionaphthene.]

REACTIONS OF C WITH ORGANIC OH (OR SH) COMPOUNDS (OR THEIR METALLIC DERIVATIVES)

Reactions of \bar{C} with alcohols. [\bar{C} reacts with alcs. in general yielding the corresp. acetates: e.g., \bar{C} with MeOH (1:6120) yields methyl acetate (1:3005), \bar{C} with EtOH (1:6130) yields EtOAc (1:3015), etc.; for studies on rate of reactn. of \bar{C} with EtOH in ether (1), or with β -chloroethyl alc. in dioxane (182) (183), or with benzyl alc. or cyclohexanol (182) see indic. refs.] — For use of \bar{C} in quant. detn. of OH groups in prim. and sec. alcs. see (186) (187) (188) cf. (185).

[Special interest, however, attaches to reaction of \bar{C} with ter-alcohols: under ord. conditions these react with \bar{C} to exchange Cl for OH yielding alkyl chloride + AcOH (e.g., \bar{C} + ter-butyl alc. giving ter-BuCl + AcOH); note, therefore, that under special conditions \bar{C} with ter-alcs. also gives the corresp. esters; e.g., \bar{C} with ter-butyl alc. (1:6140) in dry ether + Mg (189) (190) or dimethylaniline (191) or in xylene with pyridine (192) gives (yields: 98% (192), 83% (189), 63–68% (191), 45–55% (190)) ter-butyl acetate (1:3057); other ter-alcs. (189) and other acid chlorides (191) behave similarly.]

[For reactn. of \tilde{C} with cellulose (or cotton) see (193) (194) (195); with polyoxymethylenes see (196).]

[Č with mercaptans yields the corresp. thiolacetates: e.g., \bar{C} with C_2H_5SH gives (80% yield (197)) ethyl thiolacetate, $CH_3CO.S.C_2H_5$, b.p. 116–117°, $D_4^{25}=0.9755$, $n_D^{28}=1.4503$ (197).]

Reactions of C with phenols. C can react with phenols in either or both of two modes: on one hand it can acetylate the phenolic OH yielding the corresp. phenol acetates, or in the pres. of suitable cat. or solvents it can condense with one or more of the nuclear H atoms yielding phenolic ketones. Furthermore the phenol acetates can more or less readily be caused to rearr. into phenolic ketones (Fries rearr.) so that the chemistry of the two classes is closely related and so voluminous that it cannot be given extensive discussion here.

[\tilde{C} with phenol (1:1420) directly (198) (199) or in C_6H_6+Mg (200) gives (yields: 92% (200), 90% (199)) phenyl acetate (1:3571); other mono-, di-, and polyhydric phenols behave analogously.]

[\bar{C} with phenol (1:1420) + FeCl₃ in CS₂ (156) (201) or phenyl acetate (above) + AlCl₃ in nitrobenzene at 20–25° for 24 hrs. (202) gives (yields: 75% (202), 33% (201)) p-hydroxy-acetophenone (1:1527), m.p. 109° (for extensive review of the Fries rearr. reactn. see (203)); the corresp. analogous reactns. of \bar{C} with other mono-, di-, and polyhydric phenols are legion and will not be cited here.]

[For study of series of mol. cpds. of C with various benzeneazophenols see (230).]

Reaction of \bar{C} with phenol ethers. With phenol ethers where no phenolic OH remains to interfere \bar{C} reacts in the pres. of suitable cat. in the Friedel-Crafts sense: e.g. $[\bar{C}$ (2 moles) with methyl phenyl ether (anisole) (1:7445) (1 mole) + AlCl₃ (2 moles) gives (75% yield

(204)) (205) p-methoxyacetophenone (p-acetylanisole) (1:5140); note that $\ddot{\mathbf{C}}$ + anisole do not react in the pres. of AlF₃ or ZnF₂ (111). — Countless analogous condensations of $\ddot{\mathbf{C}}$ with other phenol ethers cannot be discussed here].

Reaction of $\tilde{\mathbf{C}}$ with enols (or their metallic derivatives). [The reaction of $\tilde{\mathbf{C}}$ with ethyl acetoacetate (1:1710) leads according to circumstances to either or both of two very closely similar derivatives; one of these is ethyl O-acetylacetoacetate (ethyl P-acetoxycrotonate) (A) [Beil. III-373, III₁-(135), III₂-(255)], b.p. 212-214° sl. dec. (206), $D_4^{20}=1.060$ (207), $n_D^{20}=1.4447$ (207); the other is ethyl α -acetylacetoacetate (ethyl diacetylacetate) (B) [Beil. III-751, III₁-(263), III₂-(467)], b.p. 209-211° (208), $D_4^{20}=1.093$ (207), $n_D^{20}=1.4687$ (207); note that the latter (B) as liquid is 100% enolized (209) (210) and this prop. is used (211) for detn. of both A+B in their mixtures. — Note furthermore that the O-ester (A) by suitable htg. (212) (213) (214) (215) (216) can be converted to the isomer (B).]

[$\bar{\mathbf{C}}$ with cthyl acetoacetate (1:1710) in pres. of pyridine (217) or $\bar{\mathbf{C}}$ with its Na enolate in ether (219) or its Cu enolate in ether or C_6H_6 (220) gives mainly the O-acetyl deriv. (A) (above); $\bar{\mathbf{C}}$ with ethyl sodioacetoacetate in ether (221) (222) (223) (226) or pet. ether (216) or with the Ca enolate in C_6H_6 (224) or $\bar{\mathbf{C}}$ with ethyl acetoacetate + Mg in C_6H_6 (225) (226) gives (yields: 65% (224), 46-52% (225)) ethyl diacetylacetate (B above) (Cu enolate, m.p. 151° (226)).]

[For study of influence of \bar{C} on rate of enolization of ethyl acetoacetate see (228); for formn. of ethyl O-acetylacetoacetate (isomer A above) from \bar{C} + ketene diethylacetal (30% yield together with other prods.) see (229).]

Reaction of $\tilde{\mathbf{C}}$ with acids or their salts. [$\tilde{\mathbf{C}}$ on htg. with NaOAc or other metal salts of AcOH yields acetic anhydride (1:1015); this reactn. is well known and will not be amplified here; $\tilde{\mathbf{C}}$ with salts of acids other than acetic gives in some cases the corresp. mixed anhydride, in others only the anhydride of the second acid. E.g., $\tilde{\mathbf{C}}$ (1 mole) with dry Na isovalerate (1 mole) gives at 120° the mixed anhydride contg. 1 acetyl and 1 isovaleroyl radical (231); on the other hand, $\tilde{\mathbf{C}}$ with dry Na cinnamate gives only cinnamic anhydride (231); many other examples are known.]

[\bar{C} on htg. with AcOH under appropriate conditions (232) (233) (234) loses HCl giving good yields Ac₂O (1:1015).]

Note that \bar{C} in Ac₂O behaves as a weak acid and can actually be titrated with NaOAc in Ac₂O using methyl orange as indicator (235).

REACTION OF C WITH AMINES (OR THEIR DERIVATIVES)

Reaction of $\bar{\mathbf{C}}$ with primary and secondary amines. $\bar{\mathbf{C}}$ readily reacts with such amines to yield under ord. conditions the N-acetylated derivative: e.g., $\bar{\mathbf{C}}$ with MeNH₂ gives N-methylacetamide [Beil. IV-58, IV₁-(329), IV₂-(563)], very sol. aq., m.p. 27-28°, b.p. 206°; countless other examples are known. Note that only 1 acetyl group is introduced into each amino group; also that $\bar{\mathbf{C}}$ with a mixture of two amines gives mainly (or even exclusively) the N-acetyl deriv. of the more negative accompanied by the hydrochloride of the more positive (236). See also below under $\bar{\mathbf{O}}$'s.

Reaction of \bar{C} with tertiary amines. \bar{C} (1 mole) with pyridine (1 mole) directly (237) (238) or in C_6H_6 (237) ppts. an addn. prod. (presumably N-acetylpyridinium chloride), white cryst. turning red in light, m.p. abt. 100°, after darkening at 90°; for use of this cpd. in cleavage of phenol ethers see (237). — For use of \bar{C} + pyridine in toluene as means of quant. detn. of OH groups see (186).

[Č (1 mole) with Et₈N (1 mole) in 10 vols. dry C₆H₆ (239) or Č in equal. vol. pyridine or picoline (238) yields dehydroacetic acid (1:0700), m.p. 209°.]

[Note here also a novel method of intermolecular dehydrohalogenation: e.g., C with

lauroyl chloride (3:9858) + Et₂N in dry ether ppts. Et₃N.HCl and yields (240) a mixt. of acetylketene (detene dimer) + lauroylketene and other prods. — Note further that since dehydroacetic acid (above) may be viewed as ketene tetramer, its formation from Č with ter-amines (above) may (241) involve preliminary formation of acetylketene followed by Diels-Alder addn. with a second identical molecule to give dehydroacetic acid.]

Reaction of \tilde{C} with other miscellaneous nitrogenous systems. [\tilde{C} with diazomethane in dry ether yields (242) diazoacetone (acetyldiazomethane) [Beil. I_1 -(396), I_2 -(823)] yel. liq., b.p. 49° at 13 mm. (242).]

[C with oximes often is used to effect either dehydration to nitriles or Beckmann rearr. or both (for review see {243}).]

[C with acetanilide refluxed for 7 hrs. gives (244) diphenylacetamidine; other anilides behave in analogous fashion (244). — However, C with acetanilide + AlCl₃ in CS₂ (245) or other inert solvent (246) gives Friedel-Crafts reactn. forming (57% yield (245)) p-(acetylamino)acetophenone [Beil. XIV-48, XIV₁-(366)], m.p. 166-167°.]

[C with thiosemicarbazide results in acetylation followed by elimination of HCl and ring closure yielding (247) (248) the hydrochloride, m.p. 110° (248), of 5-amino-2-methyl-1-thiodiazole-3,4 [Beil. XXVII-629], m.p. 235° (248). — For study of reactn. of C with Schiff's bases see (249).]

REACTION OF C WITH VARIOUS ORGANOMETALLIC COMPOUNDS

Reaction of \bar{C} with Grignard reagents. [The normal reaction of \bar{C} with 1 mole RMgX is to eliminate MgXCl and yield the corresp. ketone; e.g., \bar{C} with EtMgBr in pres. of CdCl₂ gives (46% yield (250)) ethyl methyl ketone (1:5405); in the presence of excess RMgX, however (and sometimes without excess), the ketone may react further to yield the corresp. tertiary alcohol; e.g., \bar{C} with C₆H₈MgBr gives 39% yield (251) diphenyl-methyl-carbinol; countless other examples cannot be included here.]

[Certain divergences from the above normal reaction have, however, now been recognized; these appear to be largely a function of the particular types of RMgX employed. E.g., \bar{C} (0.5 mole) with benzyl MgCl (0.37 mole) in dry ether gives (instead of the expected phenylacetone (1:5118)) 24% yield (252) of o-methylacetophenone (1:5524).]

[Furthermore Č with Grignard reagents derived from tertiary alkyl halides is often reduced and the reactn. prod. then contains (in addn. to the normal prods.) other material derived from the reduction prods. E.g., Č (in excess) with ter-BuMgCl gives (40% yield (253) (254)) ter-butyl methyl ketone (pinacolone) (1:5425); note, however, that further study (255) (256) (13) has shown the formation of numerous other prods. including 2-methylpropane (isobutane), 2-methylpropene-1 (isobutylene), carbon monoxide, ethyl acetate, pinacolyl acetate, and mesityl oxide. — For study of reactn. of Č with ter-AmMgCl (254) (13) and other ter-RMgX cpds. (254) see indic. refs. — Note that even RMgX cpds. from even primary halides may effect reduction; e.g., Č with n-BuMgCl gives (255) 13% hexanol-2 (1:6210) + 8% EtOH (1:6130).]

[Note also that \bar{C} with 2,4,6-trimethylbenzyl MgBr (mesityl MgBr) gives (257) mesitylene but no 2,4,6-trimethylacetophenone (acetomesitylene) although \bar{C} with 2,4,6-triphenyl-phenyl MgBr does give (258) the corresp. 2,4,6-triphenylacetophenone.]

Reaction of \tilde{C} with other miscellaneous organometallic compounds. [\tilde{C} with diphenylmethylsodium reacts to replace Na by H yielding (259) diphenylmethane (1:7120); \tilde{C} with phenylsilver gives (260) 21% acetophenone (1:5515) + 40% biphenyl (1:7175); \tilde{C} with phenylcopper gives (260) 48-54% acetophenone (1:5515).]

[\bar{C} with E₂Mg gives (261) 3-methylpentanol-3 (1:6189) (not *ter*-butyl alc. as was formerly supposed); \bar{C} with dibenzylzinc in pet. ether gives (262) 9% ketones; \bar{C} with dibenzylcadmium in ether gives (262) 18% phenylacetone (1:5118); \bar{C} with Et₂Hg gives

- (263) EtHgCl + butanone-2 (1:5405), but \tilde{C} with dibenzylmercury or with benzylmercuric chloride shows little reaction (262) even after refluxing 2 weeks.]
- [\bar{C} with tetraphenyltin in s.t. at 100° for 15 hrs. gives (very small yield (264)) of acetophenone (1:5515); for reactn. of \bar{C} with tetraethyllead and use in detn. of latter in gasoline see (265).]
 - [C with triphenylbismuth in CCl₄ yields (266) acetophenone (1:5515).]
- [\overline{C} (2 moles) with Ni(CO)₄ (1 mole) in pet. ether gives (267) 4CO + NiCl₂ + biacetyl the latter sepg. as a 1:1 addn. cpd. with the NiCl₂.]
 - D Acetanilide: cryst. from hot aq., m.p. 114°. [From C with aniline (2 moles) followed by recrystallization to remove aniline hydrochloride. Note that even with aniline + aq. at room temp. acetanilide formn. occurs to extent of 35-45% but its proportion diminishes with increase of temp. (268).]
 - Acet-p-toluidide: cryst. from hot aq. or dil. alc., m.p. 153°. [From C + p-toluidine (2 moles) followed by recrystallization to remove p-toluidine hydrochloride.]
 - D Acet-α-naphthalide: m.p. 159°.
 - D Acet-β-naphthalide: m.p. 132°.
 - β-Acetophenylhydrazide (β-acetylphenylhydrazine) (C_6H_5 .NH.NH.COCH₃) [Beil. XV-241, XV₁-(63)]: m.p. 128–129°. [Note that α-acetphenylhydrazide [Beil. XV-236, XV₁-(62)], m.p. 124°, is obtd. from α ,β-diacetylphenylhydrazine [Beil. XV-245, XV₁-(64)], m.p. 107–108°, by partial hydrolysis.]
 - β-Acet-p-nitrophenylhydrazide [Beil. XV-478]: yel. ndls. from alc., m.p. 205-206°.
 β-Acet-2,4-dinitrophenylhydrazide [Beil. XV-492]: yel. pr. from alc., m.p. 201° (269).
- 3:7065 (1) Branch, Nixon, J. Am. Chem. Soc. 58, 2499-2504 (1936). (2) Walden, Z. physik. Chem. 70, 578 (1910). (3) Whitmore, Rec. trav. chim. 57, 567 (1938). (4) Bruhl, Ann. 203, 11 (1880). (5) Koehl, Wenzke, J. Am. Chem. Soc. 59, 1418 (1937). (6) Timmermans, Bull. soc. chim. Belg. 30, 216 (1921). (7) Thorpe, J. Chem. Soc. 37, 186-189 (1880). (8) Martin, Partington, J. Chem. Soc. 1936, 162. (9) Kohlrausch, Pongratz, Z. physik. Chem. B-22, 381 (1933). (10) Mathews, Fehland, J. Am. Chem. Soc. 53, 3216 (1931).
- (11) Walden, Z. physik. Chem. 55, 222 (1906). (12) von Auwers, Schmidt, Ber. 46, 473 (1913). (13) Whitmore, Sutherland, Wagner, Clapper, Lewis, Lux, J. Am. Chem. Soc. 63, 651 (1941). (14) Monsanto Chemical Works, Brit. 397,775, Sept. 21, 1933; Cent. 1933, II 3194. (15) Béchamp, Compt. rend. 40, 946 (1855); 42, 226 (1856). (16) Aschan, Ber. 31, 2346-2347 (1898). (17) Brooks, J. Am. Chem. Soc. 34, 492-499 (1912). (18) Scheuble, Ger. 251,806, Oct. 8, 1912; Cent. 1912, II 1503. (19) British Dyestuffs Corp. & Coffey, Brit. 261,240, Dec. 9, 1926; Cent. 1927, II 620. (20) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-104 (1933).
- (21) Ritter, Ann. 95, 208 (1855). (22) Kanonnikow, Ber. 7, 1650 (1874). (23) Kato, Fujino, Kikuchi, J. Spc. Chem. Ind. Japan (Suppl.) 37-B, 170-171 (1934); Cent. 1934, II 1440; C.A. 28, 5406 (1934). (24) Friedel, Compt. rend. 68, 1557 (1869). (25) Demole, Ber. 10, 1790-1791 (1877). (26) I.G., Ger. 539,624, Nov. 28, 1931; Cent. 1932, I 739. (27) Britton (to Dow Chem. Co.), U.S. 1,805,162, May 12, 1931; Cent. 1931, II 631; C.A. 25, 3670 (1931). (28) Traube, Krahmer, Ber. 52, 1294 (1919). (29) B.A.S.F., Ger. 146,690, Dec. 1, 1903; Cent. 1904, I 65. (30) Henle, Schirm (to M.L.B.), Ger. 397,311, July 1, 1924; French 568,331, March 22, 1924; Cent. 1924, II 1401-1402.
- (31) Henle (to I.G.), U.S. 1,792,163, Feb. 10, 1931; Cent. 1931, I 2934; C.A. 25, 1843 (1931). (32) Montonna, J. Am. Chem. Soc. 49, 2114-2115 (1927). (33) Kempf, J. prakt. Chem. (2) 1, 414 (1870). (34) Eggert, Grimm (to I.G.), Ger. 655,683, Jan. 25, 1938; Cent. 1938, I 2445; C.A. 32, 3773, 6672 (1938). (35) I.G., French 754,986, Nov. 17, 1933; Cent. 1934, I 942. (36) I.G., French 755,052, Nov. 18, 1933; Cent. 1934, I 942-943. (37) Hale, U.S. 1,850,205, March 22, 1932; Cent. 1933, II 2192; C.A. 26, 2750 (1932). (38) Mugdan, Wimmer (to Consortium für Elektrochem. Ind.), Ger. 549,725, April 30, 1932; Cent. 1932, II 122. (39) Brown, J. Am. Chem. Soc. 60, 1325-1328 (1938). (40) Chem. Fabrik vorm. Weiler-ter-Meer, Ger. 350,050, March 11, 1922; Cent. 1922, IV 155.
- (41) Nesmeyanov, Kahn, J. Gen. Chem. (U.S.S.R.) 4, 1243-1246 (1936); Cent. 1936, I 4288; not in C.A. (42) Nesmeyanov, Kahn, Ber. 67, 370-373 (1934). (43) Gerhardt, Ann. chim. (3)

37, 294-298 (1853); Ann. 87, 68-71 (1853). (44) Geuther, Ann. 123, 113-121 (1862). (45) Verein Chem. Ind., Ger. 63,593, June 8, 1892; Friedlander, 3, 8. (46) Wohl, Ger. 151,864, June 9, 1904; Cent. 1904, II 69. (47) Mugdan (to Consortium für Elektrochem. Ind.), U.S. 944,372, Dec. 28, 1909; C.A. 4, 643 (1910). (48) I.G., Brit. 289,959, May 31, 1928; Cent. 1928, II 711. (49) Hochstetter, Ger. 284,617, May 31, 1915; Cent. 1915, II 215. (50) Chem. Fabrik von Heyden, Ger. 123,052, July 29, 1901; Cent. 1901, II 518.

(51) M.L.B., Ger. 210,805, June 16, 1909; Cent. 1909, II 79. (52) Gal, Ann. chim. (3) 68. 188-190, 196-199 (1862). (53) Nametkin, Bryusova, Fedoseeva, J. Applied Chem. (U.S.S.R.) 12. 1698-1701 (1939); C.A. 34, 7283 (1940). (54) Schlubach, Elsner, Angew. Chem. 47, 130-131 (1934). (55) Masters (to Elko Chem. Co.), U.S. 1,819,613, Aug. 18, 1931; Cent. 1931, II 2932; C.A. 25, 5678 (1931). (56) Stellmann, French 785,075, Aug. 1, 1935, Cent. 1935, II 3301; C.A. 30. 490 (1936). (57) Adams, Uhlich, J. Am. Chem. Soc. 42, 606 (1920). (58) Rabcewicz-Zubkowski, Roczniki Chem. 9, 523-531 (1929); Cent. 1929, II 2767; C.A. 24, 61 (1930). (59) Givaudan et Cie, Swiss 169,040, July 16, 1934; Cent. 1934, II 3555. (60) Weber, Hennion, Vogt. J. Am. Chem. Soc. 61, 1456-1457 (1939).

(61) Steinhauser (to I.G.), Ger. 561,399, Oct. 13, 1932; Cent. 1932, II 3961; I.G., Brit. 308,666, March 25, 1929; Cent. 1929, II 1467; French 671,938, Dec. 20, 1929, Cent. 1930, I 2163. (62) Wiezevich, Frolich (to Standard Oil Development Co.), U.S. 2,062,344, Dec. 1, 1936; Cent. 1937, I 4863; C.A. 31, 708 (1937). (63) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994; C.A. 26, 2747 (1932). (64) Britton, Reed (to Dow Chem. Co.), U.S. 1,870,601, Aug. 9, 1932; Cent. 1932, II 3305, C.A. 26, 5578 (1932). (65) Chick, Wilsmore, Proc. Chem. Soc. 24. 77-78 (1908); Cent. 1908, II 1018. (66) Eschenbach, Ger. 638,441, Nov. 16, 1936; Cent. 1937, I 2024; C.A. 31, 1042 (1937). (67) Vol'nov, J. Gen Chem. (U.S.S.R.) 9, 2269-2282 (1939); C.A. 34, 5048 (1940). (68) Soc. des Usines Chimiques Rhône-Poulenc, Brit. 329,721, June 19, 1930; Cent. 1930, II 1611. (69) Soc. des Usines Chimiques Rhône-Poulenc, Brit. 330,511, July 10, 1930; Cent. 1930, II 2184. (70) Smith, J. Chem. Soc. 1927, 1100.

(71) Aschan, Ber. 46, 2162-2168 (1913). (72) Chapman, J. Chem. Soc. 127, 2818-2819 (1925). (73) Richter, Ber. 49, 1026 (1916). (74) Shilov, J. Chem. Ind. U.S.S.R. 7, 110-115 (1930). Cent. 1930, II 463-464; C.A. 25, 4524 (1931). (75) Joist, Lob, Z. Elekatrochem. 11, 941 (1905). (76) Mailhe, Compt. rend. 180, 1111-1113 (1925); Cent. 1925, I 2554. (77) Barredo, Anales soc. españ. fis quím. **37**, 274-277, 278-281, 282-290 (1941); C.A. **37**, 24-25 (1943); Cent. **1943**, I 938-939 (1943). (78) Kaufmann, Funke, Fette u. Scifen 44, 386-390 (1937); Cent. 1938, I 1259; C.A. 32, 815 (1938). (79) Govaert, Natuurw. Tijdschr. 15, 149-153 (1933); C.A. 28, 740 (1934). (80) Benrath, Hertel, Z. wiss. Phot. 23, 30-40 (1924); Cent. 1924, II 822; C.A. 19, 440 (1925).

(81) Hertel, Becker, Clever, Z. physik. Chem. B-27, 303-315 (1934). (82) Watson, Roberts, J. Chem. Soc. 1928, 2781-2786. (83) Shaw, J. Chem. Soc. 123, 2234 (1923). (84) Kharasch. Hobbs, J. Org. Chem. 6, 705-712 (1941). (85) Watson, J. Chem. Soc. 1928, 1137-1141. (86) Aschan, Ber. 45, 1913-1919 (1912). (87) Staudinger, Anthes, Ber. 46, 1421-1422 (1913). Aschan, Ber. 46, 2162-2168 (1913). (89) Gustus, Stevens, J. Am. Chem. Soc. 55, 374-377 (1933).

(90) Gustus, Stevens, J. Am. Chem. Soc. 55, 378-386 (1933).

(91) Stevens, J. Am. Chem. Soc. 56, 450-452 (1934). (92) von Peski, Rec. trav. chim. 40, 106 (1921). (93) Elliott, Kleist, Wilkins, Webb, J. Chem. Soc. 1928, 1221, 1229. (94) Krajcinovic. Ber. 59, 2117-2119 (1926). (95) Krajcinovic, Arhiv Hem. Farm. 5, 2-13 (1931); C.A. 25, 3955 (1931). (96) Collie, Hilditch, J. Chem. Soc. 91, 787-789 (1907). (97) Skraup, Preglinger, Monatsh. 31, 367 (1910). (98) D'Ans, Friederich, Z. anorg. allgem. Chem. 73, 355-357 (1911). (99) Borgeson, Wilkinson, J. Am. Chem. Soc. 51, 1455 (1929). (100) Clarke, Hartmann, J. Am. Chem. Soc. 46, 1731-1733 (1924).

(101) Black, Bergmann, Ber. 53, 966-968 (1920). (102) Chretien, Oechsel, Compt. rend. 206. 254-256 (1938). (103) deFazi, Hemmler, Atti accad. Lincei (6) 12, 583-586 (1930); Cent. 1931, I 2858; C.A. 25, 4769 (1931). (104) Jacquemin, Vosselmann, Compt. rend. 49, 372 (1859). (105) Diels, Odada, Ber. 44, 3334-3335 (1911). (106) Lachowicz, Ber. 17, 1283 (1884). (107) Schroeter, Ber. 42, 3357-3358 (1909). (108) Biltz, Heidrich, Ann. 457, 203 (1927). (109) Biltz, Jeltsch, Ber. 56, 1918 (1923). (110) Naegeli, Gruntuch, Lendorff, Helv. Chim. Acta 12,

255 (1929).

(111) Calloway, J. Am. Chem. Soc. 59, 1474-1479 (1937). (112) Meslans, Ann. chim. (7) 1, 405-423 (1894). (113) Blicke, J. Am. Chem. Soc. 46, 1516-1517 (1924). (114) Henne, Midgely, J. Am. Chem. Soc. 58, 884-886 (1936). (115) Wright, J. Am. Chem. Soc. 58, 2653-2654 (1936). (116) Voznesenskii, J. Gen. Chem. (U.S.S.R.) 9, 2148-2152 (1939); C.A. 34, 4053 (1940). (117) Böeseken, Rec. trav. chim. 20, 103-104 (1901). (118) Kozlov, Bogdanovskaya, Silogul, J. Gen. Chem. (U.S.S.R.) 6, 315-317 (1936); Cent. 1936, II 1896; C.A. 30, 4813 (1936). (119) Meerwein, Maier-Hüser, J. prakt. Chem. (2) 134, 67-68, 75-77 (1932). (120) Wedekind, Ann. 323, 253-254 (1902).

- (121) Spindler, Ann. 231, 272 (1885). (122) Levaillant, Compt. rend. 200, 1054 (1935). (123) Levaillant, Compt. rend. 190, 56 (1930). (124) Combes, Ann. chim. (6) 12, 204-213 (1887); Compt. rend. 103, 814 (1886). (125) Gustavson, J. prakt. Chem. (2) 37, 108-110 (1888). (126) Tommasi, Quesneville, Bull. soc. chim. (2) 19, 204-205 (1873). (127) Pospekhov, Sbornik Rabot Kiev. Tekh. Inst. Kozhevenno-Obuvnoi Prom. 3, 268-270 (1940); C.A. 37, 4359-4360 (1943). (128) Varvoglis, Ber. 70, 2395-2396 (1937).
 (129) Varvoglis, Praktika Akad. Athenon 13, 42-44 (1938); Cent. 1938, II 1394-1395; C.A. 34, 5050 (1940).
 (130) Wohl, Mylo, Ber. 45, 328-329 (1912).
- (131) Neunhoeffer, Nerdel, J. prakt. Chem. (2) 144, 63-66 (1936). (132) Hopff, Nenitzescu, Isacescu, Cantuniari, Ber. 69, 2248-2249 (1936). (133) Hopff, Ber. 64, 2742-2743 (1931). (134) Nenitzescu, Chicos, Ber. 68, 1585-1587 (1935). (135) Nenitzescu, Cantuniari, Ber. 65, 1449-1453 (1932). (136) Kenner, Statham, Ber. 69, 17 (1936). (137) McGinnis, Robinson, J. Chem. Soc. 1941, 406. (138) Schoeller, Zollner (to Schering-Kahlbaum, A.G.), U.S 1,737,203, Nov 26, 1929; Cent. 1930, II 1133; Brit. 282,412, Feb. 15, 1928; Cent. 1929, I 143. (139) Frolich, Wiezevich (to Standard Oil Development Co.), U.S. 2,006,198, June 25, 1935; Cent. 1936, I 2827; C.A. 29, 5457 (1935). (140) Nemtzescu, Gavat, Ann. 519, 260-271 (1935).
- (141) Colonge, Mostafavi, Bull. soc. chim. (5) 6, 335-342; 342-354 (1939). (142) Cornillot, Alquier, Compt. rend. 201, 837-838 (1935). (143) Nelles, Bayer (to I.G.), Brit. 461,080, March 11, 1937; Cent. 1937, II 2597; C.A. 31, 4676 (1937); Ger. 461,080, Feb. 25, 1937; Cent. 1937, II 2597; C.A. 31, 3501 (1937). (144) Kroeger, Sowa, Nieuwland, J. Org. Chem. 1, 163-169 (1937). (145) Nenitzescu, Cantuniari, Ber. 65, 810-812 (1932). (146) Nenitzescu, Ionescu, Ann. 491, 202-208 (1931). (147) Nenitzescu, Vantu, Bull. soc. chim. (5) 2, 2209-2216 (1935). (148) Unger, Ber. 65, 467-472 (1932). (149) Nenitzescu, Cioranescu, Cantuniari, Ber. 76, 277-283 (1937). (150) Nenitzescu, Cioranescu, Ber. 69, 1820-1823 (1936).
 (151) Hurd, Christ, J. Am. Chem. Soc. 59, 120 (1937). (152) Darzens, Compt. rend. 150,
- 707-708 (1910). (153) Wieland, Bettag, Ber. 55, 2249-2252 (1922). (154) Friedel, Crafts, Ann. chim. (6) 1, 507 (1884). (155) Calloway, Green, J. Am. Chem. Soc. 59, 809-811 (1937). (156) Nencki, Stoeber, Ber. 30, 1769 (1897). (157) Wertyporoch, Ber. 66, 1237 (1933). (158). Kashtanov, J. Gen. Chem. (U.S.S.R.) 2, 515-523 (1932); Cent. 1933, I 600; C.A. 27, 975 (1933). (159) Krishnamurti, Cent. 1929, I 2156 (not in C.A.). (160) Kashtanov, J. Gen. Chem. (U.S.S.R.) 3, 229-233 (1933); Cent. 1933, II 2512; C.A. 28, 1687 (1934).
- (161) Bredereck, Lehmann, Schonfeld, Fritzsche, Ber 72, 1416, 1424 (1939). (162) Ray, Dutt, J. Indian Chem. Soc. 5, 108 (1928). (163) Chakrabarty, Dutt, J. Indian Chem. Soc. 5, 517 (1928). (164) Chopin, Bull. soc. chim. (4) 35, 610-614 (1924). (165) Sorge, Ber. 35, 1069-1070 (1902) (for other older work see Beil. VII-308). (166) Gastald, Cherchi, Gazz. chim. ital. 45, II 274, Note (1915). (167) O. C. Dermer, Wilson, Johnson, V. H. Dermer, J. Am. Chem. Soc. 63, 2881-2883 (1941). (168) O. C. Dermer, R. A. Billmeier, J. Am. Chem. Soc. 64, 464-465 (1942). (169) Weygand, Mensdorff, Ber. 68, 1831-1832 (1935). (170) Zaki, Fahim, J. Chem. Soc. 1942, 307-308.
- (171) Allen, Org. Syntheses, Coll. Vol. 2 (1st ed.), 3-5 (1943); 14, 1-3 (1934). (172) Lock, Monatsh. 74, 77-84 (1942); Cent. 1942, II 1901. (173) Dziewonski, Marusinska, Bull. intern. acad. polon. sci., Classe sci. math. nat. A-1938, 316-323; Cent. 1939, I 1171, C.A. 33, 1712 (1939). (174) Haworth, Mavin, J. Chem. Soc. 1932, 2720-2723. (175) Kon, Weller, J. Chem. Soc. 1939, 792-794. (176) Long, Henze, J. Am. Chem. Soc. 63, 1939-1940 (1941). (177) Grieve, Hey, J. Chem. Soc. 1933, 970. (178) Silver, Lowy, J. Am. Chem. Soc. 56, 2429-2430 (1934). (179) Fieser, Hershberg, J. Am. Chem. Soc. 61, 1278-1279 (1939). (180) Fieser, Cason, J. Am. Chem. Soc. 61, 1742 (1939).
- (181) Johnson, May, Org. Syntheses, Coll. Vol. 2 (1st ed.), 8-9 (1943); 18, 1-2 (1938). (182) Kommppa, J. prakt. Chem. (2) 122, 329-330 (1929). (183) Leimu, Ber. 70, 1042 (1937). (184) Palomaa, Leimu, Ber. 66, 813-815 (1933). (185) Smith, Bryant, J. Am. Chem. Soc. 57, 841-845 (1935). (186) Smith, Bryant, J. Am. Chem. Soc. 57, 61-65 (1935). (187) Christensen, Pennington, Dimick, Ind. Eng. Chem., Anal. Ed. 13, 821-823 (1941). (188) Kaufmann, Funke, Ber. 70, 2549-2554 (1937). (189) Spassow, Ber. 70, 1928-1930 (1937). (190) Spassow, Org. Syntheses **20.** 21-22 (1940).
- (191) Hauser, Hudson, Abramovitch, Shivers, Org. Syntheses 24, 19-21 (1944). (192) Bryant, Smith, J. Am. Chem. Soc. 58, 1016 (1936). (193) Hess, Ber. 54, 2869, 2872, 2881 (1921). (194) Zechmeister, Ber. 56, 577 (1923). (195) Weltzien, Singer, Ann. 443, 71-112 (1925). (196) Staudinger, Luthy, Helv. Chim. Acta 8, 53-56 (1925). (197) Baker, Reid, J. Am. Chem. Soc. 51 1568 (1929). (198) Hoeflake, Rec. trav. chim. 36, 30-32 (1916). (199) Adickes, Brunnert, Lücker, J. prakt. Chem. (2) 130, 172-173 (1931). (200) Spassow, Ber. 75, 779-780 (1942). (201) Irvine, Robinson, J. Chem. Soc. 1927, 2091. (202) Rosenmund, Schnurr, Ann. 460, 88
- (1928). (203) Blatt, Chem. Revs. 27, 413-436 (1940). (204) Straus, Ann. 374, 139, Note (1910).

(205) Pratt, Robinson, Williams, J. Chem. Soc. 125, 202 (1924). (206) Nef, Ann. 266,102-105 (1891). (207) von Auwers, Ann. 415, 228-229 (1918). (208) Claisen, Zedel, Ann. 277, 172 893). (209) Meyer, Ber. 45, 2854–2855 (1912). (210) von Auwers, Ann. 415, 185–186 (1918). (211) Seidel, Thier, Uber, Dittmer, Ber. 69, 650–653 (1936). (212) Wislicenus, Körber, Ber.

34, 218, 3768 (1901). (213) Wislicenus, Ber. 38, 546-548 (1905). (214) Bouveault, Bongert, Bull. soc. chim. (3) 27, 1163-1164 (1902). (215) Dieckmann, Stein, Ber. 37, 3373 (1904). (216) Machemer (to A. Wacker Ges. für Elektrochem. Ind.), Ger. 713,810, Nov. 15, 1941; Cent. 1942, I 2065; not in C.A. (217) Claisen, Haase, Ber. 33, 1242-1246 (1900). (218) Nef, Ann. 266, 206-207 (1893). (219) Mingasson, Bull. soc. chim. (4) 45, 716-718 (1929). (220) Michael, Carlson, J. Am. Chem. Soc. 58, 353 (1936).

(221) James, Ann. 226, 210-213 (1884). (222) Elion, Rec. trav. chim. 3, 248-252 (1884). (221) James, Am. 220, 210-213 (1884). (222) Finol, Rec. trav. crim. 3, 240-252 (1884). (223) Michael, Ber. 38, 2088-2090 (1905). (224) Packendorff, Ber. 64, 948-949 (1931). (225) Spassow, Org. Syntheses 21, 46-47 (1941). (226) Spassow, Ber. 70, 2383-2384 (1937). (227) Seidel, Ber. 65, 1209 (1932). (228) Rice, Sullivan, J. Am. Chem. Soc. 50, 3054 (1928). (229) McElvain, Kundiger, J. Am. Chem. Soc. 64, 255, 258 (1942). (230) Fischer, Taurinisch.

Ber. 64, 236-239 (1931).

(231) Autenrieth, Thomae, Ber. 57, 423-437 (1924). (232) Kanonnikow, Saytzeff, Ann. 187, 192 (1877). (233) M.L.B., Ger. 396,696, June 10, 1924; Cent. 1924, II 1401: Henle (to M.L.B.), Ger. 411,519, March 30, 1925; Cent. 1925, II 92. (234) I.G., Swiss 153,481, June 1, 1932; Cent. 1932, II 3014. (235) Usanovich, Yatsimirskii, J. Gen. Chem. (U.S.S.R.) 11, 957-958 (1941); C.A. 36, 6444 (1942). (236) Dains, J. Am. Chem. Soc. 28, 1183-1188 (1906). (237) Prev. Ber. 75, 543 (1942). (238) Dennstedt, Zimmermann, Ber. 19, 75-78 (1886). (239) Wedekind, Ann. 318, 100-101 (1901); Ann. 323, 247-249 (1902). (240) Sauer (to du Pont Co.), U.S. 2,238,826, April 15, 1941; Cent. 1942, II 1403; C.A. 35, 4970 (1941).

(241) Hurd, Abernathy, J. Am. Chem. Soc. 62, 1148 (1940). (242) Arndt, Amende, Ber. 61, 1124 (1928). (243) Blatt, Chem. Revs. 12, 215-260 (1933). (244) Friedmann, Backeberg, J. Chem. Soc. 1938, 469-470. (245) Niyogy, Proc. Indian Acad. Sci. A-4, 305 (1936). (246) von Schickh (to I G.), Ger. 715,930, Jan. 9, 1942; Cent. 1942, I 1561; not in C.A. (247) Fromm, Ann. 447, 304 (1926). (248) Freund, Meinecke, Ber. 29, 2516 (1896). (249) Tanasescu, Silberg,

Ann. 447, 304 (1926). (248) Freund, Meinecke, Ber. 29, 2516 (1896). (249) Tanasescu, Silberg, Bull. soc. chim. (5) 3, 224-239 (1936). (250) Gilman, Nelson, Rec. trav. chim. 55, 528-530 (1936). (251) Gilman, Fothergill, Parker, Rec. trav. chim. 48, 748-751 (1929). (252) Austin, Johnson, J. Am. Chem. Soc. 54, 656-659 (1932). (253) Whitmore, Badertscher, J. Am. Chem. Soc. 56, 825-826 (1932). (254) Whitmore, Badertscher, J. Am. Chem. Soc. 55, 1564 (1933). (255) Whitmore, Rec. trav. chim. 57, 566-567 (1938). (256) Whitmore, Wheeler, J. Am. Chem. Soc. 60, 2899-2900 (1938). (257) Smith, Webster, Guss, J. Am. Chem. Soc. 59, 1078-1082 (1937). (258) Kohler, Baltzley, J. Am. Chem. Soc. 54, 4015-4026 (1932). (259) Bergmann, J. Chem. Soc. 1936, 412-413. (260) Gilman, Straley, Rec. trav. chim. 55, 823, 825 (1936).

 Soc. 1936, 412-413. (2007) Gilman, Stratey, Rec. true. Crim. 50, 525, 525 (1950).
 (261) Gilman, Schulze, J. Am. Chem. Soc. 49, 2328-2330 (1927). (262) Gilman, Nelson, J. Am. Chem. Soc. 51, 742 (1939). (263) Mel'nikov, Rokitskaya, J. Gen. Chem. (U.S.S.R.) 7, 464-466 (1937), Cent. 1937, II 1557; C.A. 31, 4266 (1937). (264) Bost, Borgstrom, J. Am. Chem. Soc. 51, 1923 (1929). (265) Kiemstadt, Z. angew. Chem. 42, 1107-1108 (1929). (266) Challenger, Company of the company of t Ridgway, J. Chem. Soc. 121, 112-113 (1922). (267) Reihlen, Gruhl, von Hessling, Ann. 472, 277, 285-286 (1929). (268) Vles, Rec. trav. chim. 53, 961-962 (1934). (269) Strain, J. Am. Chem. Soc. 57, 758 (1935).

1-CHLOROBUTEN-3-YNE-1 C4H3Cl Beil. S.N. 13 (1-Chloro-2-vinylacetylene) CH₂=CH-C=C-Cl

B.P. 55-57° at 760 mm. (1) (2) (3) (4)

 $D_4^{20} = 1.0032$ (1) (2) $n_D^{20} = 1.4663$ (1) (2) 1.0034 (4) $D_7^7 = 1.021$ (4) $n_D^7 = 1.4698$ (4)

Colorless oil, not explosive when pure (3) (4). — C rapidly polymerizes on stdg. into black brittle solid sensitive to heat and shock (1); polymerization of C catalyzed by u.v. light, peroxide, ozonides, etc. (2). After addn. of hydroquinone (3) C can be distd. at ord. press.

[For prepn. of C from vinylacetylene by actn. of alkaline alk. hypochlorite solns. at 0° (vield 60-65% (4), 10% (1)) see (1) (2) (3) (4).]

 \bar{C} treated as directed at -10° with conc. $HCl + CuCl + NH_4Cl$ gives (56% yield (4)) 1,2-dichlorobutadiene-1,3 (3:9057) q.v.

C with NH₄OH/AgNO₃ gives a white ppt.; with Ilosway reagt. a yel. ppt. (4).

3:7070 (1) Jacobson, Carothers, J. Am. Chem. Soc. **55**, 4667–4669 (1933). (2) Jacobson (to du Pont), U.S. 1,967,864, July 24, 1934; Cent. **1936**, I 1709; C.A. **28**, 5834 (1934). (3) Klebanskii, Tzyurikh, Dolgopol'skii, Bull. acad. sci. U.R.S.S. **1935**, No. 2, 189–226; Rubber Chem. Tech. **9**, 383–408 (1936); Cent. **1935**, II 3844, C.A. **30**, 1259 (1936). (4) Klebanskii, Volkenshtein, Orlova, J. Gen. Chem. (U.S.S. R.) **5**, 1255–1267 (1935); Cent. **1936**, I 3414; C.A. **30**, 1025 (1936); J. prakt. Chem. (2) **145**, I-17 (1936).

B.P.
$$D_4^{21} = 0.8950$$
 (2) $D_D^{21} = 1.4115$ (2) $D_D^{21} = 0.8950$ (2) $D_D^{21} = 1.4115$ (2) $D_D^{21} = 0.9107$ (1) $D_D^{21} = 1.4166$ (1)

 $\bar{\rm C}$ forms with abs. EtOH an azeotrope, b.p. 53.6–54.0° at 760 mm., $D_4^{15}=0.8945,$ contg. 88.5% by wt. of $\bar{\rm C}$ (1).

[For form. from d,l-1,2-dichlorobutane (3:7680) + alc. KOH (together with *cis*-(3:7110) and *trans* (3:7110) stereoisomers of 1-chloro-butene-1) see (1).]

3:7075 (1) Navez, Bull. soc. chim. Belg. 39, 435-443 (1930). (2) Kroeger, Sowa, Nieuwland, J. Org. Chem. 1, 167 (1936).

3:7080 2-CHLOROBUTADIENE-1,3 Cl C₄H₅Cl Beil. S.N. 12 (Chloroprene)
$$H_2C=CH-C=CH_2$$

B.P. $D_4^{20} = 0.9585$ (2) $D_D^{20} = 1.4583$ (1) $D_D^{20} = 1.4583$ (1) $D_D^{20} = 1.4583$ (1) $D_D^{20} = 1.4583$ (1) $D_D^{20} = 0.9583$ (1) $D_D^{20} = 0.9583$ (1) $D_D^{20} = 0.9583$ (1) $D_D^{20} = 0.9575$ (31) $D_D^{20} = 0.9575$ (31)

Colorless liq. with ethereal odor suggesting C_2H_5Br . Only slightly sol. aq. but miscible with most org. solvs.

 \bar{C} was first reported in 1931 (1) and given the name chloroprene (1) because of its analogy to 2-methylbutadiene-1,3 (isoprene) in structure and reactions. Despite its immense practical importance in the manufacture of various types of synthetic rubbers and plastics comparatively little information on \bar{C} itself has been released for publication in the scientific literature.

[For a study of the toxicity and pathology of \bar{C} see (3); for study of poisoning by \bar{C} and its treatment see (4).]

[For studies of detn. of C (5) by diazometric methods (6) (7) see indic. refs.]

PREPARATION OF C

Č has been prepared from vinylacetylene by addn. of HCl, from dichlorobutenes by elimination of 1 HCl, and from various other sources. Comparatively little on these methods has appeared in the scientific literature, and most of the information is available only through patents. Such of the latter as are here cited must be regarded only as illustrative as no guarantee of complete patent coverage can be offered.

From vinylacetylene. $ildе{C}$ is formed from vinylacetylene (8) by addn. of HCl from aqueous soln. in pres. of catalysts (usually copper salts). The initial step comprises 1,4 addition, and the primary product is 4-chlorobutadiene-1,2 (isochloroprene) (3:7225). Under certain conditions this may be isolated as the major reaction product, but it readily isomerizes (especially in the presence of cuprous chloride and/or other salts (9)) yielding chloroprene. When sufficient amounts of HCl are present further addition to \hat{C} may also occur leading to 2,4-dichlorobutene-2 (3:5550) (see also below).

[For prepn. of C from vinylacetylene (8) with conc. aq. HCl in pres. of $Cu_2Cl_2 + NH_4Cl$ at 30° for 4 hrs. (65% yield) see (1) (47); for studies of this process in foreign laboratories see (10) (11) (12) (2) (24). For examples of patents on this process see (13)-(23) incl. For analogous prepn. of certain homologs of \bar{C} such as 2-chloro-3-methylbutadiene-1,3 (3:7290) and 2-chloro-3,4-dimethylbutadiene-1,3, etc., see (25) cf. (26).]

From dichlorobutenes. [For prepn. of C from 3,4-dichlorobutene-1 (1,2-dichlorobutene-3) (3:5350) with powdered KOH or alc. NaOH see (27) (28); for 2,3-dichlorobutene-1 (3:9074) by thermal dehydrochlorination at 530° without cat. see (29); from 2,4-dichlorobutene-2 (3:5550) by dehydrochlorination (and isomerization) in pres. of fused KOH at 180-190° (30) or over silica gel or clay at 245-275° (31) cf. (30) see indic. refs.; from 1,2-dichlorobutenes by dehydrochlorination with inorg. or org. bases in pres. of org. solvs. see (32).]

From other sources. [For prepn. of $\bar{\rm C}$ from 2,2,3-trichlorobutane (3:5680) by thermal dehydrochlorination over MgCl₂/MgSO₄ cat. see (33); from polychlorobutanes of 55-66% chlorine content (corresp. to dichloro-and trichlorobutanes) by thermal dehydrochlorination at 400-500° see (34) (note that 1-chlorobutadiene-1,3 (3:7210) is also formed; for separation of it from $\bar{\rm C}$ see (35)): for formn of $\bar{\rm C}$ from vinyl chloride (3:7010) with acetylene in pres. of aq. Cu₂Cl₂/NH₄Cl see (36).]

CHEMICAL BEHAVIOR OF C

Addition Reactions

With chlorine. [\bar{C} (2 moles) with Cl₂ (1 mole) in CHCl₃ at -10° in pres. of hydroquinone gives mainly (37) cf. (38) (39) 1,2,4-trichlorobutene-2 (1,3,4-trichlorobutene-2) (3:9062) accompanied by other products such as 1,2,3-trichlorobutene-1 (37), b.p. 40-42° at 10 mm., $D_4^{15} = 1.3190$, $n_D^{15} = 1.4902$ (giving on oxidn. α,β -dichloropropionic acid); note: data also consistent with 2,3,4-trichlorobutene-1 (3:9064) and 1,2-dichlorobutadiene-1,3 (3:9057), b.p. 45-48° at 10 mm. (37), $D_4^{15} = 1.1905$ $n_D^{15} = 1.5065$ (37).]

With bromine. [C (0.3 mole) with Br₂ (0.25 mole) in CHCl₃ at 0-5° gives mainly (40) 2-chloro-1,4-dibromobutene-2, b.p. 98-101° at 10 mm. (oxidizing with KMnO₄ to bromoacetic acid), accompanied by other products; note that in pres. of anti-oxidants distn. range of prod. is much wider perhaps owing to formn. of geom. stereoisomers.]

With iodine chloride. [\tilde{C} with ICl in CHCl₃ at -5° to 0° gives (70% yield (41)) a prod. regarded as 2.4-dichloro-1-iodobutene-2.]

With hydrogen chloride. [\bar{C} with conc. aq. HCl in pres. of Cu₂Cl₂ (42) adds HCl giving 2,4-dichlorobutene-2 (3:5550); for behavior of \bar{C} in liq. HCl see (43).]

With hydrogen bromide. [C (0.96 mole) with dry HBr (0.88 mole) in AcOH at -5° gives (72% yield on Br₂ (44)) 2-chloro-4-bromobutene-2, b.p. 150-152°; $D_4^{20} = 1.5264$, $D_4^{15} = 1.5335$; $n_2^{20} = 1.5160$, $n_2^{15} = 1.5185$; note that this prod. with aq. KMnO₄ oxidizes to AcOH + bromoacetic acid and adds 1 mole Br₂ giving 2-chloro-2,3,4-tribromobutane, b.p. 104.5-106° at 10 mm., $D_4^{15} = 2.1907$.]

With hydrochlorous acid. [The behavior of \bar{C} with HOCl appears not to have been reported; 1,4 addition to \bar{C} might be expected to yield 1,2-dichlorobuten-2-ol-4 and/or 2,4-dichlorobuten-2-ol-1, but neither is reported from any source; an isomer, viz., 2,3-

dichlorobuten-1-ol-4, b.p. 72-73° at 10 mm., $D_4^{20} = 1.3198$, $D_4^{15} = 1.3243$, $n_D^{20} = 1.4956$, $n_D^{15} = 1.4978$, has been reported (45) by indirect means.]

With hypotromous acid. [Č with HOBr (from N-bromoacetamide) gives mainly (45) (note 3,4 addition) 2-chloro-4-bromobuten-1-ol-3, b.p. 77.0-77.25° at 10 mm.; $D_4^{20} = 1.6710$, $D_4^{15} = 1.6770$; $n_D^{20} = 1.5228$, $n_D^{15} = 1.5249$; this prod. in CHCl₃ adds 1 mole Br₂ giving 3-chloro-1,3,4-tribromobutanol-2, m.p. 69.5-71°.]

With alkyl hypoiodite. [\bar{C} with MeOI (from MeOH + HgO + I₂) gives (62% yield (46)) 2-chloro-4-iodo-3-methoxybuten-1, b.p. 76.5-77.0° at 10 mm., $D_4^{20} = 1.7135$, $D_4^{15} = 1.7209$; $n_2^{20} = 1.5312$, $n_2^{15} = 1.5338$. — \bar{C} with EtOI (from EtOH + HgO + I₂) gives (46% yield (46)) 2-chloro-4-iodo-3-ethoxybuten-1, b.p. 82-83° at 10 mm.; $D_4^{20} = 1.6163$, $D_4^{15} = 1.6231$; $n_2^{20} = 1.5198$, $n_2^{15} = 1.5220$. — Note for both these cases the same type of 3.4 addn. observed for HOBr above.]

With sulfur dioxide. [\bar{C} in ether contg. pyrogallol treated with SO₂ at 100–105° in s.t. for 12 hrs. gives in very small amt. (2.5% (47)) an addition prod. 3-chloro-1-thiacyclopenten-3 dioxide (chloroprene sulfone).]

With naphthoquinone-1,4. \tilde{C} (2 moles) with α -naphthoquinone (1:9040) (1 mole) in C_6H_6 refluxed 3 hrs. and the intermediate addition prod. suspended in alc. NaOH and oxidized with air gives (1) 2-chloroanthraquinone (3:4922).

With maleic anhydride. \bar{C} (1+ moles) with maleic anhydride (1:0625) (1 mole) warmed at 50° then boiled with aq. gives (77% yield (1)) 4-chloro-1,2,3,6-tetrahydrophthalic acid, cryst. from aq., m.p. 173-175° cor. (1).

POLYMERIZATION OF C

Č readily polymerizes at 30-35° in light from a 150-watt lamp in 48-80 hours (26); for study of various types of polymers from Č alone see (1). Furthermore, Č with various other unsaturated compounds undergoes copolymerization processes. The practical importance of the polymers and copolymers thus obtained can scarcely be overestimated, but the field is so large, so interlocked, and so rapidly developing that any attempt to organize it is quite beyond the scope of this book. Attention is here directed, however, to a few scientific papers of interest in this connection.

[For studies on structure of polychloroprene see (48) (49); for study of polymers of \bar{C} by ozonization and HNO₃ oxidn. see (50); for detn. of unsaturation in polymers of \bar{C} see (51); for permeability of polychloroprene to gas see (52).]

[For study of influence of tetralin peroxide (53) in nitrobenzene (54) or of high-frequency field (55) (56) on polymerization of \bar{C} see indic. refs.; for photopolymerization of \bar{C} see (57); for study of kinetics of polymerization of \bar{C} in di-n-butyl phthalate soln. in pres. of dibenzoyl peroxide see (58); for detection of free radicals in peroxide polymerization of \bar{C} see (59).

3:7680 (1) Carothers, Williams, Collins, Kirby, J. Am. Chem. Soc. 53, 4203-4225 (1931). (2) Zelinskii, Kozlov, Shter, Bull, acad. sci. U.R.S.S., Classe sci. math. nat. 1934, 141-151; Cent. 1935, I 1946; [C.A. 28, 5713 (1934)]. (3) von Oettingen, Hueper, Diechmann-Gruebler, Wiley, J. Ind. Hyg. Toxicol. 18, 240-270 (1936). (4) McNally, Ind. Med. 6, 270-283 (1937); C.A. 31, 8063 (1937). (5) Peregud, Caoutchouc and Rubber (U.S.S.R.) 1937, No. 7-8, 63/70; Cent. 1938, I 1477; C.A. 32, 3197 (1938). (6) Terent'ev, Org. Chem. Ind. (U.S.S.R.) 4, 535-542 (1937); [C.A. 32, 6580 (1938)]. (7) Senderikhina, Trudy Moskov. Sanit. Inst. im. Erismana 1939, 86-101; [C.A. 36, 2233 (1942)]. (8) Nieuwland, Calcott, Downing, Carter, J. Am. Chem. Soc. 53, 4197-4202 (1931). (9) Carothers (to du Pont Co.), U.S. 2, 104, 789, Jan. 11, 1938; Cent. 1938, I 4108; C.A. 32, 1718 (1938). (10) Klebanskii, Dolgopol'skii, Chevychalov, Caoutchouc and Rubber (U.S.S.R.) 10, No. 1, 31-34; No. 2, 19-27 (1937); Cent. 1937, II 872; C.A. 32, 4006 (1938).

Hurukawa, Nakamura, J. Soc. Rubber Ind. Japan 12, 103-106, 106-109 (1939); C.A. 33, 9717 (1939).
 Furukawa, Nakamura, J. Soc. Chem. Ind. Japan 41, 198-200 (1938); C.A. 32, 9557 (1938).
 Collins (to du Pont Co.), U.S. 1,950,435, March 13, 1934; Cent. 1936, I 1708; C.A. 28, 3270-3271 (1934).
 Perkins (to Carbide and Carbon Chem. Corp.), U.S.

2,027,550, Jan. 14, 1936; Cent. 1936, II 1796; C.A. 30, 1395 (1936). {15} Carothers, Collins (to du Pont Co.), U.S. 1,950,431, March 13, 1934; not in Cent.; C.A. 28, 3271 (1934): French 721,532, March 4, 1932; Cent. 1932, II 2107; C.A. 26, 4061 (1932): Brit. 387,325, Jan. 24, 1933; not in Cent.; C.A. 27, 4718 (1933): Ger. 588,708, Nov. 24, 1933; not in Cent.; C.A. 28, 2015 (1934): Australian 3619/31: Czechoslovakian 51,643: Dutch 31,084: Italian 301,326: Japanese 96,820: Norwegian 52,261; Spanish 123,629: Swedish 79,586: Swiss 164,539. (16) Carothers, Collins (to du Pont Co.), U.S. 2,178,737, Nov. 7, 1939; C.A. 34, 1334 (1940). {17} Carter (to du Pont Co.), U.S. 2,207,784, July 16, 1940; C.A. 34, 7936 (1940). {18} Carter, Downing (to du Pont Co.), U.S. 2,221,941, Nov. 19, 1940; C.A. 35, 1412 (1941). {19} I.G., Brit. 458,100, Dec. 14, 1936; not in Cent.; C.A. 31, 3070 (1937): French 805,238, Nov. 14, 1936; Cent. 1937, I 2022; [C.A. 31, 1284 (1937): French 805,621, Nov. 25, 1936, Cent. 1937, I 2456; C.A. 31, 4344 (1937):

(21) du Pont, Brit. 395,131, Aug. 3, 1933; Cent. 1933, II 2455; C.A. 28, 375 (1934). (22) du Pont, French 721,532, March 4, 1932; Cent. 1932, II 2107; C.A. 26, 4061 (1932). (23) Klebanskii, Trenke, Russian 46,916, May 31, 1936; Cent. 1936, II 3852; C.A. 33, 4079 (1939). (24) Klebanskii, Tzyurikh, Dolgopol'skii, Bull. acad. sci. U.R.S.S. 1935, No. 2, 189-226; J. Research Assoc. Brit. Rubber Mfrs. 4, 505-506 (1935); C.A. 30, 1259 (1936); Rubber Chem. and Tech. 9, 383-408 (1936). (25) Carothers, Coffman, J. Am. Chem. Soc. 54, 4071-4076 (1932). (26) Jacobson, Carothers, J. Am. Chem. Soc. 55, 1624-1627 (1933). (27) Petrov, Sopov, J. Gen. Chem. (U.S.S.R.) 15, 981-987 (1945); C.A. 40, 6407 (1946). (28) Carothers (to du Pont Co.), U.S. 2,038,538, April 28, 1936, Cent. 1936, II 3358; C.A. 30, 3838 (1936). (29) Hearne, Adams (to Shell Development Co.), U.S. 2,391,827, Dec. 25, 1945; C.A. 40, 1347 (1946). (30) Klebanskii, Chevychalova, Belen'kaya, J. Applied Chem. (U.S.S.R.) 9, 1985-1992 (1936); C.A. 31, 2580 (1937)

(31) Klebansku, Chevychalova, Sintet. Kauchuk 1935, No. 6, 16-21; Cent. 1936, I 1975; C.A. 39, 1024 (1936). (32) I.G., French 819,963, Oct. 29, 1937; Cent. 1938, II 950; C.A. 32, 3203 (1938): Ger. 683,097, Oct. 10, 1939, [C.A. 36, 3704 (1942)]. (33) Tishchenko, Churbakov, Russ. 51,994, Oct. 31, 1937; C.A. 34, 1336 (1940). (34) Carter, Johnson (to du Pont Co.), U.S. 2,381,037, Aug. 7, 1945, C.A. 39, 4888 (1945). (35) Carter, Willett (to du Pont Co.), U.S. 2,381,038, Aug. 7, 1945, C.A. 39, 4888 (1945). (36) Eringer, French 811,433, April 14, 1937; Cent. 1937, II 2914; [C.A. 31, 8996 (1937)]: Brit. 480,320, Feb. 17, 1938; C.A. 32, 6104 (1938). (37) Petrov, J. Gen. Chem. (U.S.S.R.) 13, 102-107 (1943); C.A. 38, 329 (1944). (38) Carothers, Berchet, J. Am. Chem. Soc. 55, 1628-1631 (1933). (39) Carothers, Berchet (to du Pont Co.), U.S. 1,965,369, July 3, 1934; Cent. 1935, I 3724; [C.A. 28, 5716 (1934)]. (40) Petrov, J. Gen. Chem. (U.S.S.R.) 13, 108-112 (1943), C.A. 38, 330 (1944).

(41) Petrov, J. Gen. Chem. (U.S.S.R.) 13, 155-158 (1943); C.A. 38, 1466 (1944). (42) Carothers, Berchet, Collins, J. Am. Chem. Soc. 54, 4066-4070 (1932). (43) Gebauer-Fuelnegg (to Marsene Corp. of America), U.S. 1,980,396, Nov. 13, 1934; Cent. 1935, I 3859; [C.A. 29, 376 (1935)]. (44) Petrov, J. Gen. Chem. (U.S.S.R.) 10, 1418-1424 (1940); C.A. 35, 3593 (1941). (45) Petrov, J. Gen. Chem. (U.S.S.R.) 2322-2243 (1939); Cent. 1940, II 611; C.A. 34, 5050 (1940). (46) Petrov, J. Gen. Chem. (U.S.S.R.) 10, 819-825 (1940); Cent. 1940, II 2734; C.A. 35, 2112 (1941). (47) Backer, Blass, Rec. trav. chim. 61, 787-788 (1942). (48) Bunn, Proc. Roy. Soc. (London) A-180, 58-60, 66 (1942); Rubber Chem. and Tech. 15, 790-797 (1942). (49) Clews, Proc. Roy. Soc. (London) A-180, 100-107 (1942); Rubber Chem. and Tech. 15, 847-853 (1942). (50) Klebanskii, Vasil'eva, J. Gen. Chem. (U.S.S.R.) 6, 359-369 (1936); Cent. 1936, II 1895; J. prakt. Chem. (2) 144, 251-264 (1936); Rubber Chem. and Tech. 10, 126-134 (1937)

(51) Klebanskii, Rakhlina, J. Gen. Chem. (U.S.S.R.) 7, 1299-1305 (1937); Cent. 1938, I 1478; C.A. 31, 6921 (1937). (52) Reitlinger, J. Gen. Chem. (U.S.S.R.) 14, 420-427 (1944); C.A. 39, 4776 (1945). (53) Medvedev, Chilikina, Klimenkov, Acta Physicochim. U.R.S.S. 11, 751-766 (1939); C.A. 34, 3159 (1940). (54) Chilikina, Medvedev, Acta Physicochim. U.R.S.S. 12, 293-302 (1940); C.A. 34, 7708 (1940). (55) Yakubovich, Evdokimova, Arch. sci. biol. (U.S.S.R.) 55, No. 3, 93-100 (1939); C.A. 34, 2687 (1940). (56) Balandin, Eidus, Terent'eva, Compt. rend., acad. sci. U.R.S.S. 27, 343-348 (1940); C.A. 34, 7757 (1940). (57) Bolland, Melville, Rubber Technol. Conf. (London) 1938, 239-252; Cent. 1939, II 2766; C.A. 32, 8396-8397 (1938). (58) Medvedev, Gindin, Lazareva, J. Phys. Chem. (U.S.S.R.) 13, 1389-1402 (1939); C.A. 35, 371 (1941). (59) Medvedev, Koritskaya, Alekseeva, J. Phys. Chem. (U.S.S.R.) 17, 391-407 (1943); C.A. 38, 4903 (1944).

56.4°

at 685 mm. (5)

3: 7085 CHLOROMETHYL METHYL ETHER
$$C_2H_5OCl$$
 (Chlorodimethyl ether; CH_3OCH_2 I_1 -(304) I_2 -(645)

B.P. F.P. 61° (1) -103.5° (9) $D_4^{20} = 1.0703$ (6) 59-60° (2) (3) (29) 1.0605 (5) 59.5° at 759 mm. (4) 59.4° at 760 mm. (5) $D_4^{15} = 1.0771$ (6) 59.1-59.3° at 766 mm. (6) 59.15° at 760 mm. (7) 57.7° at 750 mm. (8) $n_2^{20} = 1.39737$ (10)

 \tilde{C} is frequently but incorrectly designated as "chloromethyl ether"; care should therefore be taken to avoid confusion of \tilde{C} with the closely related "bis-(chloromethyl) ether" (3:5245) which has the structure ClCH₂OCH₂Cl.

Č is insol. cold aq. but on stdg. or warming soon dissolves with hydrolysis (see below). — Č is sol. in cold conc. HCl but can be salted out with CaCl₂.

 \bar{C} forms azeotropes with various org. cpds.: e.g., \bar{C} with acetone (1:5400) forms a const.-boilg. mixt., b.p. 56.1°, contg. 13% \bar{C} (7); \bar{C} with CS₂ forms a const.-boilg. mixt., b.p. 43.1°, contg. 25% \bar{C} (7).

[For prepn. of \bar{C} from aq. formaldehyde soln. (formalin) (1:0145) in MeOH by passage of HCl gas at room temp. (yields: 64-66% (11)) (3) (12) (14) see indic. refs.; from paraformaldehyde (trioxymethylene) (1:0080) in dry MeOH by passage of HCl gas (yields: 80% (6) (15), 66% (16), 60% (17), 50-60% (18)) (19) (13) (20) (23) (note that the prod. conts. MeOH (1:6120), formaldehyde dimethylacetal (methylal) (1:0105), and acetone (1:5400) (1) (15), and that htg. should be avoided since it promotes methylal formn. (15)).

[For formn. of \bar{C} from dimethyl ether [Beil. I-281, I₁-(139), I₂-(269)] with Cl₂ in diffuse daylight (79% yield (21)) (4) or in CHCl₃ or CCl₄ solns. + cat. in light (75); from acetaldehyde dimethylacetal (1:0125) with Cl₂ at not above 60° (other prods. are also formed (22)) see indic. refs.]

Further substitution of \bar{C} . [\bar{C} with Cl_2 in semi-darkness at 12° for 40 hrs. gives mainly (23) bis-(chloromethyl) ether (3:5245).]

Reactions involving the halogen atom of $\bar{\mathbf{C}}$ with inorganic reactants. $\bar{\mathbf{C}}$ is insol. in cold aq. but upon shaking or warming rapidly dissolves yielding soln. contg. formaldehyde (1:0145) + MeOH (1:6120) + HCl (note that paraformaldehyde (1:0080) is formed only on very slow hydrolysis with insufficient water for complete reactn. (18).

[\bar{C} with alc. KSH yields mainly (24) a polymeric thioformaldehyde, (CH₂S)_n, sol. aq. but cryst. from alc., m.p. 123-124° (24); \bar{C} with dry KSH. ½H₂O at 5-10° gives methoxymethyl mercaptan, CH₃OCH₂SH, liq. with disagreeable odor, b.p. 52° at 15 mm., $D_{12}^{12} = 1.0738$, $n_{12}^{12} = 1.4909$ (24); \bar{C} with 2K₂S.H₂O gives (24) bis-(methoxymethyl) sulfide, CH₄OCH₂-S-CH₂OCH₃, liq. with disagreeable odor, b.p. 62° at 15 mm., $D_{21.5}^{21.5} = 1.0418$. $n_{12}^{21.5} = 1.4575$ (24).]

[C with mixt. of HNO₃ (D = 1.5) + conc. H₂SO₄ + fumg. H₂SO₄ (70% SO₃) and appropriate cooling gives in 15 min. nitromethoxymethyl nitrate, oil, b.p. 48° at 15 mm., + (nitromethoxy)methoxy methyl nitrate, highly explosive oil, b.p. 88-89° at 9 mm. (25).]

[$\bar{\mathbf{C}}$ with SO₃ below 0° gives (27% yield (17)) chloromethyl methyl sulfate [Beil. I-582, I₂-(647)], b.p. 92° at 18 mm., $D_{18}^{18} = 1.473$.]

[C in either liq. or gaseous phase with various finely divided metals at 50-250° and press.

from 100-200 atm. yields (26) ethylene oxide (1:6105) and other products. — \bar{C} with metallic Zn at ord. temp. gives (27) formaldehyde dimethylacetal (1:0105) + β -chloroethyl methyl ether (3:7265) + CH₃Cl (3:7005) + resins. — \bar{C} with ZnCl₂.H₂O vigorously stirred at 27° gives (28) b_2 -(chloromethyl) ether (3:5245).]

[For rate of reactn. of C with KI in acetone see (29).]

[Č on adding to cold soln. of NH₃ in ether (30) or with aq. or alc. NH₄OH (4) gives NH₄Cl (pptd. in ether method) + hexamethylenetetramine.]

[C with equal wt. CuCN refluxed 4 hrs. (31) or with 3 wt. pts. Hg(CN)₂ at room temp. for several hrs. (33) gives (yields: 74% (31), 70% (32)) (8) methoxyacetonitrile [Beil. III-242, III₁-(93), III₂-(174)], b.p. 120-121° cor. at 759 mm., $D_4^{20} = 0.9492$, $n_D^{20} = 1.3831$ (31); note that AgCN does not (33) give this result.]

[C with silver cyanate in dry ether in cold gives (30) methoxymethyl isocyanate, colorless lachrymatory oil, b.p. 87.5° cor. (30); C with KSCN in dry C₆H₆ refluxed 2 days gives (34) methoxymethyl isothiocyanate, lachrymatory oil, b.p. 138° at 770 mm.]

Reactions involving the halogen atom of \tilde{C} with organic reactants. By virtue of its very reactive halogen atom, \tilde{C} may conveniently be employed for introducing the methoxymethyl radical in place of reactive H atoms; these may be located in OH groups of alcohols, phenols, or enols or in aromatic nuclei; various acceptors for the resulting HCl are employed or \tilde{C} may be used with metallic derivatives of the reactants; examples of the various combinations are cited below.

[Č with MeOH (1:6120) (12) (35) or with NaOMe (1) (12) gives (small yield (1)) formaldehyde dimethylacetal (methylal) (1:0105); Č with EtOH (1:6130) + pyridine in cold (36) or Č with NaOEt (37) gives (13.3% yield (36)) ethyl methoxymethyl ether (ethylmethyl-formal), b.p. 65.4° at 760 mm., $D_4^{20}=0.84198$, $n_D^{20}=1.36426$ (36) (for corresp. prepn. of mixed formals from Č with n-PrOH, n-BuOH, n-AmOH, and n-hexyl alc. + pyridine (yields all 17-23%) see (36)). — Č with benzyl alc. (1:6480) + pyridine in dry ether gives (47% yield (35)) benzyl methoxymethyl ether, b.p. 208-211° at 756 mm. (35).]

[C with phenol + pyridine does not react (35), but C with K phenolate (38) or Na phenolate (16) (39) gives (70% yield (16)) methoxymethyl phenyl ether, b.p. 188-189° (39), 189-190° (16); for many analogous cases with other phenols see (16) (39).]

[C with sodium salts of phenolic aldehydes gives the corresp. ethers: e.g., C with Na salt of salicylaldehyde (1:0205) in alc. gives (33% yield (40)) (39) o-(methoxymethoxy)-benzaldehyde; for numerous other examples of this type of reaction with phenolic aldehydes see (39) (40) (41) (42) (43).]

[\bar{C} with ethyl cyano-sodio-acetate in dry ether gives (6% yield (44)) ethyl cyano-methoxymethyl-acetate; \bar{C} with diethyl malonate (1:3581) + Na in dry ether (45) or in $C_6H_6(46)$ gives (49% yield (45)) (46) diethyl methoxymethylmalonate, b.p. 121–122° at 15 mm.; \bar{C} with diethyl benzylmalonate + Na in dry ether gives (78% yield (47)) diethyl benzylmethoxymethyl-malonate, m.p. 49–50°, b.p. 194–195° at 19 mm. (47); \bar{C} with ethyl aceto-acetate + Na in dry ether gives (51% yield (48)) O-(methoxymethyl) ether, viz., ethyl β-(methoxymethoxy)crotonate, b.p. 109–110° at 18 mm. (48), accompanied by (42% yield) diethyl α ,γ-diacetylglutarate, b.p. 178° at 10 mm. (48), the latter also being obtd. in good vield from \bar{C} + the Cu enolate of ethyl acetoacetate in dry ether (48).]

[\bar{C} with triphenylmethylsodium gives (49) methyl β,β,β -triphenylethyl ether, cryst. from propyl alc. or lgr., m.p. 137° (49); \bar{C} with diphenylmethylsodium gives (50) methyl β,β -diphenylethyl ether, b.p. 198° at 19 mm. (50).]

[C with salts of organic acids yields the corresp. methoxymethyl esters: e.g., C with dry Pb formate (but not with K or Ca formates (18)) on htg. under reflux gives (20% yield (3) (18)) methoxymethyl formate, b.p. 102-103°; C with fused KOAc (3) or NaOAc (3) (51) (but not Pb or Zn acetates (3)) gives (35-40% yield (3)) methoxymethyl acetate [Beil.

II-151, II₁-(70), II₂-(163)], b.p. $117-118^{\circ}$ (3); for corresp. react. with Pb propionate or Na *n*-butyrate see (3).]

[$\tilde{\mathbf{C}}$ in $\mathbf{C_6H_6}$ with $\mathbf{ZnCl_2}$ + HCl gas at 55-65° gives (52) cf. (28) benzyl chloride (3:8535). — $\tilde{\mathbf{C}}$ with chlorobenzene (3:7903) + dehydrating agts. gives (28) p-chlorobenzyl chloride (3:0220). — $\tilde{\mathbf{C}}$ with toluene + SnCl₄ gives (35-40% yield (53)) p-methylbenzyl chloride (p-xylyl chloride) (3:8660) together with other prods.]

[\bar{C} in AcOH soln. without cat. condenses with aromatic nuclei: e.g., \bar{C} with toluene in AcOH gives (25% yield {15}) a mixt. of o-xylyl chloride (3:8710) and p-xylyl chloride (3:8660); for analogous reactns. of \bar{C} in AcOH with o-xylene (1:7430), m-xylene (1:7420), pseudocumene (1:7470), mesitylene (1:7455), naphthalene (1:7200), tetralin (1:7550), anisole (1:7445), etc., see {15}.

[By virtue of its reactive halogen atom \bar{C} reacts readily with Grignard reagents giving (54) the corresp. methyl ethers: e.g., \bar{C} with n-BuMgBr gives (67% yield (55)) (56) n-amyl methyl ether (1:7905); \bar{C} (2 moles) with decamethylene-bis-MgBr gives (53% yield (57)) dodecanediol-1,12-dimethyl ether; \bar{C} with CH₃—C=C—MgBr gives (58) CH₃.C=C.CH₂OCH₃; \bar{C} with Br—Mg.C=C—MgBr gives (63% yield (32)) 1,4-dimethoxybutyne-2; \bar{C} with C₆H₅MgBr gives (60% yield based on initial C₆H₅Br (59)) benzyl methyl ether (1:7475); \bar{C} with benzyl MgCl gives mainly (60) cf. (61) (62) methyl β -phenylethyl ether (ω -methoxyethylbenzene) [Beil. VI-479, VI₁-(238)], b.p. 185–187° (61), accompanied by some ρ -tolylcarbinol methyl ether and ρ -tolylcarbinol methyl ether, cf. (60).]

[In the pres. of appropriate catalysts $\bar{\mathbb{C}}$ adds to olefinic unsatd. linkages, addition occurring as if $\bar{\mathbb{C}}$ dissociated into (Cl-) and (CH₃O.CH₂-) radicals; examples of these addition reactions are given as follows: $\bar{\mathbb{C}}$ with ethylene + BiCl₃ at 80° under 700–800 lbs. press. for 7 hrs. gives (63) γ -chloro-n-propyl methyl ether; $\bar{\mathbb{C}}$ with propylene + BiCl₃ similarly gives (63) γ -chloro-n-butyl methyl ether; $\bar{\mathbb{C}}$ with 2-methylpropene-1 (isobutylene) + HgCl₂ on stdg. in s.t. 4 days at room temp. gives (60% yield (64)) 2-chloro-4-methoxy-2-methylbutane, b.p. 136° at 751 mm. $D_4^{20} = 0.9455$, accompanied by some ter-butyl chloride (3:7045); but $\bar{\mathbb{C}}$ with isobutylene + TiCl₄ as directed (65) gives the corresp. alc., viz., 3-chloro-3-methylbutanol-1; $\bar{\mathbb{C}}$ with 2-methylbutene-2 (trimethylcthylene) (1:8220) with ZnCl₂ as directed (63) or with HgCl₂ in s.t. at room temp. for 48 hrs. (64) gives (40% yield (64)) 2-chloro-4-methoxy-2,3-dimethylbutane, b.p. 153° at 761 mm., 46-46.5° at 14 mm., $D_4^{20} = 0.9528$, accompanied by some ter-AmCl (3:7220); $\bar{\mathbb{C}}$ with cyclohexene (1:8070) + ZnCl₂ in CS₂ stirred 5 hrs. at 0°, then 3 hrs. at room temp., gives (28.7% yield (66)) cf. (64) (o-chlorocyclohexyl)methyl methyl ether (2-chloro-1-(methoxymethyl)cyclohexane), b.p. 88-91° at 17 mm., $D_4^{20} = 1.1552$ (66).]

[\bar{C} with butadiene-1,3 + ZnCl₂ in s.t. at room temp. for 24 hrs. gives (70% yield (64)) a mixt. of 1-chloro-5-methoxypentene-2, b.p. 168° at 758 mm., 56° at 10 mm., $D_4^{20} = 1.0022$ (from 1,4- addn. (?)) + 3-chloro-5-methoxypentene-1, b.p. 148° at 756 mm., 35° at 10 mm., $D_4^{20} = 0.9740$ (from 1,2 addn. (?)) (note that these two prods. represent synionic mesomers); \bar{C} with cyclohexadiene-1,3 (1:8057) + HgCl₂ under CO₂ at 0° stood 24 hrs. gives (38% yield (64)) (4-chlorocyclohexenyl)methyl methyl cther, b.p. 81° at 10 mm., $D_4^{20} = 1.0636$ (64).]

[$\bar{\mathbb{C}}$ (1 mole) + vinylacetylene (1 mole) + BiCl₃ (trace) + pyrogallol (trace) in dry ether at 5-15° for 9 hrs. (with periodic addns. of BiCl₃) gives (67) 34.8% yield 1-chloro-5-methoxypentadiene-2,3, b.p. 60-61° at 10 mm., $D_4^{20} = 1.0427$, $n_D^{20} = 1.4893$ (by 1,4 addn.), together with 15% yield of 3-chloro-5-methoxypentadiene-1,3, b.p. 46° at 10 mm., $D_4^{20} = 1.0351$, $n_D^{20} = 1.4846$, together with other prods.; note that of the two preceding dienes the former with Cu₂Cl₂ + HCl in ether at 20-40° for 2 hrs. readily isomerizes (81% yield (67)) to the latter; for further reactions of the pair see (67).]

 $[\tilde{C} \text{ with } 4.67\% \text{ dislvd. ZnCl}_2 \text{ shaken with CO at } 25-50^\circ \text{ at } 275-625 \text{ pounds press. for } 8 \text{ hrs. gives } (68) \text{ methoxyacetyl chloride } (3:5225).]$

Č with tertiary amines yields the corresp. quaternary ammonium salts: e.g., Č with Me₃N in dry ether gives (69) methoxymethyl-trimethyl-ammonium chloride (chloroplatinate, m.p. 228–229°, picrate, m.p. 198°); Č with pyridine in dry ether gives (69) methoxymethyl-pyridinium chloride (chloroplatinate, m.p. 182–185° (70), 180–182° dec. (35), HgCl₂ cpd., m.p. 91° (69)); Č with quinoline in CHCl₃ gives (69) methoxymethyl-quinolinium chloride (chloroplatinate, m.p. 232–234°; chloroaurate, m.p. 126–127°); for other quaternary salts see (69).

- Methoxymethyl benzoate: oil, b.p. 283° (71). [From C with NaOBz at 100° (71).]
- ---- Methoxymethyl p-nitrobenzoate: unreported.
- Methoxymethyl 3,5-dinitrobenzoate: unreported.
- —— S-(Methoxymethyl)isothiourea picrate: m.p. 163° (72). [From C + thiourea in cold acetone giving (90% yield (72)) corresp. hydrochloride, m.p. 112° dec., which is then converted to the picrate.]
- ---- N-(Methoxymethyl)phthalimide: cryst. from dry MeOH, m.p. 120-121° (73), 118° (74). [Prepn. reported only by indirect means (73) (74).]

3:7685 (1) Löbering, Fleischmann, Ber. 70, 1680-1683 (1937). (2) Straus, Heinze, Ann. 493, 215-216 (1932). (3) Clark, Cox, Mack, J. Am. Chem. Soc. 39, 712-714 (1917). (4) Friedel, Bull. soc. chm. (2) 28, 171-172 (1877). (5) Rau, Nurayanawarmy, Proc. Indian Acad. Sci. A-1, 217-218 (1935). (6) Karvonen, Ann. Acad. Sci. Fennicac A-3, No. 7, 1-103; Cent. 1912, II 1268. (7) Lecat, Ann. soc. sci. Bruxelles 47, I 66 (1927); Cent. 1927, II 904. (8) Kohlrausch, Ypsilanti, Z. physik. Chem. B-29, 291 (1935). (9) Timmermans, Bull. soc. chim. Belg. 27, 334-343 (1913); Cent. 1914, I 618. (10) Karvonen, Ann. Acad. Sci. Fennicae A-5, No. 6, 105.

(11) Marvel, Porter, Org. Syntheses, Coll. Vol. 1 (2nd ed), 377-379 (1941); (1st ed.), 369-371 (1932), 9, 58-60 (1929). (12) Henry, Bull. acad. roy. Belg. (3) 25, 439-440 (1893); Ber. 26, Referate 933 (1893). (13) Litterschied, Thimme, Ann. 334, 1-49 (1904). (14) Favre, Compt. rend. 119, 284 (1894); Bull soc. chim. (3) 11, 1095-1096 (1894). (15) Vavon, Bolle, Calin, Bull. soc. chim. (5) 6, 1025-1033 (1939). (16) Reychler, Bull. soc. chim. (4) 1, 1195-1198 (1907). (17) Houben, Arnold, Ber. 40, 4306-4310 (1907). (18) Wedekind, Ber. 36, 1383-1386 (1903). (19) Wedekind, Ger. 135,310, Oct. 16, 1902; Cent. 1902, II 1164. (20) Farren, Fife, Clark, Garland, J. Am. Chem. Soc. 47, 2420-2421 (1925).

(21) Kleber, Ann. 246, 97-102 (1888). (22) Reichert, Bailey, Nieuwland, J. Am. Chem. Soc. 45, 1554-1555 (1923). (23) Litterscheid, Ann. 330, 114-116 (1903). (24) deLettre, Bull. soc. chim. Belg. 26, 323-336 (1912); Cent. 1912, II 1192. (25) Houben, Pfankuch, Ber. 59, 88-89 (1926). (26) du Pont Co., Brit. 435,110, Oct. 10, 1935; Cent. 1936, I 877; C.A. 30, 1387 (1936). (27) Fileti, de Gaspari, Gazz. chim. ital. 27, II 293-296 (1897). (28) Stephen, Short, Gladding, J. Chem. Soc. 117, 511, 517, 522 (1920). (29) Conant, Kuner, Hussey, J. Am. Chem. Soc. 47, 497 (1925). (30) Jones, Powers, J. Am. Chem. Soc 46, 2526-2527 (1924).

(31) Henze, Rigler, J. Am. Chem. Soc. **56**, 1351 (1934). (32) Gauthier, Ann. chim. (8) **16**, 306, 336-337 (1909). (33) Sommelet, Ann. chim. (8) **9**, 497-498 (1906); Bull. soc. chim. (4) **1**, 372-373 (1907). (34) Johnson, Guest, Am. Chem. J. **41**, 340-341 (1909). (35) Cocker, Lapworth, Walton, J. Chem. Soc. **1930**, 446-448, 451-453. (36) Palomaa, Kantola, Ber. **65**, 1593-1598 (1932). (37) Henry, de Sonay, Bull. acad. roy. Belg. **1908**, 6-17, Cent. **1908**, I 2014. (38) Breslauer, Pictet, Ber. **40**, 3786 (1907). (39) Hoering, Baum, Ger. 209,608, May 7, 1909; Cent. **1909**, I 1680-1681. (40) Pauly, Wasder, Ber **56**, 606-610 (1923).

(41) Pauly, Feuerstein, Ber. 62, 303 (1929).
(42) Pauly, Strassberger, Ber. 62, 2280 (1929).
(43) Smith, Laforge, J. Am. Chem. Soc. 56, 2431 (1934).
(44) Foldi, von Fodor, Demjen, Szekeres, Halmos, Ber. 75, 760 (1942).
(45) Simonsen, J. Chem. Soc. 93, 1780 (1908).
(46) Fischer, Nenitzescu, Ann. 443, 125 (1925).
(47) Simonsen, J. Chem. Soc. 117, 565-566 (1920).
(48) Simonsen, Storey, J. Chem. Soc. 95, 2108-2109, 2111-2112 (1909).
(49) Schlenk, Bergmann, Ann. 464, 17-18 (1928).
(50) Bergmann, J. Chem. Soc. 1936, 413.

(51) de Gaspari, Gazz. chrm. ital. 27, II 297-298 (1897). (52) Lock, Ber. 74, 1568-1574 (1941); Cent. 1942, I 189. (53) Sommelet, Compt. rend. 157, 1443-1445 (1913); Cent. 1914, I 462-463: Compt. rend. 180, 1349-1351 (1925), Cent. 1925, II 399. (54) Hamonet, Bull. soc. chrm. (4) 3, 254-258 (1908). (55) Gredy, Bull. soc. chim. (5) 3, 1094 (1936). (56) Kirrmann, Bull. soc. chim. (4) 39, 989 (1926). (57) Chuit, Helv. Chim. Acta 9, 268 (1926). (58) Yvon, Compt. rend. 180, 748-749 (1925); Cent. 1925, II 17. (59) Reychler, Bull. soc. chim. (4) 1, 1198-1200 (1907). (60) Bottomley, Lapworth, Walton, J. Chem. Soc. 1938, 2215-2216.

(61) Madinaveitia, Bull. soc. chim. (4) 25, 604 (1919). (62) Müller, Cent. 1932, I 811. (63) Scott (to du Pont Co.), U.S. 2,024,749, Dec. 17, 1935; Cent. 1936, I 4074; C.A. 30, 1067 (1939):

Brit. 423,520, Feb. 28, 1935; Cent. 1935, II 920; C.A. 29, 4374 (1935). (64) Straus, Thiel, Ann. 525, 151-182 (1936). (65) Martin (to du Pont Co.), U.S. 2,143,021, Jan. 10, 1939; Cent. 1939) II 227; C.A. 33, 2907 (1939). (66) Nenitzescu, Przemetzki, Ber. 69, 2706-2707 (1936). (67, Dykstra, J. Am. Chem. Soc. 58, 1747-1749 (1936). (68) Scott (to du Pont Co.), U.S. 2,084,284, June 15, 1937; Cent. 1937, II 2261; C.A. 31, 5383 (1937). (69) Litterscheid, Thimme, Ann. 334, 49-62 (1904). (70) Litterscheid, Ann. 316, 168-169 (1901).

(71) Walker, Plastic Products 9, 187-188 (1933); Cent. 1933, II 2517; C.A. 28, 1662 (1934).
(72) Sprague, Johnson, J. Am. Chem. Soc. 59, 2439-2441 (1937).
(73) Sachs, Ber. 31, 1230 (1898).
(74) Hopkins, J. Am. Chem. Soc. 45, 542 (1923).
(75) Salzberg (to du Pont Co.),

U.S. 2,065,400, Dec. 22, 1936; Cent. 1937, I 3715; C.A. 31, 1046 (1937).

3: 7090 d,l-3-CHLOROBUTENE-1 H H C₄H₇Cl Beil. I —
$$(\gamma$$
-Chloro- α -butylene; CH_3 — C — CH_2 I_1 — I_2 -(174)

B.P. 63° at 760 mm. (1)
$$D_4^{20} = 0.9001$$
 (1) $n_D^{20} = 1.4151$ (10) 64-65° (2) 1.4150 (5) (3) (2) 64° at 750 mm. (5) 1.4153 (1) 63.5° at 751 mm. (10) 24.2-24.6° at 178 mm. (3) -5° at 26 mm. (4)

For important discussion of the relationship and conversion of \bar{C} to 1-chlorobutene-2 see the latter (3:7205).

[For the prepn. of a mixt. of \bar{C} and 1-chlorobutene-2 from butadiene-1,3 + HCl see (5) (1) (6) (7); for prepn. of \bar{C} from methyl-vinyl-carbinol (buten-1-ol-3) + conc. HCl see (3) (4) (8).]

[For study of reaction with Mg, Zn, etc., see (9); for study of hydrolysis under various conditions see (10); for behavior with cuprous cyanide see (11).]

- Methyl-vinyl-carbinyl p-nitrobenzoate: m.p. 43-44° (12). [Note that this prod. has been prepd. only by indirect means (12) and may (because of allylic rearr.) possibly be in fact crotonyl p-nitrobenzoate (see under 3:7205).]
- Methyl-vinyl-carbinyl 3,5-dinitrobenzoate: unreported. [See also note under 3:7205.]
- ---- N-(Methyl-vinyl-carbinyl)phthalimide: m.p. 87-88° (13). [Prepd. indirectly, and structure unproved (13).]

3:7690 (1) Henne, Chanan, Turk, J. Am. Chem. Soc. 63, 3474-3476 (1941). (2) Baudrenghien, Bull. soc. chim. Belg. 31, 168 (1922). (3) Roberts, Young, Winstein, J. Am. Chem. Soc. 64, 2163 (1942). (4) Böhme, Ber. 71, 2378-2379 (1938). (5) Kharasch, Kritchevsky, Mayo, J. Org. Chem. 2, 494-496 (1938). (6) Voigt, J. prakt. Chem. (2) 151, 310 (1938). (7) Dykstra (to du Pont), U.S. 2,123,504, July 12, 1938; Cent. 1938, II 2840; C.A. 32, 6666 (1938). (8) Ganguly, J. Indian Chem. Soc. 13, 584 (1936). (9) Young, Eisner, J. Am. Chem. Soc. 63, 2113-2115 (1941). (10) Young, Andrews, J. Am. Chem. Soc. 64, 421-425 (1944).

(11) Lane, Fentress, Sherwood, J. Am. Chem. Soc. 66, 545-548 (1944). (12) Burton, J. Chem. Soc. 1929, 456. (13) Mumm, Richter, Ber. 73, 847, 857 (1940).

[For prepn. from propyn-2-ol-1 (propargyl alcohol) [Beil. I-454, I₁-(234) with PCl₃ see (1) (2).]

3:7160 (1) Henry, Ber. 8, 398 (1875). (2) Pauling, Gordy, Saylor, J. Am. Chem. Soc. 64, 1753-1756 (1942).

cis Stereoisomer

B.P. F.P. 66.6-67.0° at 760 mm. (1)
$$-117.3$$
° (18) $D_4^{20} = 0.9239$ (18) $n_D^{20} = 1.4240$ (18) 70.58° (18) $D_4^{15} = 0.9246$ (1) $D_4^{0} = 0.9420$ (1) $n_D^{13.4} = 1.4250$ (1)

trans Stereoisomer

B.P. F.P. 62.4-62.8° at 760 mm. (1)
$$-105.8^{\circ}$$
 (18) $D_4^{20} = 0.9139$ (18) $n_D^{20} = 1.4190$ (18) 62.84° (18) $D_4^{15} = 0.9185$ (1) $D_4^{0} = 0.9361$ (1) $n_D^{13.4} = 1.4217$ (1)

Ordinary C (mixt.)

B.P.
$$64-68^{\circ}$$
 (2) $D_4^{20} = 0.9179$ (3) $62-67^{\circ}$ (3) $n_D^{15} = 1.4232$ (2) $59-61^{\circ}$ at 761 mm. (4) $D_4^{15} = 0.9220$ (2)

Both stereoisomers form with abs. EtOH const.-boilg. mixts. from which $\tilde{\mathbf{C}}$ can be recovered by repeated shaking with 3 vols. aq. to remove the alc.; the azeotrope with $cis-\tilde{\mathbf{C}}$, b.p. 60.0-60.4° at 760 mm., $D_4^{15}=0.8964$, conts. 81.6% by wt. of $cis-\tilde{\mathbf{C}}$; the azeotrope with trans- $\tilde{\mathbf{C}}$, b.p. 56.8-57.2° at 760 mm., $D_4^{15}=0.8960$, conts. 84.6% by wt. of trans- $\tilde{\mathbf{C}}$ (1).

[For study of toxicity of \bar{C} see (5); for use as anthelmintic see (6).]

[For prepn. of the two geom. stereoisomers of \bar{C} from either d,l- (3:7615) or meso- (3:7580) 2,3-dichlorobutane with alc. KOH (1 mole + 25% excess) refluxed for 3 days see {1}.

[For prepn. of ord. \tilde{C} (mixt. of cis+trans stereoisomers) from 2,2-dichlorobutane (3:7415) with alc. KOH see {8}; from ord. 2,3-dichlorobutane (3:7615) with alc. KOH (1) (2) (3) (8) (9), with aq. NaHCO₃ + Na₂CO₃ under press. (yield 20% \tilde{C} accompanied by 4% butanone-2 (ethyl methyl ketone) (1:5405) + 5% butenols) (7), with aq. alkali or alkaline-earth hydroxides under press. at 118–250° (10), by passing vapor over BaCl₂ at 200–300° (11), or by passing vapor + steam at 300–400° over silica gel contg. MgCl₂ + CaCl₂, etc. (yields 21–25% \tilde{C} accompanied by 35–38% butadiene-1,3 and 6–8% butanone-2) (3) see indic. refs.; from butanone-2 (ethyl methyl ketone) (1:5405) with PCl₅ (\tilde{C} is accompanied by 2-chlorobutene-1 (3:7075) (12) and by 2,2-dichlorobutane (3:7415) (4)) see indic. refs.]

[For prepn. of C from 2,2-dichloro-3-iodobutane (see below) with alc. KOH see (2); from 2-bromo-2-chloro-3-iodobutane with alc. KOH see (2) (note that the isomeric 2-bromo-3-chloro-2-iodobutane under same circumstances gives 3-bromo-2-chlorobutene-2).]

[For prepn. of C from 2,3-dichlorobutene-2 (3:5500) with aq. alk. or alkaline-earth hydroxides under press. at 118-250° see (13).]

[C with Cl2 may add halogen, or be further substituted by halogen, or both, according to

circumstances: e.g., \tilde{C} in liq. phase with Cl₂ at 20–40° in absence of light but in pres. of cat. such as SnCl₄ or FeCl₃ adds Cl₂ giving (14) 2,2,3-trichlorobutane (3:5680); \tilde{C} in liq. phase with Cl₂ in pres. of light and of O₂ (15) or \tilde{C} with Cl₂ in pres. of NaHCO₃ at 0° (4) substitutes further giving (55% yield (4)) (15) 2,3-dichlorobutene-1 (3:9074) (accompanied by 45% 2,2,3-trichlorobutane (3:5680) (4)); \tilde{C} with Cl₂ at 350° gives (16) a mixt. of unsatd. chlorobutenes, probably 1,2-dichlorobutene-2 (3:5560) or (3:5615) and 1,3(2,4)-dichlorobutene-2 (3:5550).]

Č adds Br₂ yielding (2) 2,3-dibromo-2-chlorobutane, b.p. 182.5–186° sl. dec., 66–66.5° at 12 mm., $D_4^{15} = 1.8975$, $n_D^{15} = 1.5339$ (2) (this prod. with alc. KOH loses HBr yielding (2) 3-bromo-2-chlorobutene-2, b.p. 128–129.5°, $D_4^{15} = 1.4998$, $n_D^{15} = 1.4950$ (2)).

[\bar{C} adds ICl yielding (2) 2,2-dichloro-3-iodobutane, b.p. 69.5° at 11.5 mm., $D_4^{15} = 1.8580$, $n_D^{15} = 1.5505$ (2) (this prod. with KOH regenerates \bar{C}).]

[\bar{C} also adds HOCl but from the addn. prod. HCl splits out immediately: e.g., \bar{C} in CCl₄ with Cl₂ + aq. as directed (17) gives (85% yield (17)) 3-chlorobutanone-2 (α -chloroethyl methyl ketone) (3:7598).

[For behavior of C with dry HF yielding 2,2-difluorobutane see (18).]

[\bar{C} with steam passed at 300–400° over silica gel contg. MgCl₂ + CaCl₂ is unchanged (3) (dif. from 3-chlorobutene-1 (3:7090) or 1-chlorobutene-2 (3:7205) which lose HCl yielding butadiene-1,3 (3)). — Note that with alc. KOH the $cis-\bar{C}$ splits off HCl 2.5 times as fast as the $trans-\bar{C}$ (1).] [For dehydrohalogenation of \bar{C} yielding butadiene-1,3 see (19) (20).]

[$\bar{\mathbf{C}}$ with alcoholates or phenolates as directed (9) yields the corresp. ethers; e.g., $\bar{\mathbf{C}}$ with NaOEt yields (9) $\alpha_1\beta$ -dimethylvinyl ethyl ether.]

Č on oxidn. with boilg. aq. KMnO₄ yields (12) acetic acid (1:1010) and propionic acid (1:1025); the *cis*-Č appears to give mainly acetic acid; the *trans*-Č gives mainly propionic acid (12).

3:7105 (1) Navez, Bull. soc. chim. Belg. 39, 435-443 (1930); Cent. 1931, I 1269-1270; C.A. 25, 2412 (1931). (2) Petrov, Sapozhnikova, J. Gen. Chem. (U.S.S.R.) 7, 476-484 (1937), Cent. 1937, I 4925; C.A. 31, 4263 (1937). (3) Gutner, Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1729-1735 (1936); Cent. 1937, I 3786; C.A. 31, 4265 (1937). (4) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938), Cent. 1939, II 4222-4223, C.A. 33, 4190 (1939). (5) McCawley, Univ Calif. Pub. Pharmacol. 2, 89-97 (1942); C.A. 36, 4911 (1942). (6) Marcenac, Compt. rend. 198, 510-512 (1934); Cent. 1934, I 2786; C.A. 28, 2800 (1934). (7) Dobryanskii, Gutner, Shchigel'skaya, J. Gen. Chem. (U.S.S.R.) 7, 1315-1320 (1937); Cent. 1938, I 561, C.A. 31, 6189 (1937). (8) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 663-666 (1937); Cent. 1937, II 372; C.A. 31, 5754 (1937). (9) I.G., Brit. 332,605, Aug. 21, 1930, Cent. 1930, II 2572. (10) du Pont Co. & Cass, Brit. 549,799, Dec. 8, 1942, C.A. 38, 756 (1944).

(11) Levine, Cass (to du Pont Co), U.S. 2,323,226, June 29, 1943; C.A. 38, 119 (1944); Brit. 535,555, April 15, 1941; C.A. 36, 1337 (1942). (12) Charpentier, Bull. soc. chim. (5) 1, 1407-1411 (1934). (13) Cass (to du Pont Co), U.S. 2,291,375, July 28, 1942; C.A. 37, 656 (1943). (14) Levine, Cass (to du Pont Co), U.S. 2,323,227, June 29, 1943; C.A. 38, 119 (1944): Brit. 535,586, April 15, 1941; C.A. 36, 1337 (1942). (15) Hearne (to Shell Development Co.), U.S. 2,296,614, Sept. 22, 1942; C.A. 37, 1129 (1943). (16) N. V. de Bataafsche Petroleum Maatschappii, Brit. 468,016, July 22, 1937; Cent. 1937, II 4102; C.A. 31, 8543 (1937): French 810,112, March 15, 1937; Cent. 1937, II 4102; C.A. 32, 587 (1938). (17) Groll, Hearne (to Shell Development Co.), U.S. 2,060,303, Nov. 10, 1936; Cent. 1937, I 4154, C.A. 31, 419 (1937); Brit. 437,573, Nov. 28, 1935; French 787,529, Sept. 24, 1935; Cent. 1936, II 2227. (18) Henne, Hinkamp, J. Am. Chem. Soc. 67, 1194-1197 (1945). (19) Evans, Morris, Melchior (to Shell Development Co.), U.S. 2,379,697, July 3, 1945; C.A. 39, 4331 (1945). (20) Hearne (to Shell Development Co.), U.S. 2,379,708, July 3, 1945; C.A. 39, 4330 (1945).

trans Stereoisomer

B.P.
$$68.0-68.2^{\circ}$$
 at 760 mm. (1) $D_4^{15} = 0.9205$ (1) $n_D^{14.6} = 1.4225$ (1) $D_4^{0} = 0.9376$ (1)

cis Stereoisomer

B.P. 63.4-63.6° at 760 mm. (1)
$$D_4^{15} = 0.9153$$
 (1) $n_D^{15} = 1.4194$ (1) $D_4^0 = 0.9329$ (1)

Both stereoisomers form with abs. EtOH const.-boil. mixts. from which \bar{C} can be recovered by repeated shaking with 3 vols. aq. to remove the alc.: the azeotrope with the trans form, b.p. 61.2–61.6° at 760 mm., $D_4^{15}=0.8912$, conts. 79.8% by wt. of \bar{C} ; the azeotrope with the crs form, b.p. 57.0–58.2° at 760 mm., $D_4^{15}=0.8946$, conts. 85.2% by wt. of \bar{C} (1).

[For formn. of both trans and cs forms of \bar{C} from d,l-1,2-dichlorobutane (3:7680) with alc. KOH (1 mole + 25% excess) refluxed 3 days (some 2-chlorobutene-1 (3:7075) is also formed) see {1}.]

[The crs form of \bar{C} with alc. KOH splits off HCl 2 9 times as fast as the trans form (1).] [\bar{C} with Cl₂ in dark at 10° gives (70–75% yield (2)) 1,1,2-trichlorobutane, but no constants for latter can be found either in (2) or in prior literature.]

3:7110 (1) Navez, Bull. soc. chim Belg 39, 435-443 (1930); Cent. 1931, I 1269-1270; C.A. 25, 2412 (1931). (2) Henne, Hinkamp J. Am Chem. Soc. 67, 1197 (1945).

3:7120 1-CHLORO-2-METHYLPROPENE-1 CH₃ C₄H₇Cl Beil. I - 209
$$(\beta,\beta$$
-Dimethylvinyl chloride; isocrotyl chloride; CH₃—CH I₂— α -chloroisobutylene)

B.P.
$$D_{25}^{25} = 0.9144$$
 (3) $D_{D}^{25} = 1.4198$ (3) $D_{D}^{25} = 1.4198$ (3) $D_{D}^{25} = 1.4198$ (3) $D_{D}^{25} = 1.4198$ (3) $D_{D}^{20} = 1.4221$ (2) $D_{D}^{20} = 1.4221$ (3) $D_{D}^{20} = 1.4221$ (4) $D_{D}^{20} = 1.4221$ (7)

[See also 3-chloro-2-methylpropene-1 (3:7145).]

Note that for \tilde{C} the designation $\beta_i\beta$ -dimethylvinyl chloride is now preferred, cf. (5); great care should be used to avoid confusion of \tilde{C} with the isomeric and very closely related 3-chloro-2-methylpropene-1 (methallyl chloride) (3:7145); both these compounds are now commercial chemicals in the U.S.A.

[For prepn. of \bar{C} from 3-chloro-2-methylpropene-1 (methallyl chloride) (3:7145) see (2) (8): e.g., methallyl chloride (10 moles) with 80% H₂SO₄ (1 mole) stirred at 40° for 2½ hrs. gives an upper phase contg. 87% \bar{C} + 7% residual methallyl chloride + 6% dichlorides and polymers; after washing free from acid, drying, and distilling it yields 85% \bar{C} (8) (20).]

[For formn. of C (usually accompanied by the isomeric methallyl chloride and/or other

prods.) from 2-methylpropene-1 (isobutylene) with Cl₂ (5) (9), from 1,1-dichloro-2-methylpropane (isobutylidene dichloride) (3:7425) by actn. of NH₄OH or alc. KOH (4), from 1,2-dichloro-2-methylpropane (isobutylene dichloride) (3:7430) with alc. KOH (10) see indic. refs.]

[For formn. of \bar{C} (together with the isomeric methallyl chloride) from 1-chloro-2-methyl-propanol-2 (isobutylene chlorohydrin) (3:7752) by soln. in cold 45% H₂SO₄ and subsequent warming (giving 90% \bar{C} + 10% methallyl chloride (2) (8)), or by use of P₂O₅ (11) cf. (12); from 1,1,1-trichloro-2-methylpropanol-2 (1,1,1-trichloro-ter-butyl alc. = "Chlore-tone") (3:2662) with Zn dust + boilg. alc. (13), or from isobutyraldehyde (1:0120) by actn. of PCl₅ (4) see indic. refs.]

C forms with aq. a const.-boilg. mixt., b.p. 61.9°, contg. 7.5% aq. (2)

[For study of anesthetic props. of C see (14).]

Reactions involving further substitution of H atoms in C. [C with Cl₂ (in pres. of 1.5 moles NaHCO₃ at 0° (15)) cf. (2) reacts not only by addn. but also by substitution (the latter involving a shift of double bond) giving respectively 32% 1,1,2-trichloro-2-methyl-propane (3:5710) + 68% 1,1-dichloro-2-methyl-propene-2 (3:7480).]

Reactions involving the double bond of C. [C adds Cl2 (see preceding paragraph).]

[Č also adds HOCl (chlorohydrination); e.g., Č with $Cl_2 + aq.$, or aq. HOCl, or even alkyl or aralkyl hypochlorites as directed (16) cf. (2) (4), yields 1,1-dichloro-2-methyl-propanol-2 (β,β -dichloro-ter-butyl alc.) (3:5772), b.p. 150°.]

[\bar{C} can also undergo catalytic hydration of the double bond: e.g., \bar{C} (1 mole) with 90% H_2SO_4 (1 mole) stirred at -10° to 0° for $2\frac{1}{2}$ hrs., then poured onto cracked ice, diluted with aq., and distilled, gives 66% of the initial \bar{C} as 1-chloro-2-methylpropanol-2 (β -chloro-ter-butyl alcohol) (isobutylene chlorohydrin) (3:7752); note that other acids can also be used for this hydration, e.g., 85% H_3PO_4 , 70% HNO_3 , 60% $HClO_4$, benzenesulfonic acid, e.g., each having its own optimum conditions. Note also that some 18% of the initial \bar{C} is not hydrated but is partially isomerized to a mixt. contg. 90% \bar{C} + 10% methallyl chloride (2) (17).]

Reactions involving the halogen atom of \bar{C} . Note that in \bar{C} the halogen is extremely inert as compared with that of the isomeric methallyl chloride (3:7145); this permits removal of the latter from \bar{C} by chemical means (see below).

[$\ddot{\mathbf{C}}$ is virtually unattacked by aq. or alc. KOH even at 100° (11) (1) (2) (dif. from methallyl chloride (3:7145)). — $\ddot{\mathbf{C}}$ does not react with boilg. aq. K_2CO_3 or KOAc (1) (dif. from methallyl chloride (3:7145)).]

[Č is not normally convertible to isobutyraldehyde except under extreme conditions (5) (dif. from methallyl chloride (3:7145) which upon acid hydrolysis or even boilg, with aquives isobutyraldehyde).]

- β,β-Dimethylvinyl (isocrotyl) acetate: unreported.
- β,β-Dimethylvinyl (isocrotyl) benzoate: unreported.
- β,β-Dimethylvinyl (isocrotyl) p-nitrobenzoate: unreported.
- ----- β,β-Dimethylvinyl (isocrotyl) 3,5-dinitrobenzoate: unreported.
- ---- N-(β,β-dimethylvinyl)phthalimide: unreported.
- 3:7120 (1) Pogorshelski, J. Russ. Phys.-Chem. Soc. 36, 1120-1184 (1904); Cent. 1905, I 667-668. (2) Burgin, Hearne, Rust, Ind. Eng. Chem. 33, 385-388 (1941). (3) Hurdis, Smyth, J. Am. Chem. Soc. 65, 89 (1943). (4) Oeconomides, Compt. rend. 92, 1237 (1881); Bull. soc. chim. (2) 35, 499-500 (1881). (5) Burgin, Engs, Groll, Hearne, Ind. Eng. Chem. 31, 1413-1419 (1939). (6) Engs, Redmond, U.S. 2,077,382, April 20, 1937; Cent. 1937, II 1660; C.A. 31, 3937 (1937). (7) Aschan, Oversitt Finska Velenskaps-Soc. Förh. 58, 122 (1915). (8) Groll, Burgin (to Shell Development Co.), U.S. 2,042,223, May 26, 1936; Cent. 1937, I 1274; C.A. 30, 4875 (1936). (9) Tamele, Ott, Marple, Hearne, Ind. Eng. Chem. 33, 115 (1941). (10) Mouneyrat, Ann. chim. (7) 26, 533-534 (1900).

(11) Michael, J. prakt. Chem. (2) 64, 104 (1901). (12) Krassuski, J. prakt. Chem. (2) 64, 390 (1901); J. Russ. Phys.-Chem. Soc. 33, 1-26 (1901); Cent. 1901, I 996. (13) Jositsch, J. Russ. Phys.-Chem. Soc. 36, 920-924 (1898); Cent. 1899, I 606. (14) Abreu, Peoples, Emerson, Anesthesia and Analgesia 18, 156-161 (1939); Cent. 1939, II 2111; C.A. 33, 6959 (1939). (15) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1245 (1938); Cent. 1939, II 4222; C.A. 33, 4190 (1939). (16) Groll, Hearne (to Shell Development Co.), U.S. 2,060,303, Nov. 10, 1936; Cent. 1937, I 4154; C.A. 31, 419 (1937); N. V. de Bataafsche Petroleum Matschappij, Brit. 437,573, Oct. 31, 1935; Cent. 1936, II 2227; C.A. 30, 2199 (1936); French 787,529; Sept. 24, 1935; Cent. 1936, II 2227; C.A. 30, 4875 (1936); N. V. de Bataafsche Petroleum Matschappij, French 791,644, Dec. 14, 1935; Cent. 1936, II 2227.

3: 7125
$$d$$
, l-2-CHLOROBUTANE (sec.-Butyl chloride; CH₃—CH₂—CH—CH₃ I₁— ethyl-methyl-carbinyl chloride)

B.P. F.P. (8.4-68.6° u.c. (28)] -131.3° (1) (10) $D_4^{25} = 0.86767$ (1) (8.25° at 760 mm. (1) (2) (4) 0.87323 (1) (68° at 761 mm. (5) 0.8726 (5) (68° at 769 mm. (5) 0.8707 (6) (67.3-67.8° cor. (6) 67.3° at 761.4 mm. (7) $D_4^{15} = 0.87880$ (1) $D_4^{15} =$

Liquid with agreeable ethereal odor.

[For prepn. of \tilde{C} from butanol-2 (1:6155) by saturation with dry HCl gas and htg. in s.t. at 100° for several hrs. (9); by distillation with 18 wt. pts. 6 N HCl (50% yield (12)); with conc. HCl + ZnCl₂ (2 moles) (yields: 85–88% (13), 83% (14), 82% (5), 78% (15), 60–68% (16) (17)) (6); with PCl₃ + ZnCl₂ (yields: 67% (15), 40% (6)); with PCl₅ + ZnCl₂ (71% yield (15)); with SOCl₂ + pyridine (yields: 90% (15), 47% (5)); or with HCl in pres. of H₃PO₄ (18) see indic. refs.]

[For formn. of \bar{C} from either butene-1 or butene-2 with HCl gas by addn. to unsatd. linkage (7) (19) in pres. of cat. (20) (21) (22) see indic. refs.; from *n*-butane with Cl₂ see (4) (23); from *n*-butylamine with HNO₂ (2.8% yield \bar{C} accompanied by 36.5% butenes, 25% butanol-1, 13.2% butanol-2, 5.2% *n*-butyl chloride (3:7160) and other prods.) see (24); from sec.-butylamine with NOCl in xylene see (25).]

[For study of anthelmintic props. of C see (26).]

Pyrolysis of C. [C at 450-550° without cat. loses HCl and yields (4) (27) a mixt. contg. butene-1, cis-butene-2, and trans-butene-2 (dif. from 1-chlorobutane (3:7160) which gives only butene-1); C at 450° in pres. of anhyd. CaCl₂ as cat. gives (4) (27) the same mixt. (as does also 1-chlorobutane (3:7160)). For use of this pyrolysis in distinction of C from ter-butyl chloride (3:7045) see (23).]

Further halogenation of \tilde{C} . [\tilde{C} with Cl_2 at 200–380° gives (28) a mixt. of dichlorobutanes contg. 1,3-dichlorobutane (3:7925), 2,2-dichlorobutane (3:7415), and d,l-2,3-dichlorobutane (3:7680); note, however, that \tilde{C} with Cl_2 in pres. of light gives (29) 1,2-dichlorobutane (3:7680), 1,3-dichlorobutane (3:7925), 2,2-dichlorobutane (3:7415), and both d,l- (3:7615) and meso- (3:7580) 2,3-dichlorobutanes.]

Reactions of the halogen atom of C. [For study of rate of reactn. of C with KI in acetone at 60° see (30).]

[Č with C_6H_6 + AlCl₃ gives (yields: 82.5% (9), 69% (31)) sec.-butylbenzene (1:7490); Č with C_6H_6 + Al/Hg gives (59.5% yield (32)) ter-butylbenzene (1:7460); Č with naphthalene + AlHg gives (48% yield (32)) 1-(sec.-butyl)naphthalene.]

[$\ddot{\mathbf{C}}$ with acetanilide + AlCl₃ in ethylene dichloride (3:5130) at -5° gives (33) N-acetyl-p-(sec.-butyl)aniline, cryst. from di-isopropyl ether, m.p. 121-122° (33).]

C with Mg in dry ether gives (87% yield (34)) sec.-BuMgCl (see also below).

- **D** Ethyl-methyl-acetic acid (1:1105): b.p. 176-177°. [From Č by conversion to RMgCl and carbonation of the latter with CO₂ (yields: 76-86% (35), 72%) (by adding ether soln. directly to solid CO₂ (36)).]
- **D** Ethyl-methyl-acetic-p-toluidide: m.p. 92.5-93° u.c. (39). [From \bar{C} by conversion to RMgCl (see above) and reactn. in dry other with p-tolyl isocyanate (39).]
- Ethyl-methyl-acetic α-naphthalide: m.p. 128-129° u.c. (39). [From C̄ by conversion to RMgCl (see above) and reactn. in dry ether with α-naphthyl isocyanate (39).] [Note that this prod. does not distinguish C̄ from isobutyl chloride (3:7135) for which the corresp. isovalero-α-naphthalide has m.p. 125-126° u.c. (39).]
- —— sec.-Butyl mercuric chloride (sec.-BuHgCl): cryst. from alc., m.p. 30.5° (40). [Reported only by indirect means (40).]
- —— S-(sec.-Butyl)isothiourea picrate; m.p. 190° (41). [Not reported from C but obtd. from sec.-BuBr (0.2 g.) + thiourea (0.2 g.) refluxed in alc. (2 ml.) for 2 min., then treated with PkOH (0.2 g.) dislyd. in least possible hot alc. (41).]
- N-(sec.-Butyl)phthalimide (2-(N-phthalimido)butane): m.p. 24.5-25.5° (42). [Not reported from Č but obtd. (35% yield (42)) from sec.-BuBr with K phthalimide by htg. in s.t. at 210° for 4 hrs.; note that m.p. is too low to be recommended as deriv. for identification.]
- --- N-(sec.-Butyl)-3-nitrophthalimide: unreported.
- --- N-(sec.-Butyl)tetrachlorophthalimide: unreported.
- N-(sec.-Butyl)-o-sulfobenzoic imide (N-(sec.-butyl)saccharin): m.p. 81° (43). [Not reported from C but obtd. from sec.-BuBr or sec.-BuI with sodium saccharin in aq. butylcarbitol (1:6517) on refluxing for 30 min. (43).]
- ---- N-(sec.-Butyl)-N-(p-bromobenzenesulfonyl)-p-anisidide: unreported.
- —— p-(sec.-Butoxy)benzoic acid: m.p. 121-123° u.c. (44). [From C (?) or from sec.-BuBr with ethyl p-hydroxybenzoate (1:1534) in abs. alc. NaOEt on refluxing 1 hr. (44).] [Note, however, that this prod. does not distinguish C from the corresp. deriv. of n-amyl chloride (3:7460) whose m.p. is 123-124° u.c. (44).]
- --- sec.-Butyl 2,4,6-triiodophenyl ether: unreported.
- —— sec.-Butyl \(\alpha\)-naphthyl ether: b.p. 293.5° cor. (45). (Corresp. picrate, m.p. 100.5-101.0° cor.; Neut. Eq. calcd. 429, found 427 (45).)

1.40047 (6)

- sec.-Butyl β-naphthyl ether: b.p. 298.5° cor. (45), 298° (46). (Corresp. picrate, m.p. 86.0-86.5° cor. (45); 85° (46); Neut. Eq., calcd. 429, found 429 (46).)

3:7125 (1) Timmermans, Martin, J. chim. phys. 25, 424-425 (1927). (2) Roland, Bull. soc. chim. Belg. 37, 122 (1928). (3) Wiswall, Smyth, J. Chem. Phys. 9, 357 (1941). (4) Weston, Hass, J. Am. Chem. Soc. 54, 3337-3343 (1932). (5) Vogel, J. Chem. Soc. 1943, 638-639. (6) Norris, Green, Am. Chem. J. 26, 307-308 (1901). (7) Coffin, Sutherland, Mass, Can. J. Research 2. 267-278 (1930); Cent. 1930, II 2250; C.A. 24, 3750 (1930). (8) Dadieu, Pongratz, Kohlrausch, Monatsh. 61, 416 (1932). (9) Estreicher, Ber. 33, 438-441 (1900). (10) Timmermans, Bull. soc. chim. Belg. 36, 504 (1927).

 (11) Wendell, Am. Chem. J. 26, 318 (1901).
 (12) Norris, Am. Chem. J. 38, 641-642 (1907).
 (13) Copenhaver, Whaley, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 143, espec. Note 6 (1941). (14) Whaley, Copenhaver, J. Am. Chem. Soc. 60, 2497-2498 (1938). (15) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929). (16) Norus, Org. Syntheses, Coll. Vol. 1 (1st ed.), 137-138 (1932); 5, 28, Note 5 (1925). (17) Norris, Taylor, J. Am. Chem. Soc. 46, 756 (1924). (18) A. Wacker Soc. Elektrochem. Ind., French 687,855, Aug. 14, 1930; Cent. 1930, II 3637; C.A. 25, 709 (1931). (19) Coffin, Mass, Can. J. Research 3, 526-539 (1930); Cent. 1931, I 2430; C.A. 25, 1146-1147 (1931). (20) Strange, Kane, Brit. 500,880, March 16, 1939; Cent. 1939, II 226; C.A. 33, 5867 (1939).

(21) Kane (to Strange), U.S. 2,119,167, May 31, 1938; C.A. 32, 5413, Brit. 414,766, Sept. 6, 1934; French 769,103, Aug. 20, 1934; Cent. 1935, I 1934. (22) Winkler, Ger. 574,802, March 30, 1933; Cent. 1933, I 3497. (23) Hass, McBee, Weber, Ind. Eng. Chem. 27, 1190-1195 (1935). (24) Whitmore, Langlois, J. Am. Chem. Soc. 54, 3441-3447 (1932). (25) Ssolonina, J. Russ. Phys.-Chem. Soc. 30, 431-449 (1898); Cent. 1898, II 888. (26) Wright, Schaffer, Am. J. Hyg. 16, 325-428 (1932); Cent. 1932, II 3119; J. Parasitol. 16, 107-108 (1929); C.A. 26, 4869 (1932). (27) Hass, Weston (to Purdue Research Foundation), U.S. 1,975,456, Oct. 2, 1934; Cent. 1835, II 2880; C.A. 28, 7260 (1934). (28) Rust, Vaughan, J. Org. Chem. 6, 479-488 (1941). (29)
 Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 663-666 (1937); Cent. 1937, II 372; C.A. 31, 5754 (1937). (30) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925).

(31) Boedtker, Bull. soc. chim. (4) 45, 649 (1929). (32) Diuguid, J. Am. Chem. Soc. 63, 3527-3528 (1941). (33) U.S Industrial Alc. Co., French 811,832, April 23, 1937; Cent. 1937, II 1267; C.A. 32. 593 (1938). (34) Whitmore, Badertscher, J. Am. Chem. Soc. 55, 4159 (1933). (35) Gilman, Kirby, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 361-364 (1941); (1st ed.), 353-356 (1932). (36) Bartlett, Stauffer, J. Am. Chem. Soc. 57, 2582 (1935).
 (37) Verkade, Rec. trav. chem. 36, 204 (1916).
 (38) Schwartz, Johnson, J. Am. Chem. Soc. 53, 1063-1067 (1931).
 (39) Underwood, Gale, J. Am. Chem. Soc. 56, 2117-2120 (1934). (40) Marvel, Calvery, J. Am. Chem. Soc. **45**, 821 (1923).

(41) Brown, Campbell, J. Chem. Soc. 1937, 1699-1700. (42) Mumm, Richter. Ber. 73, 855 (1940). (43) Merritt, Levey, Cutter, J. Am. Chem. Soc. 61, 15-16 (1939). (44) Lauer, Sanders, Leekley, Ungnade, J. Am. Chem. Soc. 61, 3050 (1939). (45) V. H. Dermer, O. C. Dermer, J. Org. Chem. 3, 290-291 (1938/39). (46) Wang, J. Chinese Chem. Soc. 1, 61-62 (1933).

```
3:7135 1-CHLORO-2-METHYLPROPANE
                                                               CH<sub>3</sub>
                                                                          C<sub>4</sub>H<sub>9</sub>Cl
                                                                                           Beil. I - 124
                                                      CH<sub>3</sub>—CH—CH<sub>2</sub>
            (Isobutyl chloride;
                                                                                                 I_{1}-(40)
            isopropylcarbinyl chloride)
                                                                                                 I_{2}-(87)
                                             M.P.
  B.P.
                  at 760 mm. (1) (2) -130.3° (6) (7)
                                                                      D_4^{25} = 0.87177 (1)

D_4^{20} = 0.8810 (5)
                                             -131.2° (1) (2)
  68.8-69.2° at 769.2 mm. (3)
                                                                               0.87733 (1)
  68.5° cor.
                                   (4)
                                                                      D_4^{15} = 0.88290 (1)
  68.5° cor. at 756 mm. (5)
  68.2°
                                   (6) (7) (8)
                                                                                   n_{\rm D}^{25} = 1.39576 (1) n_{\rm D}^{20} = 1.39841 (5)
                                                                                           1.39836 (1)
                                                                                           1.3983
                                                                                                        (8)
                                                                                   n_{\rm D}^{16} = 1.40096 (1)
```

Colorless liquid. — Very spar. sol. aq.; 100 ml. aq. at 12.5° dis. 0.092 g. Č (9).

 $\bar{\mathbf{C}}$ forms with aq. a const.-boilg. mixt. (consts. not reported {10}) (use in sepn. from ter-butyl alc. (1:6140) {10}; $\bar{\mathbf{C}}$ also forms binary azeotropes with many org. compounds; e.g., $\bar{\mathbf{C}}$ with EtOH (1:6130) forms a const.-boilg. mixt., b.p. 61.45° at 760 mm., contg. 72 mole % $\bar{\mathbf{C}}$ (11); $\bar{\mathbf{C}}$ with propanol-1 (1:6150) forms a const.-boilg. mixt., b.p. 67.7° at 760 mm., contg. 78 wt. % $\bar{\mathbf{C}}$ (12); $\bar{\mathbf{C}}$ with propanol-2 (1:6135) forms a const.-boilg. mixt., b.p. 64.8° at 760 mm., contg. 83 wt. % $\bar{\mathbf{C}}$ (13); $\bar{\mathbf{C}}$ with ter-butyl alc. (1:6140) forms a const.-boilg. mixt., b.p. 65.5° at 760 mm., contg. 83 wt. % $\bar{\mathbf{C}}$ (14); $\bar{\mathbf{C}}$ with allyl alc. (1:6145) forms a const.-boilg. mixt., b.p. 67.2° at 760 mm., contg. 93 wt. % $\bar{\mathbf{C}}$ (14); $\bar{\mathbf{C}}$ with EtOH (1:6130) + aq. forms a ternary const.-boilg. mixt., b.p. 58.62° at 760 mm. (2 phases), contg. 62.6 mole % $\bar{\mathbf{C}}$ + 19.8 mole % $\bar{\mathbf{E}}$ EtOH + 17.6 mole % aq. (11).

[For prepn. of \tilde{C} from isobutyl alc. (1:6165) with dry HCl gas in s.t. at 120° for 8 hrs. (3) cf. (23) (gives 94% yield of a mixt. of \tilde{C} + ter-butyl chloride (3:7045) from which latter can be removed by 5-hr. shaking with 10% aq. KOH (3)) cf. (22); with dry HCl gas at 100° for 10 hrs. (4) or in pres. of pyridine (15) or CdO, ZnCl₂ or other cat. (16); or over Al₂O₃ at 420° (ter-butyl chloride is also formed (17)); with conc. aq. HCl + ZnCl₂ refluxed 1 hr. (15% yield (18) (19)); with PCl₃ + ZnCl₂ (yields: 85% (20), 80% (18), 32% (21)) (note that some ter-butyl chloride is formed (21)); with PCl₅ (24) or PCl₅ + ZnCl₂ (76% yield (18)); or with SOCl₂ + pyridine (88% yield (18)) (5), SOCl₂ + dimethylaniline (70% yield (18)), SOCl₂ + diethylaniline (58% yield (18)) (note that use of aniline gives only 19% yield (18)) see indic. refs.]

[For formn. of \bar{C} from 2-methylpropane (isobutane) with $Cl_2 + cat$. at 180° (60% yield (25) together with other prods.) (26) see indic. refs.; for formn. of \bar{C} from isobutylene by cat. addn. of HCl (note "abnormal" addition) see (27).]

[For formn. of \bar{C} from isobutylamine with NOCl in xylene at -15° (28) or with aqua regia (29) see indic. refs.; from *n*-butyl acetate (1:3145) by pyrolysis with AlCl₃ see (30).]

[For sepn. of \bar{C} from ter-butyl chloride (3:7045) by hydrol. of latter with aq. alk. and extraction of the resultant ter-butyl alc. with aq. see (10) (3); for sepn. of \bar{C} from more reactive alkyl chlorides (such as ter-butyl chloride (3:7045), methallyl chloride (3:7145), etc.) by esterification of the reactive chlorides by htg. at 125-225° under press. in pres. of Cu with alkali salt of a suitable acid, followed by fractional distn., see (47).]

[C on suitable htg. dec. into isobutylene and HCl; if the process is so conducted that these prods. can react at lower temp. they combine to yield ter-butyl chloride (3:7045): e.g., \bar{C} passed over pumice at 500° (31), or over clay at 250–300° (32), or over BaCl₂, ThCl₄, ThO₂, kaolin, etc., at 300° (33) (34) (35) (36), or with H₂ over reduced Ni at 270° (35) (36) yields isobutylene + HCl; for execution of this process so as to permit recombination to ter-butyl chloride (3:7045) see (37). — Note that \bar{C} on htg. in s.t. at 306° for 6 hrs. gives (3) 8% ter-butyl chloride; for study of the equilibrium in the system \bar{C} + ter-butyl chloride + HCl over range 88–237° see (38).]

[\bar{C} with Cl₂ yields (39) (26) 1,3-dichloro-2-methylpropane (3:7960) and other prods. — \bar{C} with Br₂ (1 mole) in pres. of Fe in s.t. at 100° for 6 hrs. gives (40) 1,2-dibromo-2-methyl propane (isobutylene dibromide), b.p. 148° (40).]

[C with aq. soln. or susp. of inorg. bases under press. at 120-350° yields (41) a mixt. contg. isobutyl alc. (1:6165), ter-butyl alc. (1:6140), and isobutylene. — For study of rate of hydrolysis of C in 50% alc. in pres. and abs. of dil. H₂SO₄ see (42). — In connection with hydrolysis of C to isobutyl alc. note that these two form no azeotrope (1).]

[\overline{C} with Na in liq. NH₃ gives 2-methylpropane (isobutane) (43); but \overline{C} with NaNH₂ in liq. NH₃ gives isobutylene (43).]

[\bar{C} with $C_6H_6+AlCl_3$ gives exclusively (44) (45) (46) (21) ter-butylbenzene (1:7460).] \bar{C} with Mg in dry ether in pres. of trace of MeI as cat. gives in 8 hrs. (98.9% yield (48))

- corresp. isobutyl MgCl; the ethereal soln. of this RMgCl undergoes the usual reactns. (see also below).
 - ① Isovaleric acid (1:1050) q.v. [From isobutyl MgCl with CO₂ followed by dil. non-volatile acid and subsequent distn. (49) (yield not reported).]
 - ① Isovaleranilide: m.p. 109-110° u.c. (50). [From isobutyl MgCl (above) with phenyl isocyanate in dry ether (50).] [Note that this derivative does *not* distinguish Ĉ from isoamyl chloride (3:7365) or 2-chlorobutane (3:7125) q.v.]

 - —— Isobutyl mercuric chloride: unreported.
 - —— S-(Isobutyl)isothiourea picrate: m.p. 174°(51). [This prod. has been reported from isobutyl bromide (or iodide) (but not from C) by htg. with thiourea in alc. for 2 min., followed by addn. of alc. PkOH (51).]
 - ---- N-(Isobutyl)phthalimide (1-(N-phthalimido)-2-methylpropane): lfts. from CS₂, m.p. 93° (53). [This prod. has been reported from isobutyl bromide with K phthalimide on htg. in s.t. at 210° for 3-4 hrs. (53).]
 - ---- N-(Isobutyl)-3-nitrophthalimide: unreported.
 - --- N-(Isobutyl)tetrachlorophthalimide: unreported.
 - —— N-(Isobutyl)-N-(p-bromobenzenesulfonyl)-p-anisidide: cryst. from 75% alc., m.p. 78-79° (57). [From C (?) or the corresp. isobutyl bromide with N-(p-bromobenzenesulfonyl)-p-anisidine in alc. KOH after 1 hr. refluxing (57).]
 - —— N-(Isobutyl)-o-sulfobenzoic imide (N-(isobutyl)saccharin: m.p. 75.0° (55). [Not reported from C, but obtd. from isobutyl bromide or iodide with sodium saccharin in aq. butylcarbitol (1:6517) on refluxing 30 min. (55).]
 - p-(Isobutoxy)benzoic acid: m.p. 140-141° u.c. (56). [From \bar{C} with ethyl p-hydroxybenzoate (1:1534) in abs. alc. NaOEt on refluxing 1 hr. (56).] [Note, however, that this prod. does not distinguish \bar{C} from isoamyl chloride (3:7365) for which the corresp. p-(isoamoxy)benzoic acid has m.p. 141-142° (56).]
 - —— Isobutyl 2,4,6-tri-iodophenyl ether: m.p. 48.0° cor. (52). [This prod. has been obt. from isobutyl bromide (but not Č) with 2,4,6-tri-iodophenol in alc. NaOEt (52).] [Note that it would not distinguish Č from 1-chloropentane (3:7460) or 1-chlorohexane (3:7955).]
 - —— Isobutyl α-naphthyl ether: b.p. 301.5° cor. (54). (Corresp. picrate, m.p. 104.5–105.5° cor. (54).)
 - Isobutyl β-naphthyl ether: b.p. 204.5° cor. (54), m.p. 33.0-33.5° cor. (54). (Corresp. picrate, m.p. 84.0-85.0° cor. (54).)
- 3:7135 (1) Timmermans, Martin, J. chim. phys. 23, 778-779 (1926). (2) Timmermans, Bull. soc. chim. Belg. 27, 334-343 (1913); Cent. 1914, I 618. (3) Michael, Zeidler, Ann. 393, 110-111 (1912). (4) Linnemann, Ann. 162, 16-17 (1872). (5) Vogel, J. Chem. Soc. 1943, 638-639. (6) Turkevich, Smyth, J. Am. Chem. Soc. 64, 737 (1942). (7) Turkevich, Smyth, J. Am. Chem. Soc. 62, 247 (1940). (8) Wiswall, Smyth, J. Chem. Phys. 9, 357 (1941). (9) Fühner, Ber. 57, 514 (1924). (10) Britton, Coleman, Warren (to Dow Chem. Co.), U.S. 1,984,725, Dec. 18, 1934; Cent. 1935, I 3199.
- (11) Lecat, "L'azeotropisme," Brussels, 1918. (12) Lecat, Rec. trav. chim. 45, 624 (1926). (13) Lecat, Rec. trav. chim. 46, 242 (1927). (14) Lecat, Ann. soc. sci. Bruzelles 47, I 152, 155 (1927). (15) Haack (to Chem. Fabrik von Heyden), Ger. 624,693, Jan. 30, 1936; Cent. 1936,

I 3575; C.A. 30, 4876 (1936). (16) Ricard, Allenet et Cie, Brit. 191,002, Feb. 14, 1923; French 545,290, Oct. 9, 1922; Ger. 430,682, June 30, 1926; Cent. 1923, II 907. (17) Sabatier, Mailhe, Compt. rend. 169, 124 (1919). (18) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929). (19) Norris, Taylor, J. Am. Chem. Soc. 46, 755-757 (1924). (20) Dehn, Davis, J. Am. Chem. Soc. 29, 1328-1334 (1907).

(21) Shoesmith, Mackie, J. Chem. Soc. 1928, 2336. (22) Freund, J. prakt. Chem. (2) 12, 29-33 (1875). (23) Mouneyrat, Ann. chim. (7) 20, 530 (1900). (24) Pierre, Puchot, Ann. 163, 275-278 (1872). (25) Britton, Coleman, Hadler (to Dow Chem. Co.), U.S. 1,954,438, April 10, 1934; Cent. 1934, II 3180, C.A. 28, 3739 (1934); U.S. 2,018,345, Nov. 22, 1935; Cent. 1936, I 3907; C.A. 30, 106 (1936). (26) Hass, McBee, Weber, Ind. Eng. Chem. 27, 1190-1195 (1935). (27) Britton, Rouseh (to Dow Chem. Co.), U.S. 2,069,624, Feb. 2, 1937, Cent. 1937, I 5045. (28) Ssolonina, J. Russ. Phys.-Chem. Soc. 30, 431-449 (1898); Cent. 1898, II 887. (29) Ssolonina, J. Russ. Phys.-Chem. Soc. 30, 822-825 (1898); Cent. 1899, I 254. (30) Gault, Beloff, Bull. soc. chim. (5) 5, 295-300 (1938).

(31) Nef. Ann. 318, 21-23 (1901). (32) Senderens, Bull. soc. chim. (4) 3, 827-828 (1908); Compt. rend. 146, 1213 (1908). (33) Sabatier, Mailhe, Compt. rend. 141, 238 (1905). (34) Senderens, Compt. rend. 200, 612-615 (1935). (35) Mailhe, Compt. rend. 200, 612-615 (1935). (35) Mailhe, Compt. rend. 156, 658 (1913); 138, 407 (1904). (37) Nutting, Britton, Huscher, Petrie (to Dow Chem. Co.), U.S. 1,993,719, March 5, 1935; Cent. 1935, II 2879-2880, C.A. 29, 2549 (1935). (38) Kistiakowsky, Stauffer, J. Am. Chem. Soc. 59, 165-170 (1937). (39) Hass, McBee (to Purdue Research Foundation), U.S. 2,147,577, Feb. 14, 1939; Cent. 1939, II 226; Can. 378,829, Jan. 10, 1939; Cent. 1939, I 3454; C.A. 33, 2151 (1939). (40) Herzfelder, Ber. 26, 1260 (1893).

(41) Britton, Coleman, Moore (to Dow Chem. Co), U.S. 2,067,473, Jan. 12, 1937; Cent. 1937, II 1894, C.A. 31, 1432 (1937). (42) Olivier, Berger, Rec. trav. chim. 41, 640 (1921). (43) Chablay, Ann. chim. (9) 1, 484, 496 (1914). (44) Kolowalow, J. Russ. Phys.-Chem. Soc. 27, 457 (1895); Bull. soc. chim. (3) 16, 865 (1896). (45) Boedtker, Bull soc. chim. (3) 31, 966-968 (1904). (46) Schramm, Monatsh. 9, 615-618 (1888). (47) Coleman, Moore (to Dow Chem. Co.), U.S. 2,207,611, July 9, 1940, C.A. 34, 7934 (1940). (48) Houben, Boedler, Fischer, Ber. 69, 1781 (1936). (49) Fournier, Bull. soc. chim. (4) 5, 924 (1909). (50) Underwood, Gale, J. Am. Chem. Soc. 56, 2117-2120 (1934).

(51) Brown, Campbell, J. Chem. Soc. 1937, 1700.
(52) Drew, Sturtevant, J. Am. Chem. Soc. 61, 2666 (1939).
(53) Neumann, Ber. 23, 999 (1890).
(54) V. H. Dermer, O. C. Dermer, J. Org. Chem. 3, 290-291 (1938/39).
(55) Merritt, Levey, Cutter, J. Am. Chem. Soc. 61, 15-16 (1939).
(56) Lauer, Sanders, Leekley, Ungnade, J. Am. Chem. Soc. 61, 3050 (1939).
(57) Gillespie, J. Am. Chem. Soc. 56, 2740-2741 (1934).

B.P.		F.P.		
70.5°	at 760 mm. (1)	-34.6° (8) (9)	$D_4^{25} = 1.084591 \ (1)$	
69.8°	(2)	-34.4° (1)	$D_4^{20} = 1.09151 (1)$	
69.7°	(3)	-33.8° (5)		
69.69° cor.	at 760 mm. (4)		$n_{\rm D}^{20} = 1.41167$	(1)
69.3°	(5)			
68.9-69.3°	(5a)		$D_4^{15} = 1.09843 (1)$	
68.86-69.06°	(6)			
68.85-68.87°	at 746 mm. (7)		•	

Č with MeOH (b.p. 64.7°) forms a const.-boilg. mixt., b.p. 55.5°, contg. 79% Č; Č with EtOH (b.p. 78.3°) forms a const.-boilg. mixt., b.p. 63.2°, contg. 85.5% Č (2).

[For f.p./compn. data on mixts. of \bar{C} with methylene (di)chloride (3:5020), with 1,1-dichloroethane (ethylidene (di)chloride) (3:5035), with CCl₄ (3:5100), or with 1,1,1-trichloroethane (methylchloroform) (3:5085) see (8).]

[For prepn. of \tilde{C} from acetone (1:5400) with PCl₅ [55% yield (10) (together with 45%

2-chloropropene-1 (3:7020)) (10)] see (10) (5) (11) (12); for formn. (25.5% (13)) (together with other products) from propane by vapor-phase chlorination at 400° see (13) (14).]

 $\ddot{\mathbf{C}}$ on hydrolysis by htg. with 8 vols. aq. in s.t. at 160–180° (4), or with HI at 130° (4), or on passing with steam over cat. at 550–850° (15) yields acetone (1:5400). [For behavior of $\ddot{\mathbf{C}}$ with boilg. aq. + trace of NaHCO₃ or with boilg. aq. + Fe see (13).]

Č with alc. KOH yields (12) (13) (16) (17) 2-chloropropene-1 (3:7020), b.p. 22.3° [Č with excess alc. KOH yields (18) propyne-1 (allylene), b.p. -27.5°].

Č with H₂ over Ni at 300° (19) or over BaCl₂ at 380-400° [Beil. I₂-(73)] gives 2-chloro-propene-1 (3:7020), b.p. 22.5°.

3:7149 (1) Timmermans, Delcourt, J. chim. phys. 31, 91-92 (1934). (2) Lecat, Rec. trav. chim. 46, 242 (1927). (3) Hass, McBee, Weber, Ind. Eng. Chem. 28, 338 (1936). (4) Linnemann, Ann. 161, 67 (1872). (5) Turkevich, Smyth, J. Am. Chem. Soc. 62, 2469 (1940). (5a) Kohlrausch, Köppl, Monatsh. 65, 196 (1935). (6) Gross, Physik. Z. 32, 589 (1931). (7) Maryott, Hobbs, Gross, J. Am. Chem. Soc. 63, 660 (1941). (8) van de Vloed, Bull. soc. chim. Belg. 48, 260, 262 (1939). (9) Timmermans, Bull. soc. chim. Belg. 25, 300-327 (1911); Cent. 1911, II 1015. (10) Henne, Renoll, J. Am. Chem. Soc. 59, 2435 (1937).

(11) Friedel, Ladenburg, Ann. 142, 315-316 (1867). (12) Friedel, Ann. 112, 236 (1859). (13) McBee, Hass, Chao, Welch, Thomas, Ind. Eng. Chem. 33, 176-177 (1941). (14) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,073, June 4, 1935, Cent. 1936, I 1500. (15) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; Cent. 1932, I 2994. (16) Kahover, Kohlrausch, Z. physik. Chem. B-46, 178 (1940). (17) West, Farnsworth, Trans. Faraday Soc. 27, 147 (1931). (18) Friedel, Ann. 134, 262-264 (1865). (19) Mailhe, Bull. soc. chim. (4) 29, 538 (1921).

3:7145 3-CHLORO-2-METHYLPROPENE-1 CH₃ C₄H₇Cl Beil. I - 209 (Methallyl chloride; isobutenyl chloride; CH₂—CH₂ I₁— I₂—
$$\beta$$
-methylallyl chloride; γ -chloroisobutylene)

B.P.
$$[73.74^{\circ}]$$
 (1)] $D_{4}^{20} = 0.9475 \ (7)$ $n_{D}^{20} = 1.4340 \ (7)$ $71-74^{\circ}]$ (2) $72.2^{\circ}]$ (3) (8) $71.5-72.5^{\circ}]$ (4) (5) $70-71^{\circ}$ (6) at 739 mm. (7)

[See also 1-chloro-2-methylpropene-1 (3:7120).]

Note that for \bar{C} the designation methallyl chloride is now preferred (3); great care should be used to avoid confusion of \bar{C} with the isomeric and very closely related 1-chloro-2-methyl-propene-1 = isocrotyl chloride = β , β -dimethylvinyl chloride = α -chloroisobutylene (3:7120); both these compounds are now commercial products in the U.S.A.

Commercial \bar{C} contains approx. 4% (10) of the isomeric β,β -dimethylvinyl chloride (3:7120); owing to the proximity of their boiling points the two isomers are extremely difficult to separate by distillation (8), but owing to the great reactivity of the halogen of \bar{C} (see amplification below) and the relative unreactivity of the halogen of β,β -dimethylvinyl chloride (3:7120) interference from the latter in *metathetical* reactions of comml. \bar{C} need not be expected.

[For prepn. of \bar{C} from 2-methylpropene-1 (isobutylene) with Cl_2 see (3) (2) (5) (9) (other prods. are also formed); for formn. of \bar{C} as its equilibrium mixt. (10% \bar{C}) with β,β -dimethylvinyl chloride (3:7120) by actn. of H_2SO_4 on latter see (8).]

[For use of \tilde{C} as insecticide see (11) (12); for toxicity studies on beetles see (13); for detn. of \tilde{C} (when used as industrial furnigant) by reaction with ethanolamine in dioxane

. (14) or by thermal decomposition (15) see indic. refs.; for use of $\bar{\mathbf{C}}$ in prepn. of cellulose ethers see (16) (17).]

Reactions involving further substitution of H atoms in \bar{C} . [\bar{C} with Cl_2 at room temp. (8) cf. (5) (9) or in pres. of NaHCO₃ soln. at 0° (2) gives (70% yield (8)) a mixt. of approximately equal amounts of 1,3-dichloro-2-methylpropene-1 (3:5590) and 1-chloro-2-(chloromethyl)propene-2 (3:5633) (see also next paragraph).]

Reactions involving the double bond of C. [C with Cl₂ (5) (42) or with SO₂Cl₂ (42) also (see above) adds halogen to the unsaturated linkage yielding (5) (42) 1,2,3-trichloro-2-methylpropane (3:5710), b.p. 163.5-164° at 772 mm. (5).]

[Č with Br₂, however, gives chiefly (93% yield (8)) cf. (5) (9) the expected addition prod., 1-chloro-2,3-dibromo-2-methylpropane [Beil. I-128], b.p. 57° at 5 mm., $D_4^{20} = 1.9168$, $n_D^{20} = 1.5834$ (8).]

[\bar{C} adds HCl with considerable difficulty; e.g., \bar{C} with equal vol. 12 N HCl at 3°, or \bar{C} at b.p. treated with HCl gas for 2 hrs., shows no reaction (3); however, \bar{C} with equal vol. 12 N HCl shaken for $1\frac{1}{2}$ hrs. at 63° forms 30% of the expected 1,2-dichloro-2-methyl-propane (3:7430). — \bar{C} with dry HBr gas readily reacts giving (97% yield (8)) 1-chloro-3-bromo-2-methylpropane, b.p. 49° at 15 mm., $D_4^{20} = 1.4839$, $n_D^{20} = 1.4816$ (8) (note that this "abnormal" mode of addition of HBr is presumably attributable to the presence in \bar{C} of peroxidic material (8)).]

[$\ddot{\mathbf{C}}$ with aq. HOCl below 5° (1) (7) cf. (8), or $\ddot{\mathbf{C}}$ with Cl₂/aq. (8) (18) or even org. hypochlorites (18), gives by addn. of HOCl to unsatd. linkage 1,3-dichloro-2-methylpropanol-2 (3:5977). — $\ddot{\mathbf{C}}$ with aq. HOBr (from Br₂/KBr in aq.) at room temp. for 4 hrs. gives 97.5% yield (1)) 1-bromo-3-chloro-2-methylpropanol-2, b.p. 84-85° at 20 mm., $D_{20}^{20}=1.7578$, $n_{20}^{20}=1.5171$ (1). — $\ddot{\mathbf{C}}$ in ether with aq. HgO + I₂ (HOI) at room temp. for 5-6 hrs. gives (15% yield (1)) 3-chloro-1-iodo-2-methylpropanol-2, b.p. 101-103° at 18 mm., $n_{20}^{20}=1.547$ (1).]

[$\bar{\mathbf{C}}$ can also add hypochlorite esters; e.g., $\bar{\mathbf{C}}$ with ter-BuOCl (3:7165) in MeOH + trace p-toluenesulfonic acid at 40° for 3-4 hrs. gives (35% yield (6)) β , β -dichloro-ter-butyl methyl ether (1,3-dichloro-2-methoxy-2-methylpropane), b.p. 170° at 748 mm., $D_{-}^{20} = 1.1953$, $n_{D}^{20} = 1.4595$ (6).]

[\bar{C} can also undergo cat. hydration of the double bond; e.g., \bar{C} , although but slightly sol. in 80% H₂SO₄ at 0°, grad. dissolves on stirring; and after the solution is poured onto ice and the liquid distilled (8) (19) 63% of the original \bar{C} can be recovered as β -chloro-terbutyl alcohol (isobutylene chlorohydrin) (1-chloro-2-methylpropanol-2) (3:7752). Note that other acids can also be used for this hydration, e.g., 85% H₃PO₄, 70% HNO₃, 60% HClO₄, benzenesulfonic acid, etc., each having its own optimum conditions (8). Note also that in this reaction some 32% of the initial \bar{C} is not hydrated but is partially isomerized to a mixt. contg. 10% \bar{C} with 90% β , β -dimethylvinyl chloride (3:7120) (see also below) (8).]

[$\ddot{\mathbf{C}}$ can also be rearranged to the isomeric isocrotyl chloride; e.g., $\ddot{\mathbf{C}}$ (10 moles) with 80% H₂SO₄ (1 mole) stirred at 40° for 2½ hrs. gives an upper phase which conts. abt. 87% isocrotyl chloride + 7% $\ddot{\mathbf{C}}$ + 6% dichlorides and polymers; after washing free from acid, drying, and distilling it yields 85% β , β -dimethylvinyl chloride (3:7120) (8) (20).]

[C on sulfonation with dioxane sulfotrioxide in ethylene dichloride gives (21) a complex mixt. of prods.; about 40% of the SO₃ adds to the unsatd. linkage giving a cyclic anhydride of the carbyl sulfate type, the remainder substituting to yield the three isomeric monosulfonic acids of C; neither polymerization nor disulfonation takes place; for details the original paper (21) should be consulted.]

[For polymerization of C in the pres. of peroxides see (22).]

[C condensed with C6H6 in pres. of anhydrous liq. HF at 0-10° for 20 hrs. as directed

(23) gives mainly (66% yield) 1-chloro-ter-butylbenzene (1-chloro-2-methyl-2-phenyl-propane), b.p. 111° at 90 mm., accompanied by a small amt. (10% yield) bis-(1-chloro-ter-butyl)benzene, b.p. 140° at 4 mm.]

Reactions involving the halogen atom of C. [C upon hydrolysis with boilg. aq. K2CO3 soln. for 30 hrs. (9) cf. (5) (4) (43) or C with 10% aq. NaOH at 116° under press. (reaction complete in 15 min.) (10) (24) yields the corresp. methallyl alcohol (2-methylpropen-2-ol-1). b.p. 114.49° , $D_4^{20} = 0.8515$, $n_D^{20} = 1.4255$ (10); for important extensive survey of its reactions see (25). Note, however, that the nature of the material obtd. by hydrolysis of Č (because of the reactivity of the resultant methallyl alcohol) depends upon the precise conditions: e.g., if the reaction mixture becomes acid (either through inadequate mixing or lack of suitable neutralizer) isobutyraldehyde (1:0120) is formed (for instance, C with $CaCO_3 + aq$. at 140-180° under press. gives only isobutyraldehyde); if only temporary local regions of acidity develop and these subsequently become alkaline a complex mixt. (contg. isobutyric acid (1:1030), isobutyl alcohol (1:6165), and 2,2,4-trimethylpentanediol-1,3 [Beil. I-492, I₂-(558)]) may result from the action of alk. on the isobutyraldehyde. — Note also that the principal by-product of the neut. or alk. hydrolysis of C (invariably formed to abt. 5%) is bis-(methallyl) ether, b.p. 134.34°, $D_4^{20} = 0.8163$, $n_D^{20} = 1.4276$; note that this cpd. forms with methallyl alc. a const.-boilg. mixt., b.p. 114.06° (almost identical with the b.p. of methallyl alc. itself), contg. 81.3 wt. % of bis-(methallyl) ether + 18.7 wt. % methallyl alc. (10) (for still other azeotropes in this system see (10).)]

[$\bar{\mathbf{C}}$ with metal alkoxides or even $\bar{\mathbf{C}}$ with alcohols + conc. aq. NaOH readily gives the corresp. ethers: e.g., $\bar{\mathbf{C}}$ with NaOEt (9) or alc. KOH (9) or EtOH + 50% aq. NaOH refluxed for 7 hrs. (10) (26) gives ethyl methallyl ether, b.p. 84.8-86.8°, $D_4^{20}=0.8151$, $n_D^{20}=1.4067$ (10); $\bar{\mathbf{C}}$ (2 moles) with methallyl alc. (3 moles) + 50% aq. NaOH (4 moles) refluxed 2 hrs. gives (91.9% yield (10)) bis-(methallyl) ether (for consts. see preceding paragraph). (Note that this last ether cannot be prepd. by conventional bimolecular dehydration with acid because under such conditions only isobutyraldehyde results.) — Note that in reaction with alc. NaOEt $\bar{\mathbf{C}}$ has about the same reactivity as allyl chloride (3:7035) at 35° but slightly less at 50°; $\bar{\mathbf{C}}$, however, is less reactive at 35° than crotyl chloride (1-chlorobutene-2) (3:7205), and the latter less than 1-chloro-2-methylbutene-2 (3:7485) (10). — For reactn. of $\bar{\mathbf{C}}$ with phenol (1:1420) + dry $\mathbf{K}_2\mathbf{CO}_3$ refluxed 24 hrs. in acetone and giving (72% yield (4)) corresp. methallyl phenyl ether, b.p. 89° at 10 mm., see (4).]

[\bar{C} with aq. or alc. NaSH (10) (27) or \bar{C} with aq. thiourea refluxed 2 hrs. then made alkaline (28) gives (68% yield (28)) methallyl mercaptan, b.p. 93.5° at 760 mm. (28), 92.4–92.6°, $D_4^{20}=0.9137$, $n_D^{20}=1.4872$ (10). — \bar{C} with Na₂S.9H₂O at 120° under press. (10) (27) yields bis-(methallyl) sulfide, b.p. 172.8–173.0°, $D_4^{20}=0.8836$, $n_D^{20}=1.4862$ (10); \bar{C} with Na₂S₂ at 120° under press. (10) (27) yields bis-(methallyl) disulfide (no constagiven (10)) (both the sulfide and disulfide are valuable fly repellents and fumigants (29).) — \bar{C} with NaSCN (30) or NH₄SCN (10) gives on refluxing 3–6 hrs. (yields: 94–95% (30), 70% (10)) methallyl isothiocyanate, b.p. 169–170° at 760 mm. (30), 89–90° at 50 mm. (30), 78° at 25 mm. (30), 64° at 10 mm. (30) (forms with aq. a const.-boilg. mixt., b.p. 96.3–97.5° (10)), $D_4^{20}=0.9926$ (10), $n_D^{20}=1.5220$ (10).]

[$\ddot{\mathbf{C}}$ with NaBr in dry acetone refluxed for 5 hrs. gives (15-20% yield (10)) (27) methallyl bromide [Beil. I₂-(182)], b.p. 94.2-95.2° at 774 mm., $D_4^{20}=1.31335$, $n_D^{20}=1.46886$ (31). — $\ddot{\mathbf{C}}$ with NaI in dry ethyl methyl ketone (1:5405) refluxed 3 hrs. gives (12% yield (10)) (27) methallyl iodide, b.p. 25-30° at 3-5 mm., $n_D^{20}=1.4862$ (10) (very unstable and may decompose violently even at room temp. on prolonged storage (10)); note that in this reactn. $\ddot{\mathbf{C}}$ is more reactive than allyl chloride (3:7035) but somewhat less reactive than 1-chloro-2-methylbutene-2 (3:7485) and considerably less reactive than 1-chlorobutene-2 (crotyl chloride) (3:7205) (10). $\rightarrow \ddot{\mathbf{C}}$ with CuCN in nitrobenzene at 125-130° for $\frac{1}{2}$ hr.

gives (58% yield on CuCN (10)) (27) methallyl cyanide, b.p. 136.2-136.4°, $D_4^{20} = 0.844$, $n_{20}^{20} = 1.4202$ (10); note that use of NaCN gives a prod. of somewhat higher b.p., 138.0-139.5° (10), indicating pres. (by rearr.) of some β,β -dimethylacrylonitrile, b.p. 140-142°.]

[\bar{C} (1 mole) with conc. aq. NH₄OH (10 moles) at 90° under press. reacts completely within 2 minutes giving (10) (32) mixt. of 56% methallylamine, b.p. 78.8°, $D_4^{20} = 0.782$, $n_D^{20} = 1.431$ (10) (\bar{B} .HCl, m.p. 190–191° cor. (41); \bar{B} .PkOH, m.p. 202–206° cor. (41)) + 26% di-(methallyl)amine, b.p. 148–149°, $D_4^{20} = 0.799$, $D_D^{20} = 1.446$ (10), + 8% tri-(methallyl)amine, b.p. 194–195° (32), 83–85° at 15 mm., $D_4^{20} = 0.8256$, $D_D^{20} = 1.457$ (10), together with 5% tetra (methallyl)ammonium chloride; \bar{C} htd. with primary amines behaves in analogous fashion (10) (32).]

[C with Mg in dry other under very carefully regulated conditions (using large excess of Mg + ether and slow addn. of C) gives as high as 90% yield (10) corresp. methallyl MgCl; this with acetaldehyde (1:0100) gives (65% yield (10)) the expected secondary alc. 4-methylpenten-4-ol-2, b.p. 129° (10); similarly C with Mg + acetone (1:5400) in dry ether gives (59 mole % yield (10)) 2,4-dimethylpentene-4-ol-2, b.p. 126° (10) accompanied by (37 mole % yield (10)) of the coupling prod. di-methallyl (see next paragraph); note that this coupling reaction is very difficult to suppress.]

[\bar{C} with Mg in dry ether (10) (33), or with Na in dry ether (34), gives (yields: 90 mole % (10), 65% (33)) di-methallyl (2,5-dimethylhexadiene-1,5) [Beil. I-259, I₁-(122), I₂-(237)], b.p. 114.3° at 760 mm. (10) (33), $D_2^{20}=0.7487$ (10), 0.7423 (33), $n_D^{20}=1.4293$ (33). — Coupling of \bar{C} with other reactive alkenyl chlorides can also be effected: e.g., \bar{C} with allyl chloride (3:7035) + Mg in dry ether gives (33) 47% yield 2-methylhexadiene-1,5 [Beil. I-257, I₁-(120)], b.p. 88.1° at 760 mm., $D_D^{20}=0.7198$, $n_D^{20}=1.4184$ (33), +30% di-methallyl (see above) + 12% hexadiene-1,5 (biallyl) (1:8045). — For analogous mixed couplings with 2-chloropentene-3 (piperylene hydrochloride) (3:7465) see (36).]

[$\ddot{\mathbf{C}}$ with NaNH₂ in liq. NH₃ gives (27% yield (35)) 2,5-dimethylhexatriene-1,3,5, b.p. 145° at 747 mm., 90.2° at 200 mm., m.p. -9° , $n_{\mathrm{D}}^{21}=1.5150$ (35); note that an intermediate x-chloro-2,5-dimethylhexadiene, b.p. 33-34° at 5 mm., $n_{\mathrm{D}}^{20}=1.4612$, has been detected (35).]

[$\bar{\mathbf{C}}$ reacts normally with other RMgX compounds: e.g., $\bar{\mathbf{C}}$ with MeMgBr in di-isopropyl ether (ord. ether boils too close to prod.) gives (10) 2-methylbutene-1 (1:8210); $\bar{\mathbf{C}}$ with n-BuMgCl gives (83 mole % yield (10)) (33) 2-methylheptene-1, b.p. 119.3° at 760 mm., $D_4^{20} = 0.7206$, $n_D^{20} = 1.4123$ (33) (contaminated with 2-methylheptene-2 formed by rearrof the former by the inevitable MgCl₂ (33)); $\bar{\mathbf{C}}$ with iso-AmMgCl gives (10) 2,6-dimethylheptene-1, b.p. 140-143° (10); $\bar{\mathbf{C}}$ with C_6H_5 MgBr gives (10) methallylbenzene (2-methyl-1-phenylpropene-1), b.p. 175-176° (10).]

[For reactn. of C with diethyl malonate (1:3581) and with various diethyl alkylmalonates see (37); for prepn. of methallyl substituted barbituric acids (37) (4) or thiobarbituric acids (38) see indic. refs.]

- Methallyl acetate [Beil. I-137, I₂-(150)]: b.p. 124° at 760 mm., $D_{20}^{20} = 0.9239$, $n_{D}^{20} = 1.4129$ (39). [From \bar{C} + KOAc at 150° in s.t. (5) (9) cf. (10).] [For data on the formate, propionate, and n-butyrate see (39).]
- Methallyl benzoate: yel. odorless oil, b.p. 120° at 50 mm. (40). [Prepd. indirectly (40).]
- ---- Methallyl p-nitrobenzoate: unreported.
- ---- Methallyl 3,5-dinitrobenzoate: unreported.
- M-(Methallyl)phthalimide: white cryst. from MeOH, m.p. 88.5-90° cor. (41). [From C + K phthalimide in s.t. at 150° for 3 hrs. (41).]

3:7145 (1) Hurd, Abernathy, J. Am. Chem. Soc. 63, 976-977 (1941). (2) D'yakonov, Tishchenko, J. Gen. Chem. (U.S.S.R.) 9, 1255-1264 (1939); C.A. 34, 710 (1940). (3) Burgin, Eng., Groll, Hearne, Ind. Eng. Chem. 31, 1413-1419 (1939). (4) Schales, Ber. 70, 116-121 1937). (5) Pogorshelski, J. Russ. Phys.-Chem. Soc. 36, 1129-1184 (1904); Cent. 1905, 1 667-668. (6) Emiling, Vogt, Hennion, J. Am. Chem. Soc. 63, 1624-1625 (1941). (7) Suter, Malkemus, J. Am. Chem. Soc. 63, 980 (1941). (8) Burgin, Hearne, Rust, Ind. Eng. Chem. 33, 385-388 (1941). (9) Sheshukov, J. Russ. Phys.-Chem. Soc. 16, 478-511 (1884); Ber. 17, Referate 412-415 (1884). (10) Tamele, Ott, Marple, Hearne, Ind. Eng. Chem. 33, 115-120 (1941).

(11) Hymas, Food 9, 254-257 (1940); C.A. 35, 4105 (1941). (12) Briejer, Nature 141, 1099-1100 (1938). (13) Richardson, Casanges, J. Econ. Entomol. 35, 664-668 (1942); C.A. 37, 687 (1943). (14) Winteringham, J. Soc. Chem. Ind. 61-T, 186-187 (1942); C.A. 37, 1951 (1943). (15) Winteringham, J. Soc. Chem. Ind. 61-T, 190-192 (1942); C.A. 37, 1951 (1943). (16) Hahn (to du Pont Co.), U.S. 2,082,787, June 8, 1937; Cent. 1937, II 3838. (17) Maxwell (to du Pont Co.), U.S. 2,134,086, Oct. 25, 1938; Cent. 1939, I 859. (18) Groll (to Shell Development Co.), U.S. 2,067,392, Jan. 12, 1937; C.A. 31, 1432 (1937), N. V. de Bataafsche Petroleum Matschappii, Brit. 435,096, Oct. 10, 1935; French 789,289, Oct. 25, 1935, Cent. 1936, II 865. (19) Groll, Burgin (to Shell Development Co.), U.S. 2,042,222, May 26, 1936; Cent. 1937, I 1546; C.A. 36, 4875 (1936); N. V. de Bataafsche Petroleum Matschappii, French 791,644, Dec. 14, 1935; Cent. 1936, II 2227. (20) Groll, Burgin (to Shell Development Co.), U.S. 2,042,223, May 26, 1936; Cent. 1937, I 1274; C.A. 36, 4875 (1936).

(21) Suter, Bordwell, J. Am. Chem. Soc. 65, 507-517 (1943). (22) Bauer, Götz (to Röhm & Haas Co.), Ger. 706,510, April 24, 1941; C.A. 36, 1952 (1942). (23) Calcott, Tinker, Weinmayr, J. Am. Chem. Soc. 61, 1012 (1939). (24) Tamele, Groll (to Shell Development Co.), U.S. 2,072,-015, 2,072,016, Feb. 23, 1937; Cent. 1937, II 472, C.A. 31, 2612 (1937); N. V. de Bataafsche Petroleum Maatschappij, French 764,207, May 17, 1934; Cent. 1935, I 3199. (25) Hearne, Tamele, Converse, Ind. Eng. Chem. 33, 805-809 (1941). (26) Groll, Ott (to Shell Development Co.), U.S. 2,042,219, May 26, 1936; Cent. 1937, I 1013; C.A. 30, 4871 (1936) (27) Groll, Ott (to Shell Development Co.), U.S. 2,042,219, May 26, 1936; Cent. 33, 102 (1934). (29) Williams (to Shell Development Co.), U.S. 2,043,941, June 9, 1936; C.A. 30, 5336 (1936): Can. 353,986, Nov. 5, 1935; C.A. 36,

1472 (1936). (30) Bruson, Eastes, J. Am. Chem. Soc. 59, 2012 (1937). (31) Merejkowsky, Bull. soc. chim. (4) 37, 711-713 (1925). (32) Tamele, Groll (to Shell Development Co.), U.S. 2,172,822, Sept. 12, 1939; Cent. 1939, II 4350; C.A. 34, 448 (1940). (33) Henne, Chanan, Turk, J. Am. Chem. Soc. 63, 3475 (1941). (34) Przybytek, Ber. 29, 3240-3241 (1887). (35) Kharasch, Nudenberg, Sternfeld, J. Am. Chem. Soc. 62, 2035 (1940). (36) Henne, Gilman, J. Am. Chem. Soc. 66, 392-394 (1944). (37) Doran, Shonle, J. Am. Chem. Soc. 59, 1625-1626 (1937). (38) Tabern, Volweiler, J. Am. Chem. Soc. 57, 1961-1963 (1935). (39) Ryan, Shaw, J. Am. Chem. Soc. 62, 3469 (1940). (40) Kleinfeller, Ber. 62, 1597 (1929).

(41) Adams, Cairns, J. Am. Chem. Soc. 61, 2466 (1939). (42) Mooradian, Cloke, J. Am. Chem. Soc. 68, 787 (1946). (43) Köhler (to Rohm & Haas Co.) U.S. 2,323,781, July 6, 1943; C.A. 38, 116 (1944).

3:7150
$$\alpha$$
-CHLOROETHYL METHYL ETHER H C₃H₇OCl Beil. I - 606 (α -Methoxyethyl chloride) CH₃.C.O.CH₃ I₁-(327) I₂-(674)

B.P. $72-73^{\circ}$ cor. at 751 mm. (1) $D_4^{20} = 0.9909$ (2) $n_D^{20} = 1.4004$ (1) $70-72^{\circ}$ at 746 mm. (2) 0.9902 (1) 1.3969 (2)

[For prepn. (yields: 97% (1), 95% (2)) from paraldehyde (1:0170) + methyl alc. (1:6120) + dry HCl see (1) (2) (3).]

C on stdg. polymerizes to dark tarry residue.

[Č with Br₂ at 0° gives (3) α,β -dibromoethyl methyl ether, b.p. 67-69° at 22 mm. (3).] $\tilde{\mathbb{C}}$ on shaking with aq. yields acetaldehyde (1:0100), methyl alc. (1:6120), + HCl.

3:7150 (1) Henze, Murchison, J. Am. Chem. Soc. 53, 4077-4079 (1931). (2) Wallace, Henze, J. Am. Chem. Soc. 64, 2882 (1942). (3) Baker, J. Chem. Soc. 1942, 522.

B.P. 75.0° at 773 mm. (1)
$$D_4^{20} = 0.9211$$
 (1) $n_D^{20} = 1.42330$ (1)

Colorless liq. with odor similar to allyl chloride but less strong; insol. aq.

[For prepn. of \bar{C} from buten-1-ol-4 (allylcarbinol) [Beil. I-441, I₁-(226), I₂-(480)] with PCl₃ + pyridine (41% yield) see (1).] [\bar{C} is not formed (2) (3) during reactn. of butadiene-1.3 with HCl.]

3:7151 (1) Juvala, Ber. **63**, 1993 (1930). (2) Kharasch, Kritchevsky, Mayo, J. Org. Chem. **2**, 494 (1938). (3) Ganguly, J. Indian Chem. Soc. **13**, 581, 584 (1936).

3: 7153 ACRYLOYL CHLORIDE (Propenoyl chloride)
$$CH_2$$
— CH_2 — CH_3 — CH_4 — CH_5 — CH_5 — CH_5 — CH_5 — CH_6 — CH

Colorless mobile strongly lachrymatory liq., fumg. in air.

[For prepn. of \tilde{C} from sodium acrylate with POCl₃ (yields 80% (11), 60% (1), 27% (12), 22% (9) (2) (3) (4), with SOCl₂ (19% yield (9)), or from β -chloropropionyl chloride (3:5690) by loss of HCl (35% yield (12)) when passed over suitable cat. at 280–300° (5) see indic. refs.; for prepn. of \tilde{C} from acrylic acid (1:1020) with PCl₃ (66% yield) see (13).]

[For polymerization of \tilde{C} by light (10) in pres. of a small amt. of org. base see (6); for polymerization of \tilde{C} in pres. of u.v. light or by dibenzoyl peroxide see (9).]

[\bar{C} with MeOH yields (1) methyl β -chloropropionate (3:5765), b.p. 148°; \bar{C} with EtOH yields (1) ethyl β -chloropropionate (3:8290), b.p. 162°; \bar{C} with phenol yields (1) phenyl β -chloropropionate, b.p. 154–157° at 30 mm. (1); note, however, that \bar{C} reacting with a large excess of alcs. or phenols and/or in the pres. of acid binding agents such as CaCO₃ yields (7) esters of acrylic acid.]

[C with Na acrylate yields (1) acrylic anhydride, b.p. 97° at 35 mm. (1).]

Č with C₆H₆ + AlCl₃ yields (8) (2) (by Friedel-Crafts reactn. and subsequent ring closure) indanone-1 (1:5144), m.p. 42°.

 \bar{C} in CHCl₃ treated with Br₂ in CHCl₃ yields (1) 2,3-dibromopropionyl chloride, b.p. 191-193°, 97-99° at 37 mm. (1), $D_{-}^{0}=2.181$ (1), which with warm aq. easily hydrolyzes to α,β -dibromopropionic acid, m.p. 64° (1).

 \bar{C} on hydrolysis yields (1) acrylic acid (1:1020) q.v. (for the amide, m.p. 84-85° (11), anilide, and p-toluidide corresp. to \bar{C} see 1:1020).

3:7153 (1) Moureu, Ann. chim. (7) 2, 161-174 (1894). (2) Kohler, Am. Chem. J. 42, 380 (1909). (3) van der Burg, Rec. trav. chim. 41, 23 (1921). (4) Gilman, Heckert, McCracken, J. Am. Chem. Soc. 56, 438 (1928). (5) I. G., Brit. 333,079, Aug. 28, 1930; Cent. 1930, II 2830; U.S. 2,050,752, Aug. 11, 1936; C.A. 36, 6762 (1936). (6) Fikenscher (to I. G.), Ger. 577,040, May 22, 1933; Cent. 1933, II 1250; C.A. 27, 3950 (1933). (7) Bauer, Lauth (to Röhm & Haas Co.), Ger. 570,955, Feb. 22, 1933; Cent. 1933, I 2608. (8) Ref. 1, pp. 198-202. (9) Marvel, Levesque, J. Am. Chem. Soc. 61, 3244-3246 (1939). (10) Staudinger, Urech, Helv. Chim. Acta 12, 1131 (1929).

(11) Jones, Zomlefer, Hawkins, J. Org. Chem. 9, 506-507 (1944). (12) Mowry, J. Am. Chem. Soc. 66, 371-372 (1944). (13) Rehberg, Dixon, Fisher, J. Am. Chem. Soc. 67, 209 (1945).

[For prepn. of \bar{C} from 2-methylbutyn-3-ol-2 (dimethyl-ethynyl-carbinol) on shaking as specified (1) (3) with HCl + CuCl₂ + NH₄Cl; if Cu₂Cl₂ is used or if reactn. is protracted \bar{C} is isomerized (cf. (4)) to 1-chloro-3-methylbutadiene-1,2 (3:7390) q.v.; for reverse conversion of latter to \bar{C} (and other products) by htg. with CaCO₃ + aq. see (3).]

C on htg. with aq. + CaCO₃ at 80° gives (2) the precursor 2-methylbutyn-3-ol-2.

Č with NH₄OH/AgNO₃ gives (1) a white ppt. [dif. from 1-chloro-3-methylbutadiene-1,3 (3:9200)].

3:7155 (1) Favorskii, Favorskaya, Compt. rend. 200, 839-840 (1935); Cent. 1935, II 1340; C.A.
 30, 3651 (1935). (2) Favorskaya, J. Gen. Chem. (U.S.S.R.) 9, 386-395 (1939); C.A. 33, 9281 (1939); G.A. 34, 1303 (1940).
 4) Hurd (to Commercial Solvents Corp.), U.S. 2,274,611, Feb. 24, 1942; C.A. 36, 4138 (1942).

3:7160 1-CHLOROBUTANE CH₃.CH₂.CH₂.CH₂ C₄H₉Cl Beil. I - 118
(n-Butyl chloride; I₁-(38)
n-propylcarbinyl chloride) Cl I₂-(80)
B.P. F.P.

B.P.				F.P.	
78.6°	at	760 mm.	(1)	-123.1° (1	$D_4^{25} = 0.88098 (2)$
78.50°	at	760 mm.	(2)	(2	
78.3-78.4°	at	760 mm.	(3)		$D_4^{20} = 0.8866 \qquad (8)$
78.05°	at	760 mm.	(4)		0.88648 (2)
78.4-78.7°	u.c	•	(5)		0.8859 (8)
78.4-78.6°			(6)		0.8845 (12)
78.1°	at	760 mm.	(7)		0.88387 (11)
78.0°	at	762 mm.	(8)		(19)
78°			(9)		
77.96° cor.			(10)		$D_4^{15} = 0.89197 (2)$
77.7-77.9°	at '	762.7 mm.	(11)		0.88923 (11)
77.6-77.7°	at	743 mm.	(3)		(19)
77.6°	at	748 mm.	(12)		$n_{\rm D}^{20} = 1.4023 $ (9) (6)
77.6°	at '	741.3 mm.	(13)		1.40223 (8)
77.5-77.9°	at	760 mm.	(14)		1.4021 (18)
77.5°			(15)	(16)	1.40173 (17)
77.3-77.6°			(17)		1.40159 (8)
77.0°	at	769 mm.	(8)		1.40148 (16)
76-77°	at	750 mm.	(18)		1.40147 (19)

See also Note 1.

Note 1: For further data on b.p. at press. over range 565-760 mm. see (15).

Note 2: Č is very spar. sol. aq.; e.g., 0.066 wt. % at 12° (20).

Binary systems of \tilde{C} with other org. cpds. For f.p./compn. data on mixts. of \tilde{C} with ter-BuCl (3:7045) see (21); for partial vapor press. (17) or n_D^{20} (22) of mixts. of \tilde{C} with n-heptane (1:8575) or n-BuBr see indic. refs.

Č forms azeotropes with various other org. cpds.; e.g., Č with MeOH (1:6120) forms a const.-boilg. mixt., b.p. 57.0° at 760 mm., contg. 73 wt % Č (4); Č with EtOH (1:6130) forms a const.-boilg. mixt., b.p. 65.7° at 760 mm., contg. 79.7 wt. % Č (4); Č with n-PrOH (1:6150) forms a const.-boilg. mixt., b.p. 74.8° at 760 mm., contg. about 82 wt. % Č (4); Č with iso-PrOH (1:6135) forms a const.-boilg. mixt., b.p. 70.8° at 760 mm., contg. 77 wt. % Č (4); Č with isobutyl alc. (1:6165) forms a const.-boilg. mixt., b.p. 77.65° at 760 mm., contg. 96 wt. % Č (4); Č with EtOAc (1:3015) forms a const.-boilg. mixt., b.p. 75.5° at 760 mm., contg. 55 wt. % Č (23).

[For prepn. of \tilde{C} from *n*-butyl alc. (1:6180) with dry HCl gas on protracted htg. (11) (13) (24) (25), with conc. aq. HCl + ZnCl₂ (2 moles) (yields: 76-78% (26) (27) (29), 66-72% (30), 64-66% (28), 65% (8)) (31), other metal salts (31) (32), or H₃PO₄ (33); with PCl₃ + ZnCl₂ (60% yield (30)) (34) or PCl₃ + pyridine (for important study of mechanism see (35) (36)); with PCl₅ + ZnCl₂ (74% yield (30)) cf. (35) (36); with SOCl₂ + pyridine (71% yield (8)) (for important study of mechanism see (37) (36)) see indic. refs.]

[For formn. of \bar{C} from *n*-butyl HSO₄ with HCl (25); from *n*-butyl MgBr with *p*-toluene-sulfonyl chloride (8.7% yield (38)); from *n*-butyl *p*-toluene-sulfonate as by-prod. of its reactn. with benzyl MgCl in prepn. of *n*-amylbenzene (39) cf. (40) (41); from *n*-butyl iodide with HgCl₂ in s.t. at 120–130° for 2 hrs. (10); from *n*-butylamine with HNO₂ (5.2% \bar{C} accompanied by 36.5% butenes + 25% butanol-1 + 13.2% butanol-2 + 2.8% 2-chlorobutane (42)); from *n*-butane with Cl₂ at 400–475° (together with other prods. (3)) see indic. refs.]

[For use as denaturant for alc. see (43) (for detn. of \bar{C} in denatured alc. see (4)); for use in removal of water from volatile fatty acids see (45); for study of anthelmintic props. see (46).]

Pyrolysis of \bar{C} . [\bar{C} at 450-650° without catalyst loses HCl and yields exclusively butene-1 (3) (47); however, \bar{C} passed at 450° over CaCl₂ cat. gives mixt. contg. 20% butene-1 + 80% cis + trans isomers of butene-2 (3) (47) (for influence of other cat. cf. (48) (49)).]

Further halogenation of C. [C with Cl₂ under various conditions (50) (51) (52) (53) (54) (5) gives a mixt. of 1,1-dichlorobutane (3:7550), 1,2-dichlorobutane (3:7680), 1,3-dichlorobutane (3:7925), and 1,4-dichlorobutane (3:5835) (together with higher chlorination prods.); note that the chlorination is facilitated by peroxides or by light but inhibited by O₂ (e.g., C with Cl₂ in absence of air at 0° in dark reacts 7% in 20 hrs. but in pres. of 2 mole % ascaridole 85% in same time or in light 100% in 1 min.; in pres. of 2% O₂ in dark no reactn. occurs in 96 hrs. (18). — C (2.5 moles) with SO₂Cl₂ (1 mole) + trace dibenzoyl peroxide 3 hrs. under reflux in the dark gives (55) mixt. contg. 25% 1,2-dichlorobutane (3:7680) + 50% 1,3-dichlorobutane (3:7925) + 25% 1,4-dichlorobutane (3:5835). — C (1 mole) with SbCl₅ (1 mole) gives on warming (56) 2,3-dichlorobutane (3:7615).]

 \bar{C} with Br₂ in pres. of Fe gives (57) 1,2-dibromobutane [Beil. I-120, I₂-(83)], b.p. 166°. Reactions of the halogen atom of \bar{C} . Note that in \bar{C} the chlorine atom is much less

reactive than that of sec.-butyl chloride (3:7125) or ter-butyl chloride (3:7045).

[For study of hydrolysis of C in pres. and abs. of acid see (58).]

[For study of rate of reactn. of C with LiI, NaI, or KI in acctone see (59) (60).]

[For study of rate of reactn. of C with Na n-propylate see (61).]

[Č with aniline as directed yields (62) N-(n-butyl)aniline and/or N,N-di-(n-butyl) aniline; for analogous study of Č with N-methylaniline (63), N-ethylaniline (63), o-toluidine (64), p-toluidine (64), unsym.-m-xylidine (65) see indic. refs.]

[\bar{C} with C_6H_6 + AlCl₃ gives (69% yield (66)) sec.-butylbenzene (1:7490) (note isomerization of carbon chain) (for comparison of reactivity of \bar{C} with other *n*-butyl halides see (67)); \bar{C} with C_6H_6 + Al/Hg gives both (68) sec.-butylbenzene (1:7490) and *n*-butylbenzene

(1:7515). — Č with toluene + AlCl₃ gives (45% yield (69) of a mixt. of both m- and p-sec.-butyltoluenes.]

[$\check{\mathbf{C}}$ with $\mathbf{C_6H_6}$ in dry liq. HCl at 195° under press. gives (70) 30% yield sec.-butylbenzene (1:7490) + 60% di-(sec.-butyl)benzene; for analogous behavior of $\check{\mathbf{C}}$ with toluene see (70).] [$\check{\mathbf{C}}$ with CO + AlCl₃ or similar cat. under press. yields (71) acids and ketones.]

Reaction of \tilde{C} to form organometallic cpds. [\tilde{C} with metallic Li in dry ether under N₂ gives (yields: 75–80% (72), 77% (73), 70–75% (74)) n-butyllithium (for study of rate of formn. of n-BuLi as compared with n-BuBr, C_0H_0Br , C_0H_0Br , C_0H_0Br , C_0H_0Br , C_0H_0Br , C_0H_0Rr see (85)); this prod. with dry CO₂ in ether at 0° gives (45% yield (75)) di-n-butyl ketone (1:5493) or with CO₂ in C_0H_0 at room temp. also (75) tri-n-butylcarbinol; for study of relative reactivity of n-BuLi as compared with n-BuMgBr, C_0H_0 MgBr, etc., see (76); note, however, that full chemistry of n-BuLi cannot be discussed here.]

[\bar{C} with metallic Na in pet. ether yields (77) *n*-butylsodium; on carbonation with CO₂ this prod. gives (77) (78) (80) both *n*-valeric acid (1:1060) and *n*-propylmalonic acid; for study of reactn. of *n*-BuNa with C₆H₆ see (77); note, however, that full chemistry of *n*-BuNa cannot be covered here.]

 \bar{C} with Mg in dry ether gives (yields: 98.5% (81), 91.2% (82) (83), 85% (84)) n-BuMgCl; for studies on rate of forms. of n-BuMgCl (as compared with C_6H_6MgBr , or with other n-Bu halides, etc.) (85), on effect of rapid addn. of \bar{C} on yield (83), on effect of concentration of \bar{C} (84) see indic. refs.; for study of equilibrium composition of ether solns. of n-BuMgCl see (86) (87); for study of competitive reaction of mixts. of \bar{C} with n-BuBr and with n-BuI in forms. of RMgX see (88). — For certain important reactions of n-BuMgCl see below but note that full chemistry of this cpd. cannot be included here.

[\bar{C} with Mg + trace of I₂ but without solvent at 79-82° for 3 hrs. gives (10% yield (89)) n-octane (1:8655); \bar{C} + Mg + I₂ in toluene in similar fashion gives (6% yield (89)) p-(n-butyl)toluene.]

- © n-Valeric acid (1:1060) q.v. [From \bar{C} by conversion to n-BuMgCl (see above) and carbonation with CO₂ (yields: 72-73% (90), 80% (91)) (note that this prod. may be accompanied by more or less di-n-butyl ketone (1:5493) and tri-n-butylcarbinol (91)), or by conversion of \bar{C} with KCN to n-valeronitrile and hydrolysis of the latter with 67% H₂SO₄ (52) (92).]
- n-Valeranilide: m.p. 62-63° u.c. (93), 63° cor. (94). [From Č by conversion to n-BuMgCl (see above) and reactn. in dry ether with phenyl isocyanate (93) (42) cf. (93).]
- ① n-Valero-p-toluidide: m.p. 72-73° u.c. (93). [From \bar{C} by conversion to n-BuMgCl (see above) and reactn. in dry ether with p-tolyl isocyanate (93).] [Note that this derivative does not afford good distinction from n-amyl chloride (3:7460) for which the corresp. n-capro-p-toluidide has m.p. 74-75° u.c. (93).]
- D n-Valero-α-naphthalide: m.p. 109-110° u.c. (93). [From Č by conversion to n-BuMgCl (see above) and reactn. in dry ether with α-naphthyl isocyanate (93).] [Note that this derivative does not afford good distinction from isoamyl chloride (3:7365) for which the corresp. isocaproic α-naphthalide has m.p. 110-111° u.c. (93).]
- ---- n-Butyl mercuric chloride (n-BuHgCl): m.p. 130° cor. (95), 129° (96), 127.5° (98), 126° (96), 125.5° (97), 125° (99). [Prepd. indirectly but should be easily preparable from n-BuMgCl + HgCl₂ cf. (98), since it has been similarly prepd. from n-BuMgBr (95).]
- S-(n-Butyl)isothiourea picrate: m.p. 177° (100). [From Č (1 g.) with thiourea (1 g.) in alc. (10 ml.) on refluxing for 2 hrs., then adding PkOH (1 g.), htg. until a clear soln. results, then cooling (100).]—[Note that this derivative does not dis-

- tinguish \tilde{C} from *n*-propyl chloride (3:7040) for which the corresp. S-(*n*-propyl)-isothiourea picrate has m.p. 176° (100), nor from isoamyl chloride (3:7365) for which the corresp. S-(isoamyl)isothiourea picrate has m.p. 173° (100).]
- —— N-(n-Butyl)phthalimide (1-(N-phthalimido)butane): cryst. from dil. AcOH, m.p. 34° (101), b.p. 311.8° cor. at 758 mm. (102). [Prepd. indirectly from n-butyl-amine (101) (102); direct prepn., e.g., from C + K phthalimide in pres. of KI never reported and m.p. too low to serve as good derivative.]
- N-(n-Butyl)-3-nitrophthalimide: pr. from CS₂, m.p. 71-72° (103). [From C with
 K 3-nitrophthalimide on refluxing for 10 hrs. (103); for photographs of crystals see
 (104).]
- N-(n-Butyl)tetrachlorophthalimide: pl. from alc., m.p. 153-154° (105). [From C with K tetrachlorophthalimide by htg. at 200° for 10 hrs. (105).]
- N-(n-Butyl)saccharin: cryst. from dil. alc., m.p. 38° (106). [From C with sodium saccharin in aq. butylcarbitol (1:6517) contg. KI on refluxing for 30 min. (106).]
- —— N-(n-Butyl)-N-(p-bromobenzenesulfonyl)-p-anisidide: cryst. from 75% alc., m.p. 74.5° u.c. (107). [This prod. has not been reported from C but has been obt. from n-BuBr with N-(p-bromobenzenesulfonyl)-p-anisidide in alc. KOH after 1 hr. reflux (107).]
- —— p-(n-Butoxy)benzoic acid: m.p. 147-148° (108), changing to a cloudy viscous liq. clearing sharply at 160° (108) cf. (109). [From $\bar{\mathbb{C}}$ with ethyl p-hydroxybenzoate (1:1534) in abs. alc. NaOEt on refluxing 1 hr. (108)]. [Note, however, that this prod. does not distinguish $\bar{\mathbb{C}}$ from n-propyl chloride for which the corresp. p-(n-propoxy)benzoic acid has m.p. 145.5-147°; the two prods. do, of course, have slightly different Neut. Eqs.]
- --- n-Butyl 2,4,6-triiodophenyl ether: m.p. 66° cor. (110). [This prod. has not been reported for C itself but has been obtd. from n-BuBr with 2,4,6-triiodophenol in abs. alc. NaOEt on refluxing for 30 min. (110).]
- —— n-Butyl α-naphthyl ether: b.p. 308.5° cor. (111), 310° (112) (corresp. picrate, m.p. 85.0° cor., Neut. Eq. 429 (111)).
- ---- n-Butyl β-naphthyl ether: b.p. 309.0° cor. (111), 311° (112); m.p. $33.0-33.5^{\circ}$ (111) (corresp. picrate, m.p. $67.0-67.5^{\circ}$ cor. (111), 67° (113)).
- 3:7160 (1) Timmermans, Bull. soc. chim. Belg. 30, 65 (1921). (2) Timmermans, Hennaut-Roland, J. chim. phys. 27, 408-410 (1930). (3) Weston, Hass, J. Am. Chem. Soc. 54, 3337-3343 (1932). (4) Lecat, Rec. trav. chim. 46, 242 (1927). (5) Rust, Vaughan, J. Org. Chem. 6, 479-488 (1941). (6) Smyth, McAlpine, J. Chem. Phys. 3, 348 (1935). (7) Kahovec, Kohlrausch, Z. physik. Chem. B-48, 8 (1940). (8) Vogel, J. Chem. Soc. 1943, 638-639. (9) Wiswall, Smyth, J. Chem. Phys. 9, 357 (1941). (10) Linnemann, Ann. 161, 197 (1872).
- (11) Karvonen, Ann. Acad. Sci. Fennicae, 3-A, 1-103 (1912); Cent. 1912, II 1271. {12} Groves, Sugden, J. Chem. Soc. 1937, 161. {13} Lieben, Rossi, Ann. 158, 160-161 (1871). {14} Mathews, Fehlandt, J. An. Chem. Soc. 53, 3216 (1931). {15} Lenth, J. An. Chem. Soc. 55, 3283 (1933). {16} Smyth, Rogers, J. Am. Chem. Soc. 52, 2228 (1930). {17} Smyth, Engel, J. An. Chem. Soc. 51, 2649-2650, 2655, 2658 (1929). {18} Kharasch, Berkman, J. Org. Chem. 6, 810-817 (1941). {19} Karvonen, Ann. Acad. Sci. Fennicae, 5-A, No. 6, 123 (1914). {20} Fühner, Ber. 57, 514 (1924).
- (21) Timmermans, Bull. soc. chim. Belg. 43, 630 (1934). (22) Smyth, Engel, Wilson, J. Am. Chem. Soc. 51, 1739 (1929). (23) Lecat, Ann. soc. sci. Bruxelles 48, I 116, 120 (1928). (24) Basel, Kaufler (to A. Wacker Soc. Elektrochem. Ind.), Ger. 462,993, July 20, 1928; Cent. 1932, I 1044; C.A. 23, 4133 (1928). (25) I.G., French 716,217, Dec. 17, 1932; Cent. 1933, I 3345. (26) Copenhaver, Whaley, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 142-144 (1941). (27) Whaley, Copenhaver, J. Am. Chem. Soc. 60, 2497-2498 (1938). (28) Norris, Org. Syntheses, Coll. Vol. 1 (1st ed.), 137-138 (1932); 5, 27-29 (1925). (29) Norris, Taylor, J. Am. Chem. Soc. 46, 756 (1924). (30) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929).
- (31) Ricard, Allenet et Cie, Brit. 191,002, Nov. 2, 1922; French 545,290, Oct. 9, 1927; Cent. 1923, II 907: Ger. 430,862, June 30, 1926; Cent. 1925, II 1097. (32) Frei (to du Pont Co.), U.S. 1,784,423, Dec. 9, 1930; Cent. 1931, I 2672; C.A. 25, 303 (1931): French 692,790, Nov. 30, 1930;

Cent. 1931, I 2112; C.A. 25, 1537 (1931). (33) A. Wacker Soc. Eicktrochem. Ind., French 687,855, Aug. 14, 1930; Cent. 1930, II 3637; C.A. 25, 709 (1931). (34) Polish 26,428, June 11. 1938; Cent. 1939, I 1856. (35) Gerrard, J. Chem. Soc. 1949, 1464-1469. (36) Gerrard, J. Chem. Soc. 1949, 218-230. (37) Gerrard, J. Chem. Soc. 1939, 99-103. (38) Gilman, Fothergill, J. Am. Chem. Soc. 51, 3506 (1929). (39) Gilman, Robinson, Org. Syntheses, Coll. Vol. 2 (1st ed.).

Am. Chem. Soc. 31, 3000 (1828); (197 (1818)), 1401 (1918); 19, 4-5 (1928). (40) (1918); 19, 4-5 (1928). (41) Rossander, Marvel, J. Am. Chem. Soc. 50, 1228 (1928). (42) Whitmore, Langlois, J. Am. Chem. Soc. 54, 3441-3447 (1932). (43) Bannister (to Comml. Solvents Corp.), U.S. 1,779,-687, Oct. 28, 1930; Cent. 1931, 1 376; C.A. 25, 168 (1931). (44) Hoff, J. Soc. Chem. Ind. 56, 1277 (1932). (43) (1932). (44) Hoff, J. Soc. Chem. Ind. 56, 1277 (1932). (45) Soc. 3 Apon de Distillating des 244T (1931); Cent. 1931, II 1506; C.A. 25, 4818 (1931). (45) Soc. Anon. des Distilleries des Deux-Sèvres, Danish 36,067, May 31, 1926; Cent. 1928, I 584: Austrian 117,474, April 25, 1930; Cent. 1930, II 620. (46) Wright, Schaffer, Am. J. Hyg. 16, 325-428 (1932); J. Parasilol. 16, 107-108 (1929); C.A. 26, 4869 (1932). (47) Hass, Weston (to Purdue Research Foundation), U.S. 1,975,456, Oct. 2, 1934; Cent. 1935, II 2880; C.A. 28, 7260 (1934). (48) Senderens, Compt. rend. 200, 612-615 (1935). (49) Senderens, Aboulenc, Compt. rend. 202, 104-107 (1936). (50) Perkin, J. Soc. Chem. Ind. 31, 616-624 (1912); Cent. 1912, II 1210-1212; C.A. 6, 2692-2693 (1912).

(51) Muskat, Northrup, J. Am. Chem. Soc. 52, 4053-4055 (1930). (52) Muskat (to du Pont Co.), U.S. 2,038,593, April 28, 1936; Cent. 1936, II 3358; C.A. 30, 3912 (1936). (53) Hass, McBes, Weber, Ind. Eng. Chem. 27, 1190-1195 (1935). (54) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 893-896 (1937); Cent. 1938, II 2575; C.A. 31, 5755 (1937). (55) Kharasch, Brown, J. Am. Chem. Soc. 61, 2145 (1939). (56) Meyer, Müller, J. prakt. Chem. (2) 46, 186 (1892). (57) Herzfeld, Ber. 26, 1260 (1893). (58) Olivier, Berger, Rec. trav. chim. 41, 640 (1921). (59) Conant, Hussey, J. Am. Chem. Soc. 47, 476-488 (1925). (60) Conant, Kirner, J. Am. Chem. Soc. 46, 248 (1924).

(61) Malkiel, Mason, J. Org. Chem. 8, 200 (1943). (62) Reilly, Hickinbottom, J. Chem. Soc. 111, 1026-1034 (1917); 113, 99-111 (1918). (63) Reilly, Hickinbottom, J. Chem. Soc. 117, 130-132 (1920). (64) Reilly, Hickinbottom, J. Chem. Soc. 113, 974-985 (1918). (65) Reilly, O'Neill, J. Soc. Chem. Ind. 46, T 226-228 (1927); Cent. 1927, II 918. (66) Boedtker, Bull. soc. chim. (4) 45, 648-649 (1929). (67) Calloway, J. Am. Chem. Soc. 59, 1477-1478 (1937). (68) Diuguid, J. Am. Chem. Soc. 63, 3527-3528 (1941). (69) Shoesmith, McGechen, J. Chem. Soc. 1930, 2234-2235. (70) Simons, Hart, J. Am. Chem. Soc. 66, 1310-1311 (1944).

(71) I.G., French 671,241, Dec. 10, 1929; Cent. 1930, II 620; Brit. 310,438, May 23, 1929; Cent. 1929, II 1214. (72) Gilman, Zoellner, Selby, J. Am. Chem. Soc. 54, 1957-1962 (1932). (73) Gilman, Zoellner, Selby, J. Am. Chem. Soc. 55, 1252-1257 (1933). (74) Coleman, Hermanson, Johnson, J. Am. Chem. Soc. 59, 1897 (1937). (75) Gilman, Van Ess, J. Am. Chem. Soc. 55 1260 (1933). (76) Gilman, Kirby, J. Am. Chem. Soc. 55, 1265-1270 (1933). (77) Morton. Richardson, Hallowell, J. Am. Chem. Soc. 63, 327-328 (1941). (78) Morton, LeFevre, Hechenbleikner, J. Am. Chem. Soc. 58, 757 (1936). (79) Morton, Hechenbleikner, J. Am. Chem. Soc. 58, 1699 (1936). (80) Morton, Davidson, Newey, J. Am. Chem. Soc. 64, 2242 (1942).

(81) Houben, Boedler, Fischer, Ber. 69, 1768, 1776 (1936). (82) Gilman, Zoellner, Dickey, J. Am. Chem. Soc. 51, 1580-1581 (1929). (83) Gilman, Zoellner, Dickey, J. Am. Chem. Soc. 51. 1585 (1929). (84) Gilman, Vanderwal, Bull. soc. chim. (4) 45, 641-644 (1929). (85) Gilman, Zoellner, Dickey, Selby, J. Am. Chem. Soc. 57, 1062 (1935). (86) Noller, Raney, J. Am. Chem. Soc. 62, 1749-1751 (1940). (87) Noller, Castro, J. Am. Chem. Soc. 64, 2509-2510 (1942). (88) Rudd, Turner, J. Chem. Soc. 1928, 686-691. (89) Schorigin, Issaguljanz, Gussewa, Ber. 66, 1430 (1933). (90) Gilman, Kirby, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 361-364 (especially Note 10) (1941); (1st ed.), 353-356 (espec. Note 10) (1932).

(91) Ivanov, Bull. soc. chim. (4) 37, 290-293 (1927). (92) Hass, Marshall, Ind. Eng. Chem. 23, 353 (1931). (93) Underwood, Gale, J. Am. Chem. Soc. 56, 2118-2119 (1934). (94) Schwartz, Johnson, J. Am. Chem. Soc. 53, 1063-1067 (1931). (95) Slotta, Jacobi, J. prakt. Chem. (2) 120, 276 (1929). (96) Kharasch, Marker, J. Am. Chem. Soc. 48, 3141 (1926). (97) Tiffeneau, Cent. 1921, III 26. (98) Marvel, Gauerke, Hill, J. Am. Chem. Soc. 47, 3010 (1925). (99) Marvel, Gould, J. Am. Chem. Soc. 44, 156 (1922). (100) Levy, Campbell, J. Chem. Soc. 1939, 1443.

(101) Vanags, Acta Univ. Latviensis, Kim. Fakultat, Series 4, No. 8, 405-421 (1939); Cent. 1939. II 3816; C.A. 34, 1982-1983 (1940). (102) Sachs, Ber. 31, 1228 (1898). (103) Sah, Ma, Ber. 65, 1630-1633 (1932). (104) Sah, Ma, Sci. Repts. Natl. Tsing Hua Univ. 2, 147-149 et. seq. (1933). (105) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934). (106) Merritt, Levey, Cutter, J. Am. Chem. Soc. 61, 15-16 (1939). (107) Gillespie, J. Am. Chem. Soc. 56, 2740-2741 (1934). (108) Lauer, Sanders, Leekley, Ungnade, J. Am. Chem. Soc. 61, 3050 (1939). (109) Bennett, Jones, J. Chem. Soc. 1939, 424. (110) Drew, Sturtevant, J. Am. Chem. Soc. 61, 2666 (1939).

(111) V. H. Dermer, O. C. Dermer, J. Org. Chem. 3, 290-291 (1938/39). (112) Slotta, Franke, Ber. 63, 685 (1930). (113) Wang, J. Chinese Chem. Soc. 1, 61-62 (1933).

3:7165 ter-BUTYL HYPOCHLORITE (CH₃)₃C—OCl C₄H₉OCl Beil. I — (Trimethylcarbinyl hypochlorite) I₁— I₂-(415) B.P. 79.6° at 750 mm. (1)
$$D_4^{18} = 0.9583$$
 (1) 77-79° (16)

Pale yellow mobile liquid with characteristic irritating odor. — \bar{C} violently attacks the eyes and mucous membranes. — \bar{C} is relatively stable and if protected from bright light can be kept at ordinary temps. for months with little or no decomposition (1). \bar{C} should, however, be handled with care since it is particularly susceptible to photochemical decomposition which may occur with explosive violence (2).

[For prepn. of \tilde{C} from *ter*-butyl alcohol (1:6140) + Cl₂ + alk. in pract. quant. yield see (1) (2) (3), 60% yield (16); from *ter*-butyl alc. (1:6140) + HOCl in CCl₄ see (15); for manufacture of \tilde{C} see (4).] [For use in bleaching of textles, fruits, etc., see (5) (6) (7).]

[For general survey of reactns. of \bar{C} see (8); for study of reactns. of \bar{C} with olefins (2) (13) (16) (17) (18) or olefins contg. activating groups (9) (10), with group $R_2C=N.MgX$ (3), or with Schiff's bases (11) (12) see indic. refs.; for study of \bar{C} in Friedel-Crafts reactn. see (14).]

Č on sufficient htg. or on exposure to bright sunlight yields (1) acetone (1:5400) + methyl chloride (3:7005). — [For data on stability of Č in aq. or in CCl4 see (15).]

 \bar{C} with aq. KI acidified with AcOH yields I_2 (use in detn. of \bar{C} (1)).

3:7165 (1) Chattaway, Backeberg, J. Chem. Soc. 123, 2999-3003 (1923). (2) Irwin, Hennion, J. Am. Chem. Soc. 63, 858-860 (1941). (3) Hauser, Humble, Haus, J. Am. Chem. Soc. 54, 2476-2480 (1932). (4) Deanesty, (to Shell Development Co.), U.S. 1,938,175, Dec. 5, 1933; Cent. 1934, I 1709; C.A. 28, 1053 (1934). (5) Magill (to du Pont), U.S. 2,155,728; April 25, 1939; Cent. 1939, II 1808; C.A. 33, 6069 (1939). (6) Carlisle (to du Pont), U.S. 2,152,532, March 28, 1939; Cent. 1939, II 276; C.A. 33, 5085 (1939). (7) Imperial Chem. Ind., Brit. 523,467, July 15, 1940; C.A. 34, 6470 (1941). (8) Clark, Chem. News 143, 265-267 (1931). (9) Emling, Vogt, Hennion, J. Am. Chem. Soc. 49, 2071-2079 (1927).

(11) Fusco, Musante, Gazz. chim. ital. 66, 258-264 (1936); Cent. 1936, II 2341; C.A. 31, 1777 (1937). (12) Musante, Fusco, Gazz. chim. ital. 66, 639-648 (1936); Cent. 1937, I 1674; C.A. 31, 3459 (1937). (13) N. V. de Bataafsche Petroleum Maatschappi, Freuch 740,350, Jan. 24, 1933; Cent. 1933, I 2870; C.A. 27, 2160 (1933). (14) Bergman, Lowy, J. Am. Chem. Soc. 60, 2596-2597 (1938). (15) Taylor, MacMullin, Gammal, J. Am. Chem. Soc. 47, 397-398 (1925). (16) Hanby, Rydon, J. Chem. Soc. 1946, 114-115. (17) Harford (to A. D. Little, Inc.), U.S. 2,207,983, July 16, 1940; C.A. 34, 7932 (1940). U.S. 2,107,789, Feb. 8, 1938; Cent. 1938, I 4718; C.A. 32, 2543 (1938): U.S. 2,054,814, Sept. 22, 1936; Cent. 1937, I 1015, C.A. 30, 7584 (1936). (18) Langedijk (to Shell Development Co.) U.S. 2,106,353, Jan. 25, 1938; C.A. 32, 2543 (1938); not in Cent.

B.P. F.P. 80° (1) (2) (3)
$$-94.0^{\circ}$$
 (9) $D_4^{25} = 1.0508$ (10) $n_D^{25} = 1.4057$ (1) 79-80° (4) 78.3° at 766 mm. (5) $D_-^{25} = 1.0469$ (1) 78.3° (6) 77.8-78.3° at 723.7 mm. (7) $D_4^{20} = 1.0646$ (7) $n_D^{20} = 1.4057$ (7) 77-78.5° (8) 1.0565 (5) 1.4038 (5)

[For prepn. of Č from propionic acid (1:1025) with PCl₅ (77% yield (11)), with PCl₃ (yields: 67.5% (12), 61% (13), 48% (14)) (15) (16) (note that excess PCl₃ may not be

used since its b.p., 76°, is too close to that of \bar{C} for subsequent sepn.), with PCl₃ + ZnCl₂ (91% yield (11)), with SOCl₂ (4) (note that excess SOCl₂ may not be used since its b.p., 79°, is almost identical with that of \bar{C}), with benzoyl chloride (3:6240) (yield 84-89% (8)) (17), with sodium chlorosulfonate (18), with benzenesulfonyl chloride + NaCl (18), with Cl₂ + S₂Cl₂ in cold (37% yield (19)), with SiCl₄ in xylene at 50° (50% yield (20)), or with acetonitrile + HCl gas at 0° (21) see indic. refs.; for prepn. of \bar{C} from propionic anhydride (1:1100) with phosgene (3:5000) + cat. as directed see (22).]

[\bar{C} with Cl₂ (67) in CCl₄ in sunlight (15) at 0° (23) or in dark at 40° (24) or \bar{C} with SO₂Cl₂ in CCl₄ in pres. of dibenzoyl peroxide refluxed 4–6 hrs. in dark (25) gives a mixt. contg. mainly β -chloropropionyl chloride (3:5690) accompanied also by α -chloropropionyl chloride (3:5320) yield: 60% β isomer + 40% α isomer (25)); note that in the pres. of I₂ instead of dibenzoyl peroxide only α -chloropropionyl chloride (3:5320) (45% yield (26)) is produced (25).]

[$\ddot{\mathbf{C}}$ with Br₂ (1 mole) at 80° evolves HCl and gives (100% yield (12)) (27) (28) α -bromopropionyl bromude [Beil. II-256, II₂-(230)], b.p. 153-155° (12); the reaction is accelerated by light, but the photobromination is retarded by O₂ (29).]

[C with Na propionate on htg. (14) (30) or C with Ag propionate on distn. (31) gives (80% yield (31)) propionic anhydride (1.1100).]

 $[\bar{C}$ passed over heated Ni cat. decomposes (32) into ethylene, HCl + CO, accompanied by smaller amts. methane, hydrogen, and CO₂. — \bar{C} with Na in abs. ether is claimed (33) to yield the dipropionate of hexen-3-diol-3,4 [Beil. II-242], b.p. 108-109° at 10 mm. (33).]

[C with ter-butyl MgBr in dry ether yields (34) not only the expected coupling product ter-butyl methyl ketone (pinacolone) (1:5425) but also diethyl ketone (1:5420), propanol-1 (1:6150), and propionic acid (1:1025) accompanied by the propionates of ter-butyl-ethyl-carbinol (2,2-dimethylpentanol-3) [Beil. I₁-(207), I₂-(446)] and of diethylcarbinol (pentanol-3) (1.6175) (reduction products). — C with C₆H₅MgBr in ether gives (57% yield (35)) diphenyl-ethyl-carbinol [Beil. VI-687, VI₁-(331)], m.p.95°, but C with C₆H₅MgBr with CdCl₂ in ether gives (76% yield (36)) ethyl phenyl ketone (propiophenone) (1:5525).]

 $[\bar{C}+2,5$ -dimethylpyrrole N-magnesyl bromide in dry ether gives (by rearr.) (37) 3-propionyl-2,5-dimethylpyrrole, colorless cryst. from AcOH, m.p. 102.5° (37); \bar{C} with benzimidazyl N-magnesyl bromide in dry ether yields (38) (39) N-(propionyl)benzimidazole, m.p. 125° (38) (39) (corresp. picrate, m.p. 228° (38) (39)).]

 $[\bar{C} + \text{ethyl acetoacetate} + \text{Mg in } C_6H_6 \text{ refluxed 2 hrs., treated with aq. gives (36% yield (40)) ethyl <math>\alpha$ -propionylacetoacetate, b.p. $104-106^\circ$ at 12 mm. (40) (isolated as Cu enolate, m.p. $78-79^\circ$, blue ndls. from MeOH/aq.; violet ndls. from pct. ether (40)).]

[\bar{C} with FeCl₃ (1 mole) on warming evolves HCl and gives a prod. which with aq. gives (34% yield (41)) (42) diethyl ketone (1:5420) + CO₂, or with alc. yields (43) ethyl α -propionylpropionate [Beil. III-686, III₂-(436).]

[Č with equal wt. CISO₃H stood at room temp. 5–10 days, poured into aq. (44), or Č with tripropylamine in lgr. (45) gives (cf. (42)) in small yield 3,5-dimethyl-2-ethyl-6-hydroxypyrone-4 [Beil. XVII-453], cryst. from aq. or AcOH, m.p. 151° (45).]

[$\bar{\mathbb{C}}$ with olefins or cyclo-olefins (cyclenes) in pres. of cat. adds to unsatn. yielding chloro-ketones; e.g., $\bar{\mathbb{C}}$ with ethylene + AlCl₃ at 0° gives (50% yield (46)) (47) β -chloroethyl ketone (1-chloropentanone-3) (3:9268); $\bar{\mathbb{C}}$ with trimethylethylene (2-methylbutene-2) (1:8220) + SnCl₄ gives (57% yield (48)) 2-chloro-2,3-dimethylhexanone-4, b.p. 74-78° at 17 mm., $D_4^{16} = 0.975$ (48) (note that this prod. on htg. with dimethylaniline loses HCl giving (60% yield (48)) of a mixt. of 2,3-dimethylhexen-2-one-4, b.p. 164-166° at 750 mm., $D_4^{13} = 0.872$, $n_D^{13} = 1.4535$ (semicarbazone, m.p. 209° (48)) and 2,3-dimethylhexen-1-one-4, b.p. 158-162° at 750 mm., $D_4^{13} = 0.862$, $n_D^{13} = 1.4450$ (semicarbazone, m.p. 108-110° (48)); $\bar{\mathbb{C}}$ with cyclohexene (1:8070) + SnCl₄ gives a prod. which with dimethylaniline loses HCl

to cyclohexen-1-yl ethyl ketone, b.p. 90° at 10 mm., $D_4^{13.5} = 0.981$, $n_D^{13.5} = 1.5005$ (oxime, m.p. 79°, semicarbazone, m.p. 195° (49)). — Note, however, that addn. of $\tilde{\mathbf{C}}$ to certain types of olefins is followed by *spontaneous* loss of HCl so that the unsatd. ketone forms the direct product; e.g., $\tilde{\mathbf{C}}$ with isobutylene (2-methylpropene-1) + SnCl₄ gives (30% yield (48)) 2-methylhexen-2-one-4, b.p. 147-148° at 760 mm., $D_4^{15} = 0.859$, $n_D^{15} = 1.4496$ (48) (semicarbazone, m.p. 163° (48)).]

[\bar{C} with aromatic hydrocarbons + cat. evolves HCl yielding corresp. ketones: e.g., \bar{C} with C_6H_6 + AlCl₃ in CS₂ gives (84% yield (19)) (50) ethyl phenyl ketone (propiophenone) (1:5525); \bar{C} with toluene (1:7405) + AlCl₃ in CS₂ gives (yields: 60% (51), 50% (52)) (53) ethyl p-tolyl ketone [Beil. VII-317, VII₁-(170)], b.p. 238-239°; for analogous reactions of \bar{C} with o-xylene (1:7430) (54), 2-methylnaphthalene (1:7605) (55), anthracene (1:7285) (56), phenanthrene (1:7240) (57), or acenaphthene (1:7225) (58) see indic. refs.; for analogous reactions of \bar{C} with heterocyclic systems, e.g., \bar{C} + 2-nitrofuran + TiCl₄ (59) or \bar{C} + thiophene + P_2O_5 at 210° for 10-12 hrs. (60), see indic. refs.]

[\bar{C} with alcs. reacts normally yielding corresp. esters: e.g., \bar{C} with MeOH yields methyl propionate (1:3020), \bar{C} with EtOH yields ethyl propionate (1:3070), etc.; for use of Mg in reaction of \bar{C} with tertiary alcs., e.g., \bar{C} + ter-butyl alc. (1:6140) + Mg giving (68% yield (61)) ter-butyl propionate, b.p. 115–116.5° (61), or \bar{C} + ter-amyl alc. (1:6160) + Mg giving (75% yield (61)) ter-amyl propionate, b.p. 153–156° at 710 mm. (61), see indic. refs.)

[\tilde{C} with phenols gives the corresp. phenol esters: e.g., \tilde{C} with phenol gives (62) phenyl propionate (1:3696), etc.; note, however, that these phenol esters on htg. with AlCl₃ in appropriate solvents, especially nitrobenzene, undergo the Fries rearr. yielding o- and p-propiophenols; this complete sequence is often carried through without isolation of the intermediate ester, e.g., for \tilde{C} + phenol + AlCl₃ giving directly o-hydroxypropiophenone [Beil. VIII-102, VIII₁-(547)] (50% yield) and p-hydroxypropiophenone [Beil. VIII-102 (25% yield) see (63); for key refs. on direct rearr. of phenyl propionate to these products see (64) (65); scores of analogous cases with other phenols or their ethers cannot be included here.]

[Č with certain hydroxy-azo-compounds in dry ether yields addn. cpds. usually (but not always) of 1:1 type: e.g., Č with p-hydroxy-azobenzene [Beil. XVI-96, XVI₁-(233)], m.p. 152°, in dry ether on stdg. at room temp. ppts. 1:1 cpd., m.p. 162° (66); for numerous analogous cases using homologous hydroxy-azo cpds. see (66).]

 $\ddot{\mathbf{C}}$ hydrolyzes with aq. yielding propionic acid (1:1025); for the amide, anilide, p-toluidide, and other derivs. corresp. to $\ddot{\mathbf{C}}$ see under propionic acid (1:1025).

3:7170 (1) Koehl, Wenzke, J. Am. Chem. Soc. 59, 1418 (1937). (2) John, Beetz, J. prakt. Chem. (2) 143, 344 (1935). (3) Sestini, Bull. soc. chim. (2) 11, 470 (1869). (4) Bardan, Bull. soc. chim. (4) 49, 1427 (1931). (5) Martin, Partington, J. Chem. Soc. 1936, 162. (6) Kohlrausch, Pongratz, Z. physik. Chem. B-22, 381 (1933). (7) Brühl, Ann. 203, 14-15 (1880). (8) Brown, J. Am. Chem. Soc. 60, 1326 (1938). (9) Timmermans, Mataar, Bull. soc. chim. Belg. 30, 216 (1921). (10) Walden, Z. physik. Chem. 55, 222 (1906).

(11) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (12) Fourneau, Nicolitch, Bull. soc. chim. (4) 43, 1236-1238 (1928). (13) Fierz-David, Kuster, Helv. Chim. Acta 22, 89 (1939). (14) Linnemann, Ann. 148, 255-257 (1868). (15) Michael, Ber. 34, 4046-4051 (1901). (16) Aschan, Ber. 31, 2346 (1898). (17) Chem. Fabrik vorm. Weiler-ter-Meer, Ger. 350,050, March 11, 1922; Cent. 1922, IV 155. (18) Henle, Schirm (to M. L. B.), Ger. 397,311, July 1, 1924; French 568,331, March 22, 1924; Cent. 1924, II 1401-1402. (19) Read, J. Am. Chem. Soc. 44, 1751 (1922). (20) Montonna, J. Am. Chem. Soc. 49, 2115 (1927).

(21) Colson, Compt. rend. 121, 1155 (1895). (22) Stellmann, French 785,075, Aug. 1, 1935; Cent. 1935, II 3301. (23) Kuster, Z. physiol. Chem. 130, 9-10 (1923). (24) Hertel, Becker, Z. physik. Chem. B-27, 310-311 (1934). (25) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940). (26) Wolffenstein, Rolle, Ber. 41, 735 (1908). (27) Aschan, Ber. 45, 1913-1919 (1912).

(28) Aschan, Ber. 46, 2162 (1913). (29) Kharasch, Hobbs, J. Org. Chem. 6, 709-712 (1941).

(30) Anderlini, Gazz. chim. ital. 25, II 132-133 (1895).

(31) Whitby, J. Chem. Soc. 1926, 1462. (32) Mailhe, Compt. rend. 180, 1112 (1925). (33) Anderlini, Gazz. chim. ital. 25, II 48, 129 (1895). (34) Petrov, Roslova, J. Gen. Chem. (U.S.S.R.) 10, 973-976 (1940); C.A. 35, 2467 (1941). (35) Gilman, Fothergill, Parker, Rec. trav. chim. 48 750 (1929). (36) Gilman, Nelson, Rec. trav. chim. 55, 528-530 (1936). (37) Oddo, Acuto, Gazz. chim. ital. 65, 1033 (1935); Cent. 1936, I 3832; C.A. 30, 4857 (1936). (38) Oddo, Raffia, Gazz. chim. ital. 67, 541 (1937); Cent. 1938, I 1581; C.A. 32, 1697 (1938). (39) Oddo, Ingraffia, Gazz. chim. ital. 62, 1096 (1932); Cent. 1932, I 2943. (40) Spassow, Ber. 70, 2383-2384 (1937).

(41) Hamonet, Bull. soc. chim. (2) 50, 356-357 (1888). (42) Wedekind, Ann. 323, 250, 254 (1902). (43) Hamonet, Bull. soc. chim. (3) 2, 335-338 (1889). (44) Krajcinovic, Ber. 62, 579-581 (1929). (45) Wedekind, Haeussermann, Ber. 41, 2299-2302 (1908). (46) Kenner, Statham, Ber. 69, 17 (1936). (47) Schoeller, Zullner (to Schering-Kahlbaum A.G.), U.S. 1.737-203, Nov. 26, 1929; Cent. 1930, II 1133; Brit. 282,412, Feb. 15, 1928; Cent. 1929, I 143. (48) Colonge, Mostafavi, Bull. soc. chim. (5) 6, 335-342; 342-354 (1939). (49) Colonge, Deroux, Bull. soc. chim. (5) 7, 459-468 (1941). (50) Pampel, Schmidt, Ber. 19, 2896 (1886).

(51) Sanchez, Bull. soc. chim. (4) 45, 284 (1929). (52) Willgerodt, Hambrecht, J. prakt. Chem. (2) 81, 76 (1910). (53) Klages, Ber. 35, 2252 (1902). (54) von Auwers, Ziegler, Ann. 425, 260 (1921). (55) Haworth, Bolam, J. Chem. Soc. 1932, 2249. (56) I.G., Brit. 289,585, May 24, 1928; Cent. 1928, II 1036. (57) Bachmann, Struve, J. Am. Chem. Soc. 58, 1659 (1936). (58) Dziewonski, Moszew, Roczniki Chem. 11, 415-425 (1931); Cent. 1931, II 570; C.A. 26, 2975 (1932). (59) Gilman, Burtner, Calloway, Turck, J. Am. Chem. Soc. 57, 908 (1935). (60) Steinkopf, Schubart, Ann. 424, 8-9 (1921).

(61) Spassow, Ber. 70, 1928-1929 (1937). (62) Perkin, J. Chem. Soc. 55, 547-548 (1889). (63) Torres, Amargos, Anales soc. espan. fis. quim. 21, 37-47 (1933); Cent. 1933, II 372; C.A. 27, 1624 (1933). (64) Miller, Hartung, Org. Syntheses, Coll. Vol. 2 (1st ed.), 543-545 (1943); 13, 90-92 (1933). (65) von Auwers, Potz, Noll, Ann. 535, 228-230 (1938). (66) Fischer, Taurinisch, Ber. 64, 236-239 (1931). (67) Schmidt, Schloffer (to I.G.) Ger. 738,398, July 15, 1943; C.A. 38, 3992 (1944).

3:7175 1-CHLOROBUTYNE-2 CH₃—C=C—CH₂Cl C₄H₅Cl Beil. S.N. 12 $(\gamma$ -Methylpropargyl chloride)

B.P. 81-84° (1)

Pale yel. oil.

[For prepn. of \bar{C} (44% yield) from butyn-2-ol-1 + PCl₅ in ether see (1).]

 \bar{C} in ether/acetone soln. on treatment with K_2CO_3 + phenol gives (57% yield) γ -methylpropargyl phenyl ether, b.p. 123-126° at 25 mm., $n_D^{20} = 1.3894$ (1).

3:7175 (1) Hurd. Cohen. J. Am. Chem. Soc. 53, 1074-1075 (1931).

3:7195 CHLOROMETHYL ETHYL ETHER C₃H₇OCl Beil. I - 581 CICH2.O.C2H5 I₁-(304) $I_2-(645)$

B.P. 83° at 763.1 mm. (1)
$$D_4^{20} = 1.0263$$
 (3) $n_D^{20} = 1.40398$ (1) 82° (2) 1.0127 (1) 81-82° (3) $D_4^{15} = 1.0188$ (1) $n_-^{12} = 1.0282$ (3) (?) 80° (4) 79-80° (5) (6)

·· C undergoes some decompn. at b.p.

[For prepn. from ethyl alc. (1:6130) + trioxymethylene (1:0080) + dry HCl see (3) (1); from ethyl alc. + formalin + HCl (42-44% yield (6)) see (6).

C on shaking with aq. readily hydrolyzes yielding formaldehyde (1:0145), ethyl alc. (1:6130), + HCl.

3:7195 (1) Karvonen, Ann. Acad. Sci. Fennicae, 3-A, No. 7, 1-103 (1912); Cent. 1912, II 1269; C.A. 14, 2175 (1920). (2) Litterscheid, Ann. 330, 123 (1904). (3) Farren, Fife, Clark, Garland, J. Am. Chem. Soc. 47, 2421 (1925). (4) Wedekind, Ber. 36, 1385 (1903). (5) de Gaspari, Gazz. chim. ital. 27, II 297 (1897). (6) Foran, J. Soc. Chem. Ind. 44, 173-174T (1925).

3:7200 1-CHLORO-2,2-DIMETHYLPROPANE CH₃ C₅H₁₁Cl Beil. I - 141 (Neopentyl chloride; CH₃ C-CH₂Cl
$$I_{1-}$$
(50) ter-butylcarbinyl chloride)

B.P. F.P.
$$-20^{\circ}$$
 (1) (4) $D_{4}^{20} = 0.866$ (1) $n_{D}^{20} = 1.4042$ (1) 83.9° at 750 mm. (1) 0.865 (3) 0.865 (4) 0.865 (5) 0.865 (6) 0.865 (7) 0.865 (8) 0.865 (9) 0.865 (1) 0.865 (1) 0.865 (1) 0.865 (2) 0.865 (3) 0.865 (4) 0.865 (4) 0.865 (5) 0.865 (6) 0.865 (6) 0.865 (7) 0.865 (8) 0.865 (8) 0.865 (9) 0.865 (1)

[For prepn. of \bar{C} (30% yield (3)) from neopentane (tetramethylmethane) (1:8499) by chlorination in light at 0° see (4) (3) (1). — \bar{C} cannot (1) (5) (contrary to earlier claims (6)) be prepared from neopentyl alc. (ter-butylcarbinol) (1:5812) even with SOCl₂ + pyridine (13).]

 $\ddot{\mathbf{C}}$ is stable for long periods of time even at 200° (1). — $\ddot{\mathbf{C}}$ is extraordinarily unreactive giving none of the ordinary alkyl halide reactns. except the forms. of the corresponding Grignard reagent.

Č in dil. ether soln. reacts slowly with Mg giving (1) (90% yield (8)) neopentyl MgCl. [For reactn. of R.Mg.Cl with CO₂ see (12).]

[For reactns. of \bar{C} with $C_6H_6+AlCl_3$ (2), or with metallic Na (10), or with NaPr (11) see indic. refs.]

Č is unchanged after htg. 20 hrs. at 100° with alc. KOH (1) or htg. with CuCN at 90° in a s.t. for 200 hrs. (1) or after treatment with KI in acctone (1) or after 6 hrs. refluxing with 6% Na/Hg (11).

- ① ter-Butylacetanilide (β,β-dimethyl-n-butyranilide): m.p. 131° (1), 130-131° (3), 129-130° (3). [From R.MgCl by reactn. with phenyl isocyanate (1).]
- Neopentyl mercuric chloride: m.p. 117-118° (3), 116.5-117° (1). [From RMgCl with HgCl₂ (1) (3) in dry ether (90% yield (3)).] [For reactn. of R.MgCl with di-p-tolylmercury giving di-neopentylmercury, b.p. 67-69° at 3 mm., m.p. 31-33°, see (9).] [For reactn. of RHgCl with KBr giving 82% yield neopentyl bromide, b.p. 104.8° at 732 mm., or with I₂ giving 92% yield neopentyl iodide, b.p. 70° at 100 mm., see (3).]
- 3:7200 (1) Whitmore, Fleming, J. Am. Chem. Soc. 55, 4161-4162 (1933). (2) Pines, Schmerling. Ipatieff, J. Am. Chem. Soc. 62, 2901-2902 (1939). (3) Whitmore, Wittle, Popkin, J. Am. Chem. Soc. 61, 1585-1590 (1939). (4) Fleming, Whitmore, J. Am. Chem. Soc. 54, 3460-3461 (1932). (5) Whitmore, Rothrock, J. Am. Chem. Soc. 54, 3431-3435 (1932). (6) Tissier, Ann. chim. (6) 29, 344 (1893). (7) Richard, Ann. chim. (8) 21, 341-342 (1910). (8) Whitmore, Wittle, Harriman, J. Am. Chem. Soc. 61, 1585-1586 (1939). (9) Whitmore, Rohrmann, J. Am. Chem. Soc. 61, 1591-1592 (1939). (10) Whitmore, Popkin, Bernstein, Wilkins, J. Am. Chem. Soc. 63, 124-127 (1941).
- (11) Whitmore, Zook, J. Am. Chem. Soc. 64, 1783-1785 (1942).
 (12) Bush, J. Am. Chem. Soc. 61, 965 (1939).
 (13) Whitmore, Karnatz, J. Am. Chem. Soc. 60, 2534 (1938).

```
3: 7205 1-CHLOROBUTENE-2 CH<sub>3</sub>.CH=CH.CH<sub>2</sub>Cl C<sub>4</sub>H<sub>7</sub>Cl Beil. I - 205 (Crotonyl chloride, \alpha-chloro-\beta-butylene; \gamma-methylallyl chloride) I<sub>2</sub>-(176)
```

B.P. 84°	at 750 mm. (1)	$D_4^{20} = 0.9340 \ (3)$	$n_{\rm D}^{20} = 1.4350 (1) (2) (17)$
84-85°	(2)	0.9316 (7)	1.4351 (5)
83.8°	(3)	• •	1.4352 (7)
83°	(7)		1.4356 (3)
80°	(4)		1.4359 (6)
45.6-4	5.7° at 191 mm. (5)		
43.7-4	4.0° at 177 mm. (5)		
-2°	at 18 mm. (6)		

Because of the close interrelationship of \bar{C} with the isomeric 3-chlorobutene-1 (3:7090) some confusion exists regarding the nomenclature. The compound here described (1-chlorobutene-2) is by some authors designated as crotyl chloride; this name, however, is better reserved for the equilibrium mixture of 1-chlorobutene-2 and 3-chlorobutene-1 as indicated by $\langle 7 \rangle$.

Pure \bar{C} (in the absence of catalysts) is quite stable (1) and may be kept at room temperature as long as a year (5) without significant increase in n_2^{20} . However, in the presence of FeCl₃, HCl, or CuCl₂ + HCl, \bar{C} is in part isomerized to 3-chlorobutene-1 and an equilibrium mixt. is formed. The composition of this equilibrium mixt. depends upon the temperature, catalyst, and other factors. E.g., with FeCl₃ the equilibrium mixt. conts. 50% \bar{C} ; with 1 mole HCl it conts. 75% \bar{C} . Although the two compounds can easily be separated by careful fractional distillation (5) yet consideration must always be given to the possible formation during chem. reaction of the derivatives of the other isomer. The refractive index of mixts. of 1-chlorobutene-2 and 3-chlorobutene-1 is a linear function of the composition (1). Although cis and trans stereoisomers of \bar{C} are possible, no record of their isolation has been published.

[For the prepn. of a mixt. of \bar{C} + 3-chlorobutene-1 from butadiene-1,3 + HCl see (1) (7) (8) (9); for prepn. of \bar{C} from crotonyl alcohol with PCl₃ + pyridine see (3) (6), with HCl + Cu₂Cl₂ see (1), with conc. HCl see (5).]

C passed over soda-lime in an iron furnace at 530-550° yields (11) butadiene-1,3. [Use in prepn. of 1,2,3,4-tetrabromobutane (11).]

[For study of reactivity of \bar{C} with KI soln. at 20° or NaOEt soln. at 20° and 50° see (3); for reaction with Mg, Zn, etc., see (12); for use in formn. of cellulose ethers see (13); for study of hydrolysis of \bar{C} under various conditions see (16); for behavior of \bar{C} with cuprous cyanide see (17).]

— Crotonyl 3,5-dinitrobenzoate: cryst. from alc., m.p. 54° (9). [This cpd. has never been reported from \bar{C} but only (cf., however (15)) from the corresp. bromide via reaction with silver 3,5-dinitrobenzoate in ether (9), it is possible that the material of m.p. 54° represents a mixt. of the two esters corresponding to crotonyl bromide and the isomeric 3-bromobutene-1 since from the former a 3,5-dinitrobenzoate, m.p. 51°, 50-51° (15), and from the latter a 3,5-dinitrobenzoate, m.p. 59°, have been reported (14).

3:7205 (1) Kharasch, Kritchevsky, Mayo, J. Org. Chem. 2, 494-496 (1938). (2) Baudrenghien, Bull. soc. chim. Belg. 31, 168 (1922). (3) Tamele, Ott, Marple, Hearne, Ind. Eng. Chem. 33, 118-119 (1941). (4) Ganguly, J. Indian Chem. Soc. 13, 584 (1936). (5) Roberts, Young, Winstein, J. Am. Chem. Soc. 64, 2163 (1942). (6) Böhme, Ber. 71, 2378-2379 (1938). (7) Henne, Chanan, Turk, J. Am. Chem. Soc. 63, 3474-3476 (1941). (8) Dykstra (to du Pont), U.S. 2,123,504, July 12, 1938; Cent. 1938, II 2840; C.A. 32, 6666 (1938). (9) Voigt, J. prakt. Chem. (2) 151, 310 (1938). (10) Charon, Ann. chim. (7) 17, 228-230 (1899).

(11) Jacobson, J. Am. Chem. Soc. 54, 1546 (1932). (12) Young, Eisner, J. Am. Chem. Soc. 63, 2113-2115 (1941). (13) Hahn (to du Pont), U.S. 2,082,797, June [8, 1937; Cent. 1937, II 8383; C.A. 31, 5577 (1937). (14) Newman, Rydon, J. Chem. Soc. 1936, 262-264. (15) Adamson, Kenner, J. Chem. Soc. 1935, 287. (16) Young, Andrews, J. Am. Chem. Soc. 66, 421-425 (1944). (17) Lane, Fentress, Sherwood, J. Am. Chem. Soc. 66, 545-548 (1944).

3: 7210 1-CHLOROBUTADIENE-1,3 Cl C₄H₅Cl Beil. S.N. 12
$$H_2$$
C=CH-CH=CH

B.P. 85° (1) $D_{23}^{23} = 0.9601$ (2) $n_D^{20} = 1.470$ (3) $n_D^{23} = 1.4733$ (2)

[For prepn. of \overline{C} from either 1,2-dichlorobutene-3 (3:5350) or 1,4-dichlorobutene-2 (3:5725) by htg. with 2 pts. powdered KOH to about 90° see (1) (3); from solid 1,1,2,3,4-pentachlorobutane (3:0750) in 80% yield (2) or from liq. diastereoisomer (3:9068) in 60% yield (2) with Zn dust in alc. see (2).]

C on stdg. (1) (2) polymerizes to a dark resinous mass (4).

3:7210 (1) Muskat, Northrup, J. Am. Chem. Soc. 52, 4054-4055 (1930). (2) Prins, Rec. trav. chim. 56, 119-125 (1937). (3) Muskat (to du Pont), U.S. 2,038,593, Apr. 28, 1936; Cent. 1936, II 3359; C.A. 39, 3912 (1936). (4) I. G. Farbenindustrie, French 769,472, Aug. 27, 1934; Cent. 1935, I 1946.

3: 7212 CHLOROACETALDEHYDE CH₂—CHO C₂H₃OCl Beil. I - 610
$$I_{1-}(327)$$
 Cl $I_{2-}(675)$ B.P. 85–86° (1)

85.0-85.5° cor. at 748 mm. (2) 84.5-85° at 759 mm. (3)

Colorless liq. with sharp and penetrating odor; vigorously attacks mucous membrane. — \bar{C} with aq. forms (2) a crystn. hemihydrate, \bar{C} . ½ H_2O ; this does not have a sharp m.p. but about 43–50° begins to liquefy and on further htg. yields \bar{C} , whose vapor may be dried by passing over anhydr. CuSO₄ (2) (3); this hemihydrate is sol. in aq. from which it may be recovered by evaporation in a stream of dry CO_2 ; it is also sol. in alc. or ether, sepg. unchanged on evapn. of solvent (2) (for prepn. (60% yield) from glycerol α -monochlorohydrin (3:9038) by oxidn. with HIO₄ see (40)). — \bar{C} also forms (4) with EtOH a liq. chloroacetaldehyde ethylaleoholate (chloroacetaldehyde ethyl-hemi-acetal), but in excess alc. on protracted stdg. at room temp. (4) this is converted to chloroacetaldehyde diethylacetal (3:8228), or on treatment with dry HCl yields (4) α , β -dichloroethyl ethyl ether (3:5640).

[For prepn. of \bar{C} from its crystn. trimer (3:2300) by distn. at ord. press. see (2) (5) (6); from chloroacetaldehyde diethylacetal (3:8228) by htg. at 150° in CO₂ with anhydr. oxalic acid (2), AcOH (2), or dil. H₂SO₄ (2) (7) see indic. refs.; from chloroacetaldehyde ethylalcoholate (see above) by htg. with anhydr. oxalic acid at 150° (90% yield) see (8) (note that the actn. of Cl₂ on paraldehyde (1:0170) gives acc. to conditions either \bar{C} (9) or α,α,β -trichloro-n-butyraldehyde (butylchloral) (3:5910) (10) (11)).]

[For prepn. of \tilde{C} from vinyl chloride (3:7010) with $Cl_2 + aq$. in the dark at 35° see (12) (13) (14) (15); from methylene dichloride (3:5020) with formaldehyde + SO_2Cl_2 at 300° with cat. see (16); from α,β -dichloroethyl ethyl ether (3:5640) with conc. H_2SO_4 see (17); from α,β -dichloroethyl acetate on distn. with a little ZnCl₂ (acetyl chloride also formed) (18) or from α,β -dichloroethyl benzoate similarly (benzoyl chloride also being formed) (19) or from α,β -dichloroethyl laurate (lauroyl chloride also being formed) (19) see indic. refs.]

[For form. of \tilde{C} from sodium β,β -dichloro- α -hydroxypropionate on boilg. with aq. see (20); from β -chloroethylidene-diurethane on warming with dil. HCl see (21); from acetaldehyde (1:0100) with ethyl hypochlorite followed by distn. with anhydr. oxalic acid see (22); from chloroacetaldehyde-sulfonic acid [Beil. I₂-(818)] by treatment with steam in 60% H₂SO₄ (23) or by htg. with 80% H₂SO₄ (24) see indic. refs.]

 \bar{C} gives positive fuchsin-aldehyde test (1). — \bar{C} reduces NH₄OH/AgNO₃ on warming (2). \bar{C} does not oxidize in the air (2) but is oxidized by conc. HNO₃ (2) (20) or by AgOH (20) or by dil. H₂O₂ (25) to chloroacetic acid (3:1370). — \bar{C} on treatment as directed (26) with halogen magnesium alcoholate (e.g., EtOMgCl) is reduced to β -chloroethanol (3:5552).

 \bar{C} on stdg. in s.t. is rapidly converted to an amorphous polymer (2); \bar{C} (or its hemihydrate) on shaking with $\frac{1}{2}$ vol. cold conc. H₂SO₄ yields (1) a cryst. trimer, 2,4,6-tris-(chloromethyl)-trioxane-1,3,5 (3:2300), m.p. 87-87.5°, which on distn. at ord. press. depolymerizes to \bar{C} .

The hemihydrate of \bar{C} htd. alone or in pres. of a few drops of conc. H_2SO_4 condenses with itself yielding (27) (28) α, γ -dichlorocrotonaldehyde [Beil. I-731, I₂-(789)].

[\bar{C} warmed with EtOH (4) or the ethylalcoholate of \bar{C} in EtOH treated with dry HCl gas (8) yields chloroacetaldehyde diethylacetal (3:8228), b.p. 157°, and in the latter case also (4) α,β -dichloroethyl ethyl ether (3:5640).]

[\bar{C} with KCN yields (29) (7) an oily prod. (cyanohydrin?) which by hydrolysis with HCl gives β -chlorolactic acid [Beil. III-286, III₁-(110), III₂-(209)] + AcOH; \bar{C} + NaCN+BzCl yields (30) α -benzoxy- β -chlorolactonitrile; note, however, that \bar{C} boiled with alc. KCN yields (31) EtOAc, or with aq. KCN yields (31) AcOH.]

[For behavior of \tilde{C} with AcCl (2), Ac₂O (32), see indic. refs.; \tilde{C} with ethyl diazoacetate yields (3) ethyl γ -chloroacetoacetate (3:6375); \tilde{C} with EtMgBr in ether yields (6) 1-chlorobutanol-2 (3:8025); \tilde{C} with nitromethane as directed (33) yields 1-chloro-3-nitropropanol-2, with nitroethane, 1-chloro-3-nitrobutanol-2; \tilde{C} with thioformamide (35) or \tilde{C} + formamide + P₂S₅ (34) yields thiazole [Beil. XXVII-15, XXVII₁-(207)], m.p. 116°.]

- Chloroacetaldoxime: lachrymatory oil dec. on distn. at 10 mm. (36). [From Č with 4 moles NH₂OH.HCl (36).]
- © Chloroacetaldehyde semicarbazone: ndls. from alc., m.p. 148° (37), 134-135° dec. (38), 134° (40). [From C + semicarbazide hydrochloride + NaOAc (37).]
- Chloroacetaldehyde dimethone: unreported. [Note that Č with warm alc. soln. of "dimethone" ("dimedone") (dimethyldihydroresorcinol) not only condenses normally but also loses HCl yielding (39) same prod., m.p. 227° u.c., 237.5° cor. (39), as obtd. from hydroxyacetaldehyde.]

3:7212 (1) Jones, Williams, J. Chem. Soc. 1934, 834. (2) Natterer, Monatsh. 3, 442-464 (1882). (3) Schlotterbeck, Ber. 42, 2570-2571 (1909). (4) Natterer, Monatsh. 5, 494-499 (1884). (5) Späth, Monatsh. 36, 6-7 (1915). (6) Helferich, Speidel, Ber. 54, 2634-2635 (1921). (7) Frank, Ann. 206, 339-344 (1880). (8) Fritsch, Schumacher, Ann. 279, 307-308 (1894). (9) Freundler, Bull. soc. chim. (4) 1, 70 (1907). (10) Krämer, Pinner, Ber. 3, 385 (1870); Ann. 158, 41-42 (1871). (11) Pinner, Ann. 179, 26 (1875). (12) Ernst, Lange (to I.G.), U.S. 1,806,285, May 19, 1931; Cent. 1931, II 1632; C.A. 25, 3671 (1931); Brit. 299,319, Oct. 22, 1937; Cent. 1930, I 129; C.A. 23, 3235 (1929); Ger. 496,062, Oct. 23, 1927; Cent. 1930, I 3722; C.A. 24, 3251 (1930); French 662,361, Aug. 6, 1929; Cent. 1930, I 129. (13) Brit. 299,722, Oct. 28, 1927; C.A. 23, 3479 (1929). (14) N. V. de Bataafsche Petroleum Maatschappij, French 787,529, Sept. 24, 1935; Cent. 1936, II 2227; C.A. 30, 1067 (1936). (15) Groll, Hearne (to Shell Development Co.), U.S. 2,060,303, Nov. 10, 1936; Cent. 1937, I 4155; C.A. 31, 419 (1937). (16) Frohlich, Wiezevich (to Standard Oil Development Co.), U.S. 2,042,303, May 26, 1936; Cent. 1936, II 3193; C.A. 30, 4871 (1936); Ger. 629,897; May 26, 1936; Cent. 1936, II 2448; C.A. 30, 6006 (1936). (17) Jacobsen, Ber. 4, 216 (1871). (18) Soc. des Usines Chimiques Rhone-Poulenc, Brit. 329,721, June 19, 1930; Cent. 1930, II 1611; C.A. 24, 5767 (1930). (19) Soc. des Usines Chimiques Rhone-Poulenc, Ger. 527,874, June 22, 1931; Cent. 1931, II 1350. (20) Reisse, Ann. 257, 334-336 (1890). (21) Houben, J. prakt. Chem. (2) 165, 15 (1923). (22) Goldschmidt, Endres, Direch, Ber. 58,

576-577 (1925). (23) Lepouse, Bull. soc. chim. Belg. 34, 141-142 (1925). (24) Chem. Fabrik Weiler-ter-Meer, Ger. 362,744, Oct. 31, 1922; Cent. 1923, II 1246. (25) Filachione, J. Am. Chem. Soc. 61, 1706 (1939). (26) I.G., Brit. 384,156, Dec 22, 1932; Cent. 1933, I 1351. (27) Natterer, Monatsh. 4, 539-543 (1883). (28) Lespieau, Bull. soc. chim. (4) 43, 200-201 (1928). (29) Glinsky, Ber. 6, 1256-1257 (1873). (30) MacCorquodale, Johnson, Rec. trav. chim. 51, 486 (1932).

(31) Chattaway, Irving, J. Chem. Soc. 1929, 1043. (32) Spath, Monatsh. 36, 36 (1915). (33) I. G. French 804,589, Oct. 27, 1936; Cent. 1937, I 1791, C.A. 31, 3505 (1937). (34) Hromatka (to E. Merck), Ger. 670,131, Jan. 12, 1939; Cent. 1939, I 2296; C.A. 33, 2909 (1939). (35) Willstätter, Wirth, Ber. 42, 1918 (1909). (36) Meister, Ber. 40, 3442 (1907). (37) Blaise, Bull. soc. chim. (4) 15, 671–672 (1914). (38) Kling, Bull. soc. chim. (4) 5, 415 (1909). (39) Vorländer, Z. anal. Chem. 77, 254–255 (1929). (40) Hatch, Alexander, J. Am. Chem. Soc. 67, 688 (1945).

B.P. 85-87° (1) 91-96° (2)

[For prepn. of C from 4,4-dichloro-2-methylbutane (3:7885) with alc. KOH see (1); from 3,4-dichloro-2-methylbutane (3:8075) with alc. NaOH see (2) (note, however, that the latter process very probably leads to a mixt. of C with other prods.).]

3:7215 (1) Bruylants, Ber. 8, 413-414 (1875). (2) Kondakow, Ber. 21 Referate, 439 (1888).

3: 7220 2-CHLORO-2-METHYLBUTANE
$$C_6H_{11}Cl$$
 Beil. I - 134 (ter-Amyl chloride; CH_3 I_{1} -(46) dimethyl-ethyl-carbinyl chloride) $CH_3.CH_2$ CH_3 I_{2} -(100)

B.P. F.P. (1) (2) (11)
$$-73.7^{\circ}$$
 (9) $D_4^{20} = 0.8658$ (5) $86.0-86.1^{\circ}$ (3) -72.7° (4) 0.8650 (28) 85.65° at 760 mm. (4) M.P. $85.4-85.6^{\circ}$ at 762 mm. (5) -73.3° (9) $D_4^{13.5} = 0.86989$ (10) $n_{\rm D_i}^{20} = 1.4058$ (5) $83.0-84.5^{\circ}$ at 744 mm. (6) 1.40520 (28) 1.40550 (7) 1.4055 (7) 1.4055 (7) 1.4055 (7) 1.4055 (7) 1.4055 (7) 1.4055 (7) 1.4055 (7) 1.4055 (7) 1.4055 (7) 1.4055 (8) 1.4055 (9) 1.4055 (10)

 \bar{C} with aq. forms binary const.-boilg. mixt., b.p. 76° (2); \bar{C} with aq. + ter-amyl alc. (1:6160) forms a ternary const.-boilg. mixt. (2).

[For prepn. of \bar{C} from ter-amyl alc. (1:6160) with HCl gas see (11); with conc. HCl (yield: 93–98% (12), 65% (13)) see (12) (13); with PCl₃ (41% yield (6)) or PCl₃ + ZnCl₂ (98% yield (14)) see (6) (14); with PCl₅ (80% yield (14)) see (1) (14); with SOCl₂ (yield: 99% (14), 41% (6)) see (14) (6); with acetyl chloride see (6); with oxalyl chloride (3:5060) (yield 18% (6)) see (15) (6); with diphosgene (3:5515) see (16); with p-nitrobenzoyl chloride see (17).]

[For prepn. of C from isopropyl-methyl-carbinol (2-methylbutanol-3) (1:6170) by

rearr. with conc. HCl + ZnCl₂ (80% yield (7)), or with HCl on long stdg. (97% yield (7)), or with PCl₅ (76% yield (7)), or with SOCl₂ + pyridine (73% yield (7)) see (7).]

[For prepn. of C from trimethylethylene (2-methylbutene-2) (1:8220) by addn. of HCl see (18) (19) (20); from isopropylethylene (3-methylbutene-1) (1:8200) see (5).]

[For formn. of Č from 2-methylbutane (isopentane) (1:8500) by shaking 2 min. with diisobutylene hydrochloride (3:8113) + AlCl₃ see (29).]

Č very rapidly loses HCl by boilg. aq., e.g., 88.6% in 15 min., 94.9% in 30 min., 95.4% in 60 min. (7). Note that hydrolysis with hot aq. or aq. Na₂CO₃ gives exclusively olefins (20) (6) but that with cold aq. or cold aq. NaOH some ter-amyl alc. (1:6160) is also formed (20), although the latter may result from hydration of the olefin. [For further studies of hydrolysis of Č see (2) (6) (20) (21) (22).]

 $\bar{\rm C}$ on passing over BaCl₂ + soda-lime at 350–400°C gives (85% yield (5)) a mixture of trimethylethylene (2-methylbutene-2) (1:8220) + unsym.-ethyl-methyl-ethylene (2-methylbutene-1) (1:8210).

Č with Mg in dry ether gives (yield: 73.6% (23), 38% (26)) RMgCl; this with CO₂ gives (60% yield (13)) dimethyl-ethyl-acetic acid (1:1113) q.v. (see also derivatives below). Č with Ag 3,5-dinitrobenzoate does not (24) yield expected ter-amyl 3,5-dinitrobenzoate

- Dimethyl-ethyl-acetanilide: m.p. 90-91° u.c. (25), 92° cor. (26), 91.4° (27). [From RMgCl + phenyl isocyanate (25) (26).] [Note that this same product results by rearr., however, from similar treatment of the RMgCl cpds. from 3-chlor-2-methyl-butane (3:7275) q.v.]
- ① Dimethyl-ethyl-acet-p-toluidide: m.p. $83.0-83.5^{\circ}$ u.c. (25), 83.3° (27). [From RMgCl + p-tolyl isocyanate (25).]
- Dimethyl-ethyl-acet-α-naphthalide: m.p. 137-138° u.c. (25). [From RMgCl + α-naphthyl isocyanate (25).]

3:7220 (1) Wyschnegradsky, Ann. 190, 336 (1877). (2) Ayres, Ind. Eng. Chem. 21, 899-904 (1929). (3) Brearley, Kistiakowsky, Stauffer, J. Am. Chem. Soc. 58, 44-46 (1936). (4) Timmermans, Bull soc chim. Bclg. 30, 66 (1921). (5) Leendertse, Tulleners, Waterman, Rec. trav. chim. 52, 521-524 (1933). (6) French, Schaefer, J. Am. Chem. Soc. 57, 1576-1578 (1935). (7) Whitmore, Johnston, J. Am. Chem. Soc. 60, 2265-2266 (1938). (8) Simons, Fleming, Whitmore, Bissinger, J. Am. Chem. Soc. 60, 2265-2269 (1938) (9) Turkevich, Smyth, J. Am. Chem. Soc. 64, 737 (1942). (10) Jahn, Moller, Z. physik. Chem 13, 380 (1894). (11) Bruchet, Ann. chim. (7) 10, 384 (1897). (12) Norris, Watt, Thomas, J. Am. Chem. Soc.

(11) Bruchet, Ann. chim. (7) 10, 384 (1897).
(12) Norris, Watt, Thomas, J. Am. Chem. Soc. 38, 1076 (1916).
(13) Corson, Thomas, Waugh, J. Am. Chem. Soc. 51, 1950 (1929).
(14) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929).
(15) Adams, Weeks, J. Am. Chem. Soc. 38, 2518-2519 (1916).
(16) Nekrassow, Melnikow, J. prakt. Chem. (2) 127, 216-217 (1930).
(17) Meisenheimer, Ann. 442, 202 (1925).
(18) Michael, Zeidler, Ann. 385, 269-270 (1911).
(19) Aschan, Ber. 51, 1304-1306 (1918).
(20) Woodburn, Whitmore, J. Am. Chem. Soc. 56, 1394-1395 (1934).

(21) Hughes, J. Am. Chem. Soc. 57, 708-709 (1935). (22) Hughes, McNulty, J. Chem. Soc. 1937, 1283-1291. (23) Whitmore, Badertscher, J. Am. Chem. Soc. 55, 1562 (1933). (24) Tseng, Chu, Natl. Central Unrv. (Nanking), Sci. Rept., Ser. A-1, No. 2, 5-7 (1931); C.A. 28, 2116 (1932); Cent. 1938, I 669. (25) Underwood, Gale, J. Am. Chem. Soc. 58, 2119 (1934). (26) Schwartz, Johnson, J. Am. Chem. Soc. 53, 1065 (1931). (27) Hommelen, Bull. soc. chim. Belg. 42, 249 (1933). (28) Vogel, J. Chem. Soc. 1943, 638, 640. (29) Bartlett, Condon, Schneider, J. Am. Chem. Soc. 66, 1537 (1944).

3:7225 4-CHLOROBUTADIENE-1,2 Cl C₄H₅Cl Beil. S.N. 12 H₂C—CH—C—CH₂

B.P. 88° (1)

Č represents the initial step in the formn. of 3-chlorobutadiene-1,3 ("Chloroprene") (3:7080) by addn. of aq. HCl (1) (2) to vinylacetylene; under certain conditions Č can

be isolated as the major reactn. product, but it readily undergoes isomerization to "Chloroprene" especially in the presence of certain salts, e.g., CuCl (3). When sufficient HCl is present the reactn. proceeds further (1) with formn. of 2,4-dichlorobutene-2 (3:5550).

 \ddot{C} shaken with 3 pts. 18% HCl contg. CuCl for 16 hrs. at 20° gives (4) (3) (2) butadiene-1,3 ("Chloroprene") (3:7080), the rest being chloroprene polymer. — \ddot{C} with 3% dry FeCl₃ spontaneously evolves heat and yields (4) chloroprene (3:7080).

 \bar{C} stirred with aq. Na₂CO₃ at 60–90° for 15 hrs. gives (10) (50% yield (4)) 4-hydroxy-butadiene-1,2, colorless lachrymatory, strongly vesicant liq. with sharp pungent odor, misc. aq. and org. solvents, b.p. 126–128° at 756 mm., 68–70° at 53 mm., $D_4^{20} = 0.9164$, $n_2^{20} = 1.4759$. [This prod. on cat. hydrogenation gives (4) butanol-1 (1:6180) but is unaffected by refluxing with alc. NaOEt, 25% aq. H₂SO₄, or 2% aq. HCl; for many other reactns. and derivatives see (4) (10).]

 \tilde{C} in 80% alc. or in acetone with NaI, stood for 3 hrs. then diluted with aq., gives (46% yield (4)) 4-iodobutadiene-1,2, b.p. 43-45° at 38 mm., $D_D^{20} = 1.7129$, $n_D^{20} = 1.5709$ (4), which on htg. at 125-130° polymerizes vigorously to iodoprene. — \tilde{C} with alc. NaCN yields (5) 4-cyanobutadiene-1,3 (β -vinylacrylonitrile), b.p. 135-138° at 760 mm., 65-68° at 58 mm., 48-50° at 28 mm., $D_A^{20} = 0.8644$, $n_D^{20} = 1.4880$ (5). — \tilde{C} with liq. NH₃ at -40 to -50° yields (6) (7) tris-(butadien-1,2-yl-4)amine (for extension to many other amines see (7)).

 \bar{C} added dropwise to 3 vols. conc. H₂SO₄ at -5° to $+3^{\circ}$, then poured onto ice, yields (1) 4-chlorobutanone-2 (3:7640), b.p. 120-122° at 760 mm. (1).

C with Cl₂ yields (8) (9) mixt. of 2,3,4-trichlorobutene-1 (3:9064) and 1,2,4-trichlorobutene-2 (3:9062) which reacts further to produce 1,2,2,3,4-pentachlorobutane (3:9070).

 \bar{C} in aq. Na₂CO₃ suspension, oxidized with KMnO₄, yields (1) chloroacetic acid (3:1370), but neither acetic acid nor oxalic acid. — \bar{C} in CHCl₃ treated with O₃ for 12 hrs. at 0°, then with aq., yields (1) formaldehyde (1:0145) and chloroacetaldehyde (3:7212) (the latter not detected directly but only after KMnO₄ oxidn. (1) to chloroacetic acid (3:1370)).

3:7225 (1) Carothers, Berchet, Collins, J. Am. Chem. Soc. 54, 4066-4070 (1932). (2) Klebanskii, Tzyurikh, Dolgopol'skii, Bull. acad. sci. (U.R.S.S.) 1935, No. 2, 189-226; Cent. 1935, II 3843 C.A. 36, 1259 (1936) (full English translation in Rubber Chem. Tech. 9, 383-408 (1936). (3) Carothers (to du Pont), U.S. 2,104,789, Jan. 11, 1938; Cent. 1939, I 4108; C.A. 32, 1718 (1938). (4) Carothers, Berchet, J. Am. Chem. Soc. 55, 2811-2813 (1933). (5) Coffman, J. Am. Chem. Soc. 57, 1981-1984 (1935). (6) I. G. Farbenindustrie, French 815,312, July 9, 1937; Cent. 1937, II 2750; C.A. 32, 958 (1938). (7) Carothers, Berchet (to du Pont), U.S. 2,136,177, Nov. 8, 1938; Cent. 1939, I 2497; C.A. 33, 1344 (1939). (8) Carothers, Berchet, J. Am. Chem. Soc. 55, 1628-1631 (1933). (9) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934; Cent. 1936, 1937; Cent. 1938, I 1236; C.A. 31, 3503 (1937).

[For prepn. from propionaldehyde (1:0110) with PCl₅ (36-37% yield (1)) together with other products see (1) (3) (5); for formn. (19.6%) (together with other products) from propane by vapor-phase chlorination at 400° see (6) (7) (8); for formn. from 1-chloropropene-1 (3:7030) by addn. of HCl at 0° in presence of FeCl₅ see (2).]

 \ddot{C} on hydrolysis yields propional dehyde (1:0110); for study of behavior of \ddot{C} with boilg. aq. + trace of NaHCO₃ or with boilg. aq. + Fe see (6).

Č with alc. KOH yields (5) 1-chloropropene-1 (3:7030) q.v.

3:7230 (1) Henne, Renoll, Leicester, J. Am. Chem. Soc. 63, 2477 (1941). (2) Kharasch, Engelmann, Mayo, J. Org. Chem. 2, 296, 301 (1937). (3) Kohlrausch, Köppl, Monatsh. 65, 196 (1935). (4) Hass, McBee, Weber, Ind. Eng. Chem. 28, 338 (1936). (5) Reboul, Ann. chim. (5) 14, 458-460 (1878). (6) McBee, Hass, Chao, Welch, Thomas, Ind. Eng. Chem. 33, 176-177 (1941). (7) Hass, McBee, Hinds, Gluesenkamp, Ind. Eng. Chem. 28, 1178-1179 (1936). (8) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,073, June 4, 1935; Cent. 1936, I 1500.

3: 7235
$$\alpha$$
-CHLORO-ISOBUTYRALDEHYDE CH₃ C₄H₇OCl Beil. I - 675 (2-Chloro-2-methylpropanal-1) CH₃—C-CHO I₁— I₂— I₂— B.P. 90° (1) (2) $D_{15}^{45} = 1.053$ (1) (2)

Colorless liq. with piquant odor suggestive of chloral.

[For prepn. of \bar{C} from 2-methylpropanol-1 (isobutyl alc.) (1:6165) with Cl_2 see (1) (2); from α,β -dichloroisobutyl isobutyl ether (see below) by htg. with aq. at 100° see (1) (2); from α -chloroisobutyraldehyde diisobutylacetal (see below) with anhydrous oxalic acid (1:0535) or with Ac₂O (1:1015) on htg. see (2); \bar{C} is not (2) formed by chlorination of isobutyraldehyde (1:0120).]

Č reduces Tollens' reagt., Fehling's soln., or KMnO₄ (1) (2); Č on oxidn. with alk. KMnO₄ yields (2) α-hydroxyisobutyric acid (1:0431), m.p. 79°.

C adds NaHSO₃ yielding a compd. from which C is regenerated with difficulty (1) (2).

 \bar{C} on shaking with conc. H_2SO_4 (½ vol.) yields (1) (2) the corresp. trimer, viz., para- α chloro-isobutyraldehyde (2,4,6-tris-(α -chloroisopropyl)trioxane-1,3,5) (3:3220), m.p. 107° (1) (2).

[$\bar{\rm C}$ with isobutyl alc. (1:6165) treated with HCl gas gives (2) α,β -dichloroisobutyl isobutyl ether, b.p. 192.5° at 760 mm., 83° at 15 mm., $D_4^{15}=1.031, n_D^{19}=1.437$ (2), also obtd. from isobutyl alc. directly with Cl₂ in the cold (2); note that this prod. with aq. on htg. gives $\bar{\rm C}+\alpha$ -chloroisobutyraldehyde di-isobutylacetal, b.p. 218° at 760 mm., 102° at 15 mm., $D_4^{15}=0.9355, n_D^{17}=1.428$ (2).]

[\tilde{C} (or the above α -chloroisobutyraldehyde di-isobutylacetal) with ethyl carbamate satd. with HCl gas gives (2) α -chloroisobutylidene bis-urethane (CH₃)₂C(Cl).CH(NH.-COOC₂H₅)₂, m.p. 122° (2).]

[For complex behavior of C with MeMgBr see (3).]

---- α-Chloro-isobutyraldoxime: m.p. 96-97° (4). [Prepd. indirectly from isobutylene with amyl nitrite + HCl (4).]

3:7235 (1) Brochet, Bull. soc. chim. (3) 7, 641-644 (1892). (2) Brochet, Ann. chim. (7) 10, 352-362 (1897). (3) Henry, Bull. acad. roy. Belg. 1907, 162-189; Cent. 1907, II 445; Rec. trav. chim. 26, 416, 425-429 (1907); Compt. rend. 144, 308 (1907). (4) Ipatiev, Soolonina, J. Russ. Phys.-Chem. Soc. 33, 496-501 (1901); Cent. 1901, II 1201.

3: 7240 3-CHLOROPENTENE-2 Cl
$$C_bH_9Cl$$
 Beil. I — I_1 — I_2 — CH_3 . CH_2 — CH_3 . CH_3 — CH_3 . CH_3 C

Two geometrical stereoisomers of C are possible but as yet unrecognized.

[For prepn. of \tilde{C} (together with 2-chloropentene-2 (3:7285) and other prods.) from methyl n-propyl ketone (1:5415) with PCl₅ see (1); for prepn. of \tilde{C} (together with other prods.) from diethyl ketone (propione) (1:5420) with PCl₅ (1) followed by treatment with alc. KOH (2) see (1) (2).]

Č with NaNH₂ in xylene at 130° gives (3) a little pentyne-2 (1:8040) and on subsequent pouring of the reacts, mixt, into water also pentyne-1 (1:8025).

3:7246 (1) Bourgeul, Bull. soc. chim. (4) **35**, 1634-1636 (1924); Ann. chim. (10) **3**, 368-371 (1925). (2) Favorskii, Favorskaya, J. Russ. Phys.-Chem. Soc. **54**, 305 (1922); Cent. **1923**, III 1359. (3) Bourgeul, Ann. chim. (10) **3**, 221, 341 (1925); Compt. rend. **178**, 1985 (1924).

3:7260 3-CHLOROPENTENE-1 Cl
$$C_6H_9Cl$$
 Beil. I — I_1 — I_2 — CH_3 — CH_2 — CH_2 — CH_2 — CH_2 — I_2 — I_2 — I_2 — I_3 — I_2 — I_3 — $I_$

B.P. 93-94° at 759.3 mm. (1)
$$n_{\rm D}^{23} = 1.4224$$
 (4) 92-93° (2) (3) $D_{\rm D}^{20} = 0.8978$ (1) $n_{\rm D}^{20} = 1.4254$ (1) $n_{\rm D}^{20} = 1.4254$ (1)

Note: \bar{C} by virtue of facile allylic transposition is readily converted to an equilibrium mixt. with its synionic isomer, 1-chloropentene-2 (3:7470) q.v.; reactns. of \bar{C} may therefore frequently yield also the corresponding derivatives of the isomer.

[For prepn. of \bar{C} (or its mixt. with 1-chloropentene-2 (3:7470)) from ethyl-vinyl-carbinol (penten-1-ol-3) with dry HCl (1) (3) (5) (7), with aq. HCl at 0° (6), with PCl₃ at 45° (4) or in cold with pyridine (7) or dimethylaniline (7) (55-59% (7)), with SOCl₂ alone (24% yield (7)) or in ether (24% yield (7)), or with dimethylaniline (43% yield (7)) see indic. refs.] [\bar{C} is separable from the accompanying isomer by careful fractional distillation (5) (7).]

 \tilde{C} on long shaking with aq. Na₂CO₃ gives (7) in very poor yield penten-1-ol-3 accompanied by much penten-3-ol-1 and other products. — \tilde{C} with alc. NaOEt gives (4) the corresp. ethyl ether, viz., 3-ethoxypentene-1, b.p. 102°, $D_{-}^{23} = 0.7768$, $n_{D}^{23} = 1.3986$, accompanied by the isomeric 1-ethoxypentene-2, b.p. 123°, $D_{-}^{23} = 0.7930$, $n_{D}^{23} = 1.4099$ (4).

[For extensive study of behavior of \bar{C} with KOAc + AcOH, with AgOAc, with N-methylaniline, with diethylamine, etc., see (7); for reactn. of \bar{C} with phenol in pres. of K_2CO_3 + acetone see (5).]

M-(Penten-1-yl-3)phthalimide [N-(α-ethylallyl)phthalimide]: colorless cryst. from alc., m.p. 78-79° (7). [From C on htg. with K phthalimide in a s.t. at 190-200° for 2½ hrs.; yield is only about half that obtd. from 1-chloropentene-3, the corresp. deriv. of which always accompanies that from C (7).]

3:7260 (1) Baudrenghien, Bull. soc. chim. Belg. 32, 338 (1923). (2) Mumm, Richter, Ber. 73, 858-860 (1940). (3) Mumm, Hornhardt, Diederichsen, Ber. 72, 107 (1939). (4) Prevost, Compt. rend. 187, 1053-1054 (1928). (5) Lauer, Filbert, J. Am. Chem. Soc. 58, 1388 (1936). (6) Prevost, Bull. soc. chim. (4) 49, 264-267 (1931). (7) Meisenheimer, Link, Ann. 479, 254-277 (1930).

3:7265-3:7270

Colorless liq. with odor like CHCl₃; does not fume in air (3). — Sol. in aq. at room temp. to extent of 8% by wt. (7).

[For prepn. from ethylene chlorohydrin $(3:5552) + (CH_3)_2SO_4$ (60% yield (2)) see (2); for prepn. from β -methoxyethanol (1:6405) with $PCl_3 + pyridine$ (65% yield (6)), or $SOCl_2 + dimethylaniline$ (7), or diazomethane (5) see (6) (5) (7); for prepn. from ethylene + N,N-dichlorobenzenesulfonamide see (1).]

 \bar{C} on shaking with aq. does not hydrolyze (dif. from α -chloroethers).

3:7265 (1) Sklyarov, J. Gen. Chem. (U.S.S.R.)
 9, 2121-2125 (1939); C.A. 34, 4055 (1940).
 42) Jones, Powers, J. Am. Chem. Soc. 46, 2531-2532 (1924).
 43) Fileti, de Gaspari, Gazz. cham. ital.
 44) Karvonen, Ann. Acad. Scs. Fennicae 3-A, No. 7, 1-103 (1912); Cent. 1912, II 1269; C.A. 14, 2175 (1920).
 45) Meerwein, Hinz, Ann 484, 17 (1930).
 46) Palomaa, Kenetti, Ber. 64, 798 (1931).
 47) Bennett, Heathcoat, J. Chem. Soc. 1929, 270.

3: 7270 ISOBUTYRYL CHLORIDE
$$CH_3.CH-C=O$$
 C_4H_7OCl Beil. II - 293 II_{1} -(128) $CH_3.Cl$ II_{2} -(262) II_{2} -(262) B.P. F.P. 92° (1) (2) -90° (7) $D_4^{20} = 1.0174$ (8) $n_D^{20} = 1.40789$ (8) 91.5-92.5° at 748.2 mm. (8) 1.4080 (3) 91-92° (3) 1.4070 (5) 90-92° (30) 91° at 735 mm. (4) 90-91° (5) 85-88° at 680 mm. (6)

[For prepn. of \bar{C} from isobutyric acid (1:1030) with PCl₅ (81% yield (9)), with PCl₃ (yield: 94% (6), 75% (2)) (8) (4), with PCl₃ + ZnCl₂ (82% yield (9)), with SOCl₂ (yield: 90% (30), 75% (4) (5), 70% (10), 44% (9)), with benzoyl chloride (82-88% yield (13)), or with SiCl₄ in xylene (52% yield (11)) see indic. refs.; for prepn. of \bar{C} from sodium isobutyrate with POCl₃ see (1) (12).]

[\bar{C} with isobutyric acid (1:1030) (14) or \bar{C} with pyridine in ether (15) yields isobutyric anhydride (1:1110), b.p. 182.5°.]

[\bar{C} on passing over Ni at 420° dec. (16) into HCl, CO, CO₂, H₂, CH₄ + propylene; \bar{C} + NH₃ over Al₂O₃ at 490-500° yields (17) isobutyronitrile, b.p. 108°.]

[\bar{C} with Et₃N in dry ether or lgr. at room temp. gives (18) 95% yield triethylamine hydrochloride + 57% yield dimethylketene dimer, cf. also (19) (20).]

[Č with Cl_2 (31) in CCl_4 gives (12) cf. (21) 60-70% α -chloro-isobutyryl chloride (3:5385) + 30-40% β -chloroisobutyryl chloride (3:9101); Č with SO_2Cl_2 in pres. of dibenzoyl peroxide gives (22) 20% α -chloroisobutyryl chloride (3:5385) + 80% β -chloro-isobutyryl

chloride (3:9101). — Č with Br₂ htd. in s.t. 4 hrs. at 100° gives mainly (10) α-bromoisobutyryl bromide, b.p. 163°.]

[C added to large excess of certain RMgX cpds. is in part reduced and in part undergoes ordinary coupling with formn. of ketones; e.g., C with ter-BuMgCl in ether gives (5) (4) (3) 63% ter-butyl-isopropyl-carbinol + 20% isobutyl alc. + 18% 2,2,4-trimethylpentanone-3; C with ter-AmMgCl gives (3) 44% isobutyl isobutyrate.]

[For reactn. of \bar{C} with ethyl sodio-acetoacetate see (6); with ethyl acetoacetate + Mg see (23); with ethyl isobutyrate + triphenylmethylsodium giving 55% yield ethyl $\alpha, \alpha, \gamma, \gamma$ -tetramethylacetoacetate see (24).]

[C with 2-methylbutene-2 (trimethylethylene) + SnCl₄ gives (25) 2-chloro-2,3,5-trimethylhexanone-4, b.p. 74-79° at 14 mm.; C with cyclohexene + SnCl₄ gives (26) 1-cyclohexenyl isopropyl ketone, b.p. 96° at 6 mm.]

[Č with AlCl₃ + C₆H₆ gives (27) isobutyrophenone (isopropyl phenyl ketone) (1:5528); Č with AlCl₃ + toluene gives (28) isopropyl p-tolyl ketone [Beil. VII-331, VII₁-(176)]; Č with AlCl₃ + mesitylene gives (29) 75% yield isopropyl mesityl ketone.]

Č on hydrolysis yields isobutyric acid (1:1030), b.p. 154.7°. — For the amide (30), anilide, p-toluidide, and other derivs. corresp. to Č see isobutyric acid (1:1030).

3:7270 (1) Markownikow, Zeit. für Chemie 1866, 501. (2) Recsei, Chem. Ztg. 52, 22 (1928). (3) Whitmore, Whitsker, Miner, J. Am. Chem. Soc. 63, 647, 650, 653-654 (1941). (4) Whitmore, Rec. trav. chim. 57, 565 (1938). (5) Greenwood, Whitmore, Crooks, J. Am. Chem. Soc. 60, 2029 (1938). (6) Ranganathan, J. Indian Chem. Soc. 16, 68-69 (1939). (7) Timmermans, Mattaar, Bull. soc. chim. Belg. 30, 216 (1921). (8) Bruhl, Ann. 203, 20 (1880). (9) Clark, Bell. Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (10) Smith, Lewcock, Ber. 45, 2358-2359 (1912).

Roy. Soc. Can. (3) 27, III 97-103 (1933). (10) Smith, Lewcock, Ber. 45, 2358-2359 (1912). (11) Montonna, J. Am. Chem. Soc. 49, 2114-2116 (1927). (12) Michael, Ber. 34, 4054-4055 (1901). (13) Brown, J. Am. Chem. Soc. 60, 1325-1328 (1938). (14) Toennies, Staub, Ber. 17, 850-851 (1884). (15) Wedekind, Ber. 34, 2073 (1901). (16) Mallhe, Compt. rend. 180, 111 (1925). (17) Mailhe, Bull. soc. chim. (4) 23, 380 (1918); Ann. chim. (9) 13, 212 (1920). (18) Miller, Johnson, J. Org. Chem. 1, 138-139 (1937). (19) Wedekind, Weisswange, Ber. 39, 1631-1646 (1906). (20) Wedekind, Miller, Ber. 42, 1269-1275 (1909).

(21) Henry, Bull. acad. roy. Belg. 1906, 206-226; Cent. 1906, II 227. (22) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940). (23) Spassow, Ber. 70, 2383-2384 (1933). (24) Hauser, Renfrew, Org. Syntheses 19, 43-44 (1939). (25) Colonge, Mostafavi, Bull. soc. chim. (5) 6, 349-350 (1939). (26) Colonge, Deroux, Bull. soc. chim. (5) 7, 459-468 (1940); C.A. 36, 2842 (1942). (27) Evans, J. Chem. Soc. 1936, 788. (28) Claus, J. prakt. Chem. (2) 46, 480-481 (1892). (29) Maxwell, Adams, J. Am. Chem. Soc. 52, 2964 (1930). (30) Kent, McElvain, Org. Syntheses 25, 58-60 (1945).

(31) Schmidt, Schloffer (to I.G.) Ger. 738,398, July 15, 1943; C.A. 38, 3992 (1944).

B.P. 92.9-93.0° at 760 mm. (1)
$$D_4^{20} = 0.8685$$
 (4) $n_D^{20} = 1.4081$ (4) 91.8-91.9° at 753 mm. (2) 0.878 (2) 1.4095 (2) 91° at 753 mm. (3) 45.4° at 150 mm. (1) 25-27° at 60 mm. (4)

Stable at b.p., at 100° for 24 hrs., to aq. at room temp. (2). — \ddot{C} is not present in comml. "mixed amyl chlorides" (1).

[For prepn. of \bar{C} from 2-methylbutene-3 (1:8200) + HCl in dark at room temp. in s.t. for 7 months (88% yield (2)), or + HCl at 100° (5) (6), or at -80° in presence of AlCl₃ (4)

see indicated refs.] [Note that Č cannot be prepd. from the corresp. alc., 2-methylbutanol-3 (1:6170) + HCl since only ter-amyl chloride (3:7220) results (11).]

[For formn. of \tilde{C} from either 2-methylbutene-1 (1:8210) or 2-methylbutene-2 (1:8220) at -80° in presence of AlCl₃ see (7); from isoamyl alcohol (1:6200) + HCl over Al₂O₃ at 430° see (8); from isoamyl chloride (3:7365) over ThCl₄ or BaCl₂ at 250°, finally over pumice at 200°, see (9); from 2-methylbutane (1:8500) + Cl₂ see (10) (1).]

[For study of reactn. of C with Na see (12) (13).]

Č with Mg in dry ether yields (1) (2) corresponding R.Mg.Cl whose treatment with dry O₂ followed by hydrolysis yields (1) (2) 2-methylbutanol-3 (1:6170); [3,5-dinitrobenzoate, cryst. from dil. MeOH (1) or dil. EtOH (2), m.p. 76° (1) (2); N-(α-naphthyl)-carbamate, cryst. from pet. eth., m.p. 111-112° (2) (1).] — This R.Mg.Cl should also react according to method of (11) with phenyl isocyanate to yield isopropyl-methyl-acetanilide, m.p. 78.4° (14), 75° (15), although the execution of this reactn. is not recorded.

 \ddot{C} with excess N/10 AgNO₃ is practically completely hydrolyzed in 60 hrs. (2) [dif. from isoamyl chloride (3:7365) which reacts only to extent of 3-4%].

3:7275 (1) Hass, McBee, Weber, Ind. Eng. Chem. 27, 1192-1195 (1935). (2) Whitmore, Johnston, J. Am. Chem. Soc. 55, 5020-5022 (1933). (3) Wyschnegradsky, Ann. 190, 357 (1877). (4) Leendertse, Tulleners, Waterman, Rec. trav. chim. 52, 519 (1933). (5) Berthelot, Ann. 127, 71 (1863). (6) Wurtz, Ann. 129, 368 (1864). (7) Leendertse, Tulleners, Waterman, Rec. trav. chim. 53, 717 (1934). (8) Sabatier, Mailhe, Compt. rend. 169, 124 (1919). (9) Sabatier, Mailhe, Compt. rend. 156, 658 (1913). (10) Aschan, Cent. 1918, II 939.

Underwood, Gale, J. Am. Chem. Soc. 56, 2117 (1934).
 Morton, LeFevre, Hechenbleikner, J. Am. Chem. Soc. 58, 757 (1936).
 Morton, Hechenbleikner, J. Am. Chem. Soc. 58, 1699 (1936).
 Hommelen, Bull. soc. chim. Belg. 42, 249 (1933).
 Crossley, Perkin, J. Chem. Soc. 73, 17 (1898).

B.P. 95-97° (1)

The structure of this material is inadequately supported; the prod. may very possibly be identical with 2-chloropentene-2 (3:7285) q.v.

[For prepn. of \bar{C} from 2,2-dichloropentane (3:7755) with alc. KOH see (1).] \bar{C} on further treatment with alc. KOH yields (1) pentyne-1 (1:8025), b.p. 39.7°.

3:7280 (1) Bruylants, Ber. 8, 411 (1875).

3: 7285 2-CHLOROPENTENE-2 Cl
$$C_8H_9Cl$$
 Beil. I — I_1 — I_1 — I_2 — I_3 — I_4 — I_2 — I_2 — I_3 — I_4 — I_4 — I_4 — I_5 —

Two geom, stereoisomers of C are possible but as yet unrecognized.

[For prepn. of \bar{C} from 2,2-dichloropentane (3:7755) with boilg. 10% alc. KOH see (1); from pentanone-2 (1:5415) with PCl₅ see (2).]

C with conc. H₂SO₄ followed by aq. yields (1) methyl-n-propyl ketone (pentanone-2 (1:5415), b.p. 102°.

[C with NaNH2 in xylene at 130° followed by ice water gives (3) pentyne-1 (1:8025).]

C on oxidn. with KMnO₄ yields (1) propionic acid (1:1025) + AcOH (1:1010).

3:7285 (1) Lemke, Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 1995-1998 (1937); Cent. 1939, I 2398; C.A. 32, 482 (1938). (2) Bourgeul, Ann. chim. (10) 3, 369-370 (1925); Bull. soc. chim. (4) 35, 1633 (1924). (3) Bourgeul, Ann. chim. (10) 3, 220, 370 (1925).

3: 7290 3-CHLORO-2-METHYLBUTADIENE-1,3
$$C_5H_7Cl$$
 Beil. S.N. 12 (2-Chloro-3-methylbutadiene-1,3; Cl CH_3 " β -Chloroisoprene") $H_2C=C-C=CH_2$ B.P. 93° at 760 mm. (1) $D_4^{20}=0.9593$ (1) $n_D^{20}=1.4689$ (1) 41° at 113 mm. (1) (2) 37° at 105 mm. (1)

[For prepr. of \bar{C} (40% yield (1)) from 2-methylbutene-1-yne-3 by treatment as specified (1) with HCl + Cu₂Cl₂ + NH₄Cl see (1) (2) (10); for prepr. (60% yield (3) (4)) from 2,3,3-trichloro-2-methylbutane (3:4755) with quinoline (2 moles) at 140-225° see (3) (4).]

 $\bar{\mathbf{C}}$ readily polymerizes; for details see (1) (2). [For prepn. of plastic polymers from $\bar{\mathbf{C}}$ see (5).]

 \bar{C} htd. in s.t. 16 hrs. at 160° with SO₂ in ord. (not dry) ether yields (6) (7) (10) by 1,4-addition a compd. designated (6) (7) as 1,1-dioxo-3-chloro-4-methylthiacyclopentene-3, ndls. from aq. (7) or alc. (6), m.p. 120.0-120.5° (6) (7). [For extensive study of this prod. see (7).] [The corresponding selenium analog, in very poor (2%) yield from \bar{C} + SeO₂ in CHCl₃ (8), has m.p. 110° dec. (8).]

Č (1 g.) with 1,4-naphthoquinone (1:9040) htd. at 100° for ½ hr. gives (1) on cooling 2-chloro-3-methyltetrahydroanthraquinone, white ndls. from acetone, m.p. 165-166° u.c. (1); this prod. on suspension in dil. alc. NaOH and oxidn. of the blue soln. with air until yel., followed by dilution with aq., gives (1) 2-chloro-3-methylanthraquinone, cryst. from AcOH, m.p. 214-215° u.c. (1), 215° u.c. (9).

3:7290 (1) Carothers, Coffman, J. Am. Chem. Soc. 54, 4074-4076 (1932). (2) Carothers, Coffman (to du Pont), U.S. 1,950,441, March 13, 1934; Ger. 588,708, Nov. 24, 1933; Brit. 395,301, Oct. 10, 1933; Cent 1934, II 1038. (3) Tishchenko, J. Gen. Chem. (U.S.S. R.) 6, 1116-1132 (1936); Cent. 1937, I 573; C.A. 31, 1003 (1937). (4) Tishchenko, Russ. 44,249, Sept. 20, 1935; Cent. 1936, I 3575; C.A. 32, 2962 (1938). (5) du Pont Co., Brit. 529,838, Nov. 29, 1940; C.A. 35, 7758 (1941); French 853,478, Mar. 20, 1940; C.A. 36, 2650 (1942). (6) Backer, Strating, Rec. trav. chim. 53, 542-543 (1934). (7) Backer, van der Baan, Rec. trav. chim. 56, 181-185 (1937). (8) Backer, Strating, Rec. trav. chim. 53, 1118 (1934). (9) Keimatsu, Hirano, J. Pharm. Soc. Japan 49, 140-147 (1929); C.A. 23, 3466 (129). (10) Backer, Blass, Rec. trav. chim. 61, 785-801, 924 (1942); Cent. 1943, I 1567-1569, C.A. 38, 3646-3647 (1944).

3:7295 ETHYL CHLOROFORMATE Cl.CO.OC₂H₅ C₃H₅O₂Cl Beil. III - 10 ("Ethyl chlorocarbonate") III₁-(5) III₂-(10)

B.P.
$$F.P.$$
 -80.6° (1) $D_4^{25} = 1.127$ (10) $D_2^{21.2} = 1.3949$ (8) $D_4^{20} = 1.13519$ (4) $D_4^{20} = 1.13519$ (5) $D_2^{20} = 1.39738$ (4) $D_2^{20} = 1.14419$ (6) $D_2^{20} = 1.14419$ (7) $D_2^{20} = 1.14419$ (8) $D_2^{20} = 1.14419$ (9) $D_2^{20} = 1.144$

Note 1. For D_4^1 between -75.5° (1.278) and $+84.8^{\circ}$ (1.022) see (10).

 $\ddot{\mathbf{C}}$ has strong lachrymatory properties. — [For study of toxicity see (11).] — $\ddot{\mathbf{C}}$ is comml. chemical in U.S.A.

[For prepn. of C from carbonyl chloride (phosgene) (3:5000) with abs. EtOH (1:6130) (90% yield (12)) in pres. of dimethylaniline, quantine, or antipyrine (13) or even Ca(OH)₂ (14) see indic. refs.; for formn. of C from diethyl carbonate (1:3150) with PCl₅ (15), from diethyl pyrocarbonate O(COOEt)₂ (16) with SOCl₂ (17); from pentachloroethyl chloroformate [Beil. III-13, III₁-(6)] (18) or bis-(trichloromethyl) carbonate (triphosgene) (3:1915) (19) or bis-(trichloromethyl) oxalate [Beil. III-17] (20) with EtOH, or from K xanthate, ethyl xanthate, or benzyl xanthate with Cl₂ + aq. in cold (21) see indic. refs.]

Pyrolysis of \bar{C} . \bar{C} on htg. at 250° decomposes yielding (4) EtCl (3:7015) + CO₂ (for study of this reactn. see (22) (23)); in pres. of certain hydrocarbons or esters (24) or in pres. of dimethylaniline (25) temp. of this decomposition is lowered to 150°, in pres. of quinoline to 59° (26) (27), in pres. of AlCl₃ to room temp. (28) (see also below under \bar{C} + pyridine or quinoline).

 \tilde{C} in pres. of anhydrous ZnCl₂ (29) (30) or even metallic Zn (31) decomposes at room temp. yielding (29) (30) EtCl (3:7015) + ethylene + CO₂ + HCl.

Reactions of the $-COOC_2H_5$ group of \bar{C} . \bar{C} on hydrolysis, e.g., by boilg. with aq. or dil. acid (32), yields $CO_2 + HCl + c$ thylene; on alkaline hydrolysis, however, no ethylene is formed (32); note that \bar{C} does not react with cold aq. very rapidly and may even be washed with it to remove alcohol.

[\tilde{C} at its b.p. treated with Cl₂ in sunlight undergoes further substitution by halogen yielding as final prod. (33) (34) pentachloroethyl chloroformate (ref. given above under prepn. of \tilde{C}).]

[\bar{C} with EtHSO₄ at 100° under reflux for 6-8 hrs. gives (40% yield (48)) Et₂SO₄ + EtCl (3:7015).]

Reactions of the chlorine atom of \bar{C} . [\bar{C} on reduction with 3% Na/Hg + aq. gives (51% yield (35)) salt of formic acid (1:1005).]

[C in CHCl₃ with Na₂O₂ does not react until 1-2 drops of aq. are added; vigorous actn. then ensues with forms. of the expected (but very explosive) dicarbethoxy peroxide (EtOOC—O—O—COOEt) (36).]

[\bar{C} with NaSH (37) or with \bar{C}_2H_5 —S—MgBr (38 in ether gives (68% yield (38)) O_2S -diethyl thiocarbonate [Beil. III-133, III₁-(62), III₂-(105)], b.p. 158-159° cor.; \bar{C} (2 moles) + aq. (39) or alc. (40) Na₂S, \bar{C} with BrMgSH in ether (41), or \bar{C} with aq. potassium trithiocarbonate (39), gives diethyl thiodiformate (dicarbethoxy sulfide) [Beil. III-133, III₂-(105)], b.p. 180° dec.]

[C with thallous fluoride 12 hrs. at room temp., then refluxed 2-3 hrs., gives (47% yield (42)) ethyl fluoroformate, lachrymatory oil, b.p. 57° (42).]

[For rate of reactn. of C with KI in acctone at 25° see (43).]

[\bar{C} with aq. alc. KCN at -13° (44) or with solid NaCN (contg. 0.2-7.0% moisture) at not above 90° (45) gives (yields: 90% (45), 46% (44)) ethyl cyanoformate [Beil. II-547, II₁-(238), II₂-(510)], b.p. 115-116° (46), $D_4^{20}=1.0034$ (47), $D_D^{20}=1.3821$ (47).]

 $\tilde{\mathbf{C}}$ as carbethoxylating agent. $\tilde{\mathbf{C}}$ is widely employed as a means of introducing the $-\mathrm{COOEt}$ group into other organic molecules by reactn. of the chlorine atom with the H of the alcoholic, phenolic, or enolic OH groups (or their metallic alcoholates, phenolates, enolates, etc.); under appropriate conditions $\tilde{\mathbf{C}}$ is also employed to introduce the $-\mathrm{COOEt}$ group into an aromatic nucleus. Examples of these reactns, are cited below.

[C with NaOMe yields (49) ethyl methyl carbonate [Beil. III-4, III₂-(4)], b.p. 109° C with NaOEt yields diethyl carbonate (1:3150); other alcohols behave similarly (50). — C with K phenolate or C with phenol in ether + dry K₂CO₃ gives (71% yield (51)) ethyl phenyl carbonate [Beil. VI-157], b.p. 229°; other mono-, di-, and polyhydric phenols behave

similarly. — \bar{C} (1 mole) with salicylic acid (1:0780) in pyridine at -15° (52) or in C_6H_6 with dimethylaniline (63% yield (52)) gives O-carbethoxysalicylic acid [Beil. X-69, X₁-(30)], m.p. 95° (other mono-, di-, and polyhydroxy phenolic acids behave similarly); since the carbethoxy groups so introduced may subsequently be removed by hydrolysis, this process has great value as a means of temporary blocking of phenolic groups (for further discussion and many references see (53)).]

[\bar{C} also reacts with the sodio derivatives and other metallic enolates: e.g., \bar{C} (1 mole) with ethyl cyanoacetate (2 moles) in abs. alc. + NaOEt (2 moles) gives (54) diethyl cyanomalonate [Beil. II-811, II₁-(321), II₂-(680)], b.p. 138-140° at 14 mm., $D_4^{20}=1.1128$, $D_2^{20}=1.4295$ (55). — \bar{C} with diethyl malonate (1:3581) + NaOEt in alc. (56) or \bar{C} with dry diethyl sodio-malonate (57) directly (58) (59) or in C_8H_6 refluxed for 10 hrs. (60) gives (yields: 50-80% (59), 60-65% (60)) triethyl methane-tricarboxylate (tricarbethoxymethane) [Beil. II-810, II₁-(320), II₂-(680)], m.p. 29°, b.p. 253°; note that this same prod. is also obtained (yields: 88-93% (61), 90% (62), 80% (63)) from \bar{C} with diethyl malonate (1:3581) in abs. alc. with Mg + trace CCl₄. — \bar{C} with the Na enolate of ethyl isobutyrate (1:3095) gives (75% yield (64)) diethyl dimethylmalonate [Beil. II-648, II₁-(276), II₂-(572)], b.p. 195-196° at 760 mm. — The reactn. of \bar{C} with ethyl sodioacetoacetate cannot be discussed here.]

[C with excess RMgX compounds presumably gives first the corresp. esters which by further normal reactn. with more RMgX are converted to tertiary alcohols: e.g., C with EtMgBr (excess) yields (65) triethylcarbinol (1:6218); however, the intermediate ester can often readily be obtd.; e.g., C (1 mole) with ter-BuMgCl (1 mole) in dry ether gives (56% yield (66)) ethyl trimethylacetate (ethyl pivalate (1:3117), and other cases are recorded (66); note, however, that with certain types of RMgX cpd. abnormal reactions can occur: e.g., C with benzyl MgCl yields not only the normal tribenzylcarbinol but also (67) ethyl o-toluate (1:3862). — C also reacts with the =N—MgX grouping replacing—MgX by—COOEt (sometimes followed by rearrangement): e.g., C + 3,5-dimethyl-pyrrole-N-(magnesyl bromide) gives (57-58% yield (68)) 5-carbethoxy-2,4-dimethyl-pyrrole.]

Č also reacts readily with NH₃, with primary and secondary amines, with amino acids, etc., to replace one of the H's attached to N by the —COOEt group (see also below and under ♠): e.g., Č with excess conc. aq. NH₄OH immediately (if delayed, urea is formed) evaporated to dryness gives (3) ethyl carbamate (urethane) [Beil. III-22, III₁-(9), III₂-(19)], very eas. sol. aq., cryst. from abs. alc., dry ether, CHCl₃, or C₆H₆, m.p. 48°, b.p. 184°. — [Č (1 mole) in ether with 33% aq. MeNH₂ soln. (1 mole) + aq. NaOH below 5° as directed (69) gives (88–90% yield (69)) (70) (71) ethyl N-methylcarbamate [Beil. IV-64, IV₁-(330), IV₂-(567)], oil, very sol. aq. (69 g. in 100 ml. aq. at 15.5° (72)), b.p.170°. — Countless other, analogous reactns. cannot be cited here.]

[\tilde{C} with hydroxylamine hydrochloride + conc. aq. Na₂CO₃ (73) or with dry K₂CO₃ in ether (74) gives (89.6% yield (74)) N-hydroxyurethane (carbethoxyhydroxamic acid) [Beil. III-95, III₂-(77)], oil, very sol. aq.]

Č with hydrazine hydrate in alc. refluxed ½ hr. (75) (for starting with hydrazine sulfate see (76)) gives (yields: 100% (76), 90% (75)) diethyl sym.-hydrazinedicarboxylate (sym.-dicarbethoxyhydrazine) [Beil. III-98, III₁-(46), III₂-(79)], cryst. from hot aq., ndls. from CHCl₃, m.p. 130° (75), 131° (76) (note that the half reaction product, viz., ethyl hydrazine-monocarboxylate (N-aminourethane) (ethyl carbazinate), is also known (77) (78) but is an oil. — Č (1 mole) with urea (2.1 moles) refluxed for 2-3 hrs. gives (62-65% yield (79)) ethyl allophanate (N-carbethoxyurea) [Beil. III-69, III₁-(31), III₂-(56)], m.p. 192°.

Č (1 mole) in ether with phenylhydrazine (2 moles) in ether (80) (81) (82) (76) or in aq. pyridine (83) gives (yields: 60-65% (80), 60% (76)) ethyl ω-phenylcarbazinate (β-carb-

ethoxy-phenylhydrazine) [Beil. XV-286, XV₁-(71)], cryst. from dil. alc. or C_6H_6 /lgr. as monohydrate, m.p. 85° (81) (82), anhydrous form, m.p. 82-83° (81), 80-82° (76). — \tilde{C} with p-nitrophenylhydrazine in pyridine gives (84) β -carbethoxy-p-nitrophenylhydrazine, cryst. from alc., m.p. 198-199° (84). — \tilde{C} with 2,4-dinitrophenylhydrazine in pyridine gives (84) β -carbethoxy-2,4-dinitrophenylhydrazine, cryst. from aq. alc., m.p. 168-169° (64).

 \tilde{C} (1 mole) with pyridine (1 mole) in the cold gives first a colorless addn. prod. (85) which rapidly turns red (can be used as test for pyridine (85)) and on warming rapidly decomposes with evolution of CO_2 + EtCl (3:7015); \tilde{C} similarly treated with quinoline gives a yellow amorphous solid, considerably more stable than the above pyridine cpd., but at 100° decomposing similarly but more slowly (85) in the same manner (see also above under pyrolysis).

- **©** Ethyl N-(p-tolyl)carbamate (p-tolylurethane): pr. from alc., m.p. 52-53° (21), 52° (88). [From \tilde{C} (1 mole) with p-toluidine (2 moles) in ether (21) (88).]
- N,N'-bis-(Benzyl)urea: ndls. from alc., m.p. 167.5-169° cor. (89). [From C (1 ml.) with benzylamine (3 ml.) + trace NH₄Cl refluxed 1 hr. (89); note that in this reactn. (unlike the two preceding cases) the reagent amine not only reacts with the chlorine atom of C but also ammonolyzes the carbethoxy group; the prod. is therefore a disubstituted urea rather than the ethyl N-benzylcarbamate [Beil. XII-1049], lfts. from lgr., m.p. 48-49° (90), which is formed from C + benzylamine + cold aq. NaOH (90).]
- ---- N-(Carbethoxy)phthalimide: unreported.
- --- N-(Carbethoxy)-3-nitrophthalimide: unreported.
- —— N-(Carbethoxy)-tetrachlorophthalimide: unreported. [Note that C with K tetrachlorophthalimide fails to react under reflux and explodes on htg. in s.t. (92).]
- —— S-(Carbethoxy)isothiourea picrate: m.p. 150-151° (93). [Note that Č (1 mole) with thiourea (1 mole) in conc. aq. soln. on treatment with NaHCO3 in slight excess evolves CO2 and ppts. S-(carbethoxy)isothiourea bicarbonate, bulky white ppt., insol. aq., m.p. 59-60° dec.; this ppt. on immediate treatment with dil. HCl dissolves and from the solution PkOH gives S-(carbethoxy)isothicurea picrate; the same prod. may also be obtd. from the original aq. soln. of Č + thiourea by direct addn. of PkOH (93). Note, however, that the above bicarbonate on stdg. with aq. changes spontaneously to N,N-dicarbethoxythiourea, m.p. 97° dec., + thiourea. Note, however, that Č (1 g.) with thiourea (1 g.) in EtOH (10 ml.) refluxed 30 min., then treated with PkOH (1 g.) does not yield the above prods. but instead (94) S-ethyl-isothiourea picrate, m.p. 187° (94).]

3:7295 (1) Timmermans, Bull. soc. chim. Belg. 31, 392 (1922). (2) Perkin, J. Chem. Soc. 65, 420 (1894). (3) Dumas, Ann. chim. (2) 54, 225-237 (1833); Ann. 10, 277-288 (1834). (4) Pavlevski, Ber. 25, 1449-1451 (1892). (5) Forster, Newman, J. Chem. Soc. 97, 2573 (1910). (6) Karvonen, Ann. Acad. Sci. Fennicae A-10, No. 4, 19, Cent. 1919, III 808. (7) Mizushima, Kubo, Bull. Chem. Soc. Japan 13, 178 (1938). (8) Guye, Mallet, Arch. sci. phys. Nat. Genève (4) 13, 274-296; Cent. 1902, I 1315. (9) von Auwers, Ber. 60, 2140 (1927). (10) Jaeger, Z. anorg. allgem. Chem. 101, 67 (1917).

(11) Eichholtz, Mertz, Arch. exptl. Path. Pharmakol. 171, 125-126 (1933); Cent. 1933, II 2160; C.A. 27, 5814 (1933). (12) Cappelli, Gazz. chim. ital. 50, II 8-12 (1920); C.A. 15, 524 (1921). (13) Bayer & Co., Ger. 118,536, 118,537, Feb. 28, 1901; Cent. 1901, I 651; Ger. 117,624, Jan. 29, 1901; Cent. 1901, I 428. (14) Hochstetter, Ger. 282,134, Feb. 16, 1915; Cent. 1915, I 464. (15)

Rose, Ann. 205, 247 (1880). (16) Boehm, Mehta, Ber. 71, 1797-1802 (1938). (17) Parfent'ev, Shamshurin, Trudy Uzbekskogo Gosudarst. Univ. Sbornik Rabot Khim. 15, 67-74 (1939); C.A. 35, 4351 (1941). (18) Cloez, Ann. chim. (3) 17, 302 (1846); Ann. 60, 260 (1846). (19) Marotta, Gazz. chim. ital. 59, 960 (1929); Cent. 1930, I 2546; C.A. 24, 3993 (1930). (20) Cahours, Ann. chim. (3) 19, 346-349 (1847); Ann. 64, 314 (1848).

(21) Douglass, Johnson, J. Am. Chem. Soc. 60, 1488 (1938). (22) Choppin, Frediani, Kirby, J. Am. Chem. Soc. 61, 3176-3180 (1939). (23) Choppin, Kirby, J. Am. Chem. Soc. 62, 1592-1594 (1940). (24) Wilm, Wischin, Ann. 147, 150-157 (1868). (25) Rivier, Richard, Helv. Chim. Acta 8, 495 (1925). (26) Carré, Passedouet, Compt. rend. 200, 1767-1769 (1935). (27) Carré, Bull. soc. chim. (5) 3, 1069, 1072 (1936). (28) Rennie, J. Chem. Soc. 41, 33 (1882). (29) Underwood, Baril, J. Am. Chem. Soc. 53, 2200-2201 (1931). (30) Ulsch, Ann. 226, 281-286 (1884).

(31) Geuther, J. prakt. Chem. (2) 6, 161 (Note) (1872). (32) Thiele, Dent, Ann. 302, 256-257 (1898). (33) Muller, Ann. 258, 50-66 (1890). (34) Anschutz, Emery, Ann. 273, 61-63 (1893). (35) Geuther, Ann. 205, 223-226 (1880). (36) Wieland, von Hove, Börner, Ann. 446, 46-47 (1926). (37) Salomon, J. prakt. Chem. (2) 6, 435-439 (1872). (38) Hepworth, Clapham, J. Chem. Soc. 119, 1195 (1921). (39) Holmberg, J. prakt. Chem. (2) 71, 278-279 (1905). (40) Meyer, Ber. 2, 298 (1869).

(41) Mingoia, Gazz. chim. ital. 55, 719 (1925). (42) Goswann, Sarkar, J. Indian Chem. Soc. 10, 537-539 (1933). (43) Conant, Kirner, Hussey, J. Am. Chem. Soc. 47, 489 (1925); Conant, Kirner, J. Am. Chem. Soc. 46, 249 (1924). (44) Nef, Ann. 287, 308 (1895). (45) Gluud, Nussler, Keller (to Gesellschaft fur Kohlentechnik), Ger. 592,539, Feb. 17, 1934; Cent. 1934, II 3437; C.A. 28, 3417 (1934). (46) Weddige, J. prakt. Chem. (2) 10, 197-199 (1874). (47) Haller, Muller, Ann. chim. (8) 14, 135 (1908). (48) Kraft, Lyutina, J. Gen. Chem. (U.S.S.R.) 1, 190-192 (1931); Cent. 1931, II 3197; C.A. 26, 2167 (1932). (49) Schreiner, J. prakt. Chem. (2) 22, 354 (1880). (50) Rose, Ann. 205, 241-246 (1880).

(51) Claisen, Ber. 27, 3183 (1894).
(52) Einhorn, Ber. 44, 435-436 (1911).
(53) Meyer, "Analyse und Konstitutionsermittlung organischer Vergindungen," 6th ed., pp. 448-451, 507 (1938).
(54) Haller, Ann. chim. (6) 16, 428-429 (1889).
(55) Mignonae, Rambeck, Compt. rend. 188, 1299 (1929).
(56) Conrad, Guthzeit, Ann. 214, 31-33 (1882).
(57) Adıckes, Ber. 59, 2527-2528 (1926).
(58) Michael, J. prakt. Chem. (2) 37, 476 (1888).
(59) Philippi, Hanusch, von Wacek, Ber. 54, 901 (1921).
(60) Adıckes, Bunnert, Lucker, J. prakt Chem. (2) 130, 163-166 (1931).

(61) Lund, Voigt, Org. Syntheses, Coll. Vol. 2 (1st ed.), 594-596 (1943); 17, 86-88 (1937). (62) Lund, Ber. 67, 938 (1934). (63) Backer, Lolkema, Rec. trav. chrm. 57, 1239 (1938). (64) Hudson, Hauser, J. Am. Chem. Soc. 63, 3160 (1941). (65) Mazurewitsch, J. Russ. Phys.-Chem. Soc. 42, 1582-1589 (1910); Cent. 1911, I 1500. (66) Whitmore, Badertscher, J. Am. Chem. Soc. 55, 1563-1564 (1933). (67) Austin, Johnson, J. Am. Chem. Soc. 54, 653-654 (1932). (68) Fischer, Org. Syntheses, Coll. Vol. 2, 198-200 (1943); 17, 48-50 (1937). (69) Hartmann, Brethen, Org. Syntheses, Coll. Vol. 2 (1st ed.), 278 (1943); 12, 38-39 (1932). (70) Schreiner, J. prakt. Chem. (2) 21, 124-125 (1880).

(71) von Pechmann, Ber. 28, 855-856 (1895).
(72) Fühner, Ber. 57, 514 (1924).
(73) Hantzsch, Ber. 27, 1255 (1894).
(74) Jones, Am. Chem. J. 20, 39-40 (1898).
(75) Curtuus, Heidenreich, J. prakt. Chem. (2) 52, 476-477 (1895).
(76) Ingold, Weaver, J. Chem. Soc. 127, 381-382 (1925).
(77) Stollé, Benrath, J. prakt. Chem. (2) 70, 276-277 (1904).
(78) von Auwers, Daniel, J. prakt. Chem. (2) 110, 256-257 (1925).
(79) Dains, Wertheim, J. Am. Chem. Soc. 42, 2303-2304 (1920).
(80) Heller, Ann. 263, 278-279 (1891).

(81) Widman, Ber. 28, 1927 (1895).
(82) Pieroni, Giannini, Gazz. chim. ital. 54, 170 (1924).
(83) Busch, Heinrichs, Ber. 33, 458 (1900).
(84) Longo, Gazz. chim. ital. 63, 467-468 (1933);
Cent. 1933, II 3415; C.A. 28, 122 (1934).
(85) Hopkins, J. Chem. Soc. 117, 278-282 (1920).
(86) Wilm, Wischin, Ann. 147, 157-163 (1868).
(87) Schmidt, Z. physik. Chem. 58, 516 (1907).
(88) Hofmann, Ber. 3, 656 (1870).
(89) Dermer, King, J. Org. Chem. 8, 168-173 (1943).
(90) Hantssch, Ber. 31, 180 (1898).

(91) Vles, Rec. trav. chim. 53, 964-966 (1934). (92) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409 (1934). (93) Dixon, Kennedy, J. Chem. Soc. 117, 80-84 (1920). (94) Levy, Campbell, J. Chem. Soc. 1939, 1443.

3:7300 d,l-3-CHLORO-2-METHYLBUTENE-1
$$C_5H_9Cl$$
 Beil. I - 211 $(\alpha,\beta$ -Dimethylallyl chloride) Cl CH_3 I_1 -(87) I_2 --

B.P. 93.8° at 760 mm. (1)
$$D_4^{20} = 0.9088$$
 (1) $n_D^{20} = 1.4304$ (1) 18.0-18.1° at 30 mm. (1)

Note: C by virtue of facile allylic transposition is in equilibrium with its synionic isomer, 1-chloro-2-methylbutene-2 (3:7485); reactns. of C may therefore yield also derivatives related to its isomer.

[For prepn. of C (or its mixt, with 1-chloro-2-methylbutene-2) by actn. of Cl₂ as specified (1) on "tertiary amylene" (a mixt. consisting mainly of 2-methylbutene-2 (1:8220) with some 2-methylbutene-1 (1:8210)) see (1). — The relative amt. of \bar{C} and its isomer is not constant but usually is about 60% of C with 40% of 1-chloro-2-methylbutene-2, the ratio, however, being independent of the proportion of the two olefins in the starting material.

[For formn. of C from 2-methylbutene-2 (1:8220) with Cl₂ see (2); from 2-methylbutene-1 (1:8210) see (3); from 2,3-dichloro-2-methylbutane (3.7975) + alc. KOH (3) or by thermal dehydrohalogenation at 420-450° (4) see indic. refs.]

C on hydrolysis gives not only the corresponding alc. but also that corresponding to the isomeric 1-chloro-2-methylbutene-2 (3:7485) together with a little isopropyl methyl ketone. For details see the isomer (3:7485).

 \bar{C} with HCl yields (2) 2,3-dichloro-2-methylbutane (3:7975) + 1,3-dichloro-2-methylbutane (3:9228).

C adds Br₂ giving (3) 1,2-dibromo-3-chloro-2-methylbutane, m.p. 197-198° (3).

3:7300 (1) Burgin, Engs. Groll, Hearne, Ind. Eng. Chem 31, 1416-1417 (1939). (2) Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1116-1132 (1936); Cent. 1937, I 572, C.A. 31, 1003 (1937). (3) Gutner, Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1062-1067 (1938), Cent. 1939, II 4221; C.A. 33, 3755 (1939). (4) Buc, Muessig (to Standard Oil Development Co.) U.S. 2,332,778, Oct. 26, 1943; C.A. 38, 1750 (1944).

3: 7303 1-CHLORO-2-METHYLBUTENE-1
$$CH_3$$
 C_6H_9Cl Beil. I — I_{1} — I_{2} —(187) CH_3 — CH_2 — CH_2 — CH_3 — CH_3 — CH_3 — CH_4 — CH_4 — CH_5 —

Oil with agreeable odor. — Insol. aq., sol. ether.

[For prepn. of \bar{C} from 1-chloro-2-methylbutanol-2 (3:8175) by loss of H_2O on distn. with anhyd. oxalic acid (1:0535) (44% yield (1) together with other prods.), or on treatment with PCl₅ (2) or Ac₂O + trace conc. H₂SO₄ (2) see indic. refs.; for formn. of C from 2-methylbutanediol-1,2 with PCl₅ (2) or from 1, 2-epoxy-2-methylbutane (α -ethyl- α -methylethylene oxide) with PCl₅ (1 mole) in cold (1) (2) or with SOCl₂ (2) see indic. refs.]

[C with PCl5 adds Cl2 yielding (2) a cpd. C5H9Cl3, b.p. 180-184°.]

C adds Br₂ readily (2).

B.P. 96-97° (1)

[For behavior of C with NaI in acetone see (1).]

3;7303 (1) Chalmers, Trans. Roy. Soc. Can. (3) 22, III 75-78 (1928); Cent. 1929, I 631-632; C.A. 23, 2694 (1929). (2) Seyer, Chalmers, Trans. Roy. Soc. Can. (3) 20, III 338-339 (1926); Cent. 1927, II 1811; C.A. 21, 2663 (1927).

B.P. 97.5° cor. at **750** mm. (1)
$$D_4^{20} = 0.9537$$
 (1) $n_D^{20} = 1.3950$ (1) $93-94^\circ$ at **735** mm. (2) 0.9655 (3) 1.4052 (3)

Colorless liq. which fumes in moist air.

[For prepn. (94% yield (1); 69% yield (6)) from paraldehyde (1:0170) + ethyl alc. (1:6130) + dry HCl see (1) (4); for prepn. (78% yield (5)) from acetaldehyde (1:0100) + ethyl alc. (1:6130) + dry HCl see (2) (5).]

Č on stdg. polymerizes to dark tarry residue (1).

[\bar{C} on bromination yields α,β -dibromoethyl ethyl ether (6) (7)(5).]

Č on shaking with aq. yields acetaldehyde (1:0100), ethyl alc. (1:6130), + HCl; for study of rate of hydrolysis see (8).

3:7305 (1) Henze, Murchison, J. Am. Chem. Soc. 53, 4077-4079 (1931). (2) Mohler, Sorge, Helv. Chim. Acta 23, 1209 (1940). (3) Waterman, de Kok, Leendertse, Schoenmaker, Rec. trav. chim. 56, 437-441 (1937). (4) de Kok, Leendertse, Waterman, Chem. Weekblad, 37, 579-583 (1940); C.A. 36, 4800 (1942). (5) Sherrill, Walter, J. Am. Chem. Soc. 58, 743 (1936). (6) Swallen, Boord, J. Am. Chem. Soc. 52, 654 (1930). (7) Dykstra, Lewis, Boord, J. Am. Chem. Soc. 52, 3400 (1930). (8) Mohler, Hartnagel, Helv. Chim. Acta 25, 859-863 (1942); C.A. 37, 1799 (1943).

Note that all samples of $\bar{\mathbb{C}}$ reported prior to 1935 were undoubtedly mixts. of 2-chloropentane ($\bar{\mathbb{C}}$) with 3-chloropentane (3:7330). Each of these cpds. is with great ease partially converted to the other (see text), and their mixt. cannot be separated by fractional distillation (1).

[For prepn. of \bar{C} (or its mixt. with 3-chloropentane (3:7330)) from pentanol-2 (1:6185) with conc. HCl on long stdg. at room temp. (78% yield (1)) or in s.t. at 110° (3) see (1) (2) (3); with conc. HCl + ZnCl₂ (yield: 70% (6), 49% (16)) see indic. refs.; with PCl₃ + ZnCl₂ (64% yield (6)) or PCl₅ + ZnCl₂ (56% yield (6)) see (6); with SOCl₂ + pyridine (gives least rearr. (1)) (yield: 28% (1), 67% (6)) see (1) (6); from pentene-2 on shaking 10 hrs. at room temp. with conc. HCl see (5) (4).] [Note that both pentanol-2 (1:6185) and pentanol-3 (1:6175) with HCl even at room temp. give mixts. of 2-chloropentane (\bar{C}) and 3-chloropentane (3:7330) (1).] [For formn. of \bar{C} in small amt. during reactn. of pentanol-1 (1:6205) with HCl + ZnCl₂ see (15).]

96-97°

at 729 mm.

(6)

 $\ddot{\mathbf{C}}$ is stable (no change in n_D^{20}) on htg. in s.t. at 100° for 48° (1). — However, $\ddot{\mathbf{C}}$ on shaking at 26–28° for 24 hrs. with HCl + ZnCl₂ gives a mixt. consisting of 80% $\ddot{\mathbf{C}}$ + 20% 3-chloropentane (3:7330) (1).

[For study of rate of hydrolysis by water at 80° and 180° see (7); for rate of reactn. with KI in acetone at 60° see (8); for reactn. with Na see (9).]

- Methyl-n-propyl-acetanilide: Č with Mg in dry ether yields RMgCl which upon reactn. with phenyl isocyanate and subsequent hydrolysis yields (1) (2) (4) (10) methyl-n-propyl-acetanilide, m.p. 94-96° (1), 95.2° (11), 92.6° (12), 92.5° (2), 88° cor. (13). [For m.p./compn. data and diagrams for mixts. of methyl-n-propyl-acetanilide (from Č) with diethylacetanilide (from 3-chloropentane) see (4) (2) (12).] [For crystallographic study of these two anilides see (15).]
- (11). Methyl-n-propyl-acet-p-toluidide: m.p. 90-92° u.c. (10); 80.5° (11).
- **D** Methyl-n-propyl-acet- α -naphthalide: m.p. 102.5-103.5° (10).

3:7325 (1) Whitmore, Karnatz, J. Am. Chem. Soc. 60, 2536-2538 (1938). (2) Hass, Weber, Ind. Eng. Chem., Anal. Ed. 7, 231-233 (1935). (3) Kohlrausch, Köppl, Monatsh. 65, 195 (1935). (4) Kharasch, Walling, Mayo, J. Am. Chem. Soc. 61, 1559-1564 (1939). (5) Norris, Reuter, J. Am. Chem. Soc. 49, 2630-2631 (1927). (6) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929). (7) Ayres, Ind. Eng. Chem. 21, 899-904 (1929). (8) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925). (9) Morton, LeFevre, Hechenbleikner, J. Am. Chem. Soc. 58, 757 (1936). (10) Underwood, Gale, J. Am. Chem. Soc. 56, 2117-2120 (1934).

Hommelen, Bull. soc. chim. Belg. 42, 249 (1933).
 Lauer, Stodola, J. Am. Chem. Soc. 56, 1218 (1934).
 Schwartz, Johnson, J. Am. Chem. Soc. 53, 1065 (1931).
 Hass, J. Chem. Education 13, 492-493 (1936).
 Whitmore, Karnatz, Popkin, J. Am. Chem. Soc. 60, 2541 (1938).
 Vogel, J. Chem. Soc. 1943, 638, 640.

Note that all samples of \bar{C} reported prior to 1935 were undoubtedly mixts. of 3-chloropentane (\bar{C}) with 2-chloropentane (3:7325). Each of these cpds. is with great ease partially converted to the other (see text), and the mixture cannot be separated by fractional distillation (1).

[For prepn. of $\bar{\rm C}$ (or its mixture with 2-chloropentane (3:7325)) from pentanol-3 (1:6175) with conc. HCl on long stdg. at room temp. (yield: 84% (1); 69% (3)) see (1) (3); with dil. HCl see (5); with conc. HCl + ZnCl₂ (yield: 81% (1), 70% (7), 55% (14)) see (1) (7) (14); with PCl₃ + ZnCl₂ (60% yield (7)) or PCl₅ + ZnCl₂ (73% yield (7)) see (7); with SOCl₂ + pyridine (gives least rearr. (1)) (yield: 46% (1), 42-44% (7)) see (1) (7); from pentene-2 (1:8215) + HCl in presence of FeCl₃ or AcOH see (4).] [Note that both pentanol-2 (1:6185) and pentanol-3 (1:6175) with HCl even at room temp. give mixts. of 2-chloropentane (3:7325) and 3-chloropentane ($\bar{\rm C}$) (1).] [For formn. of $\bar{\rm C}$ in small amt. during reactn. of pentanol-1 (1:6205) with HCl + ZnCl₂ see (12).]

 \tilde{C} is stable (no change in n_D^{20}) on htg. in s.t. at 100° for 48 hrs. (1). — However, \tilde{C} on shaking at 26–28° for 24 hrs. with HCl + ZnCl₂ gives a mixt. consisting of 20% \tilde{C} + 80% 2-chloropentane (1).

[For study of rate of hydrolysis by water at 80° and 180° and rate of cleavage of HCl at 180° see (12).]

- Diethylacetanilide: C with Mg in dry ether yields R.Mg.Cl which, upon reactn. with phenyl isocyanate and subsequent hydrolysis, yields (1) (3) (4) (5) diethylacetanilide, m.p. 127.5° (8), 126.8° (9), 126-127° (5), 125-128° (1), 123-124° cor. (10), 122° (3), 121° (11). [For m.p./compn. data and diagrams for mixts. of diethylacetanilide (from C) with methyl-n-propylacetanilide (from 2-chloropentane) see (4) (3) (11).] [For crystallographic study of these two anilides see (13).]
- Diethylacet-p-toluidide: m.p. 107.5-108.5° u.c. (5), 116.2° (9).
- Diethylacet-α-naphthalide: m.p. 117-118° u.c. (5).

3:7330 (1) Whitmore, Karnatz, J. Am. Chem. Soc. 60, 2536-2538 (1938). (2) Hass, J. Chem. Education 13, 493 (1936). (3) Hass, Weber, Ind. Eng. Chem., Anal. Ed. 7, 231-233 (1935).
 (4) Kharasch, Walling, Mayo, J. Am. Chem. Soc. 61, 1559-1564 (1939). (5) Underwood, Gale, J. Am. Chem. Soc. 56, 2117-2120 (1934). (6) Koelsch, McElvain, J. Am. Chem. Soc. 52, 1164-1169 (1930). (7) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929). (8) Tiffeneau, Compt rend. 204, 592 (1937). (9) Hommelen, Bull. soc. chim. Belg. 42, 249 (1933). (10) Schwartz, Johnson, J. Am. Chem. Soc. 53, 1065 (1931).

Lauer, Stodola, J. Am. Chem. Soc. 56, 1218 (1934).
 Ayres, Ind. Eng. Chem. 21, 899-904 (1929).
 Whitmore, Karnatz, Popkin, J. Am. Chem. Soc. 60, 2541 (1938).
 Vogel, J. Chem. Soc. 1943, 638, 640.

3: 7335 3-CHLORO-2-METHYLBUTENE-2
$$C_{\delta}H_{9}Cl$$
 Beil. I - 213 I_{1} — I_{2} —(Trimethylvinyl chloride) CH_{3} — C_{-} — CH_{3} I_{1} — I_{2} —(189) B.P. 97-98° (1) $D_{-}^{20} = 0.9096$ (5) $n_{D}^{20} = 1.4320$ (5) 96-99° (2) 1.4380 (3) 94-99° (3) $D_{4}^{20} = 0.925$ (3) 94° at 748 mm. (4) 91-92° at 741 mm. (5) $D_{0}^{18} = 0.9215$ (1)

[For prepn. of \bar{C} from isopropyl methyl ketone (1:5410) with PCl₅ see (3) (4); from 3-chloro-2-methylbutanol-2 (3:8030) by dehydration with P₂O₅ (50% yield (1)), anhyd. oxalic acid (6) at 130°, or strong oxygenated mineral acids such as H₂SO₄ (92% yield (7)) see indic. refs.]

[For formn. of \tilde{C} (together with other prods.) from 2,3,3-trichloro-2-methylbutane (3:4755) (8) or from 2,3-dichloro-2-methylbutane (3:7975) with alc. KOH (2), from 2-methylbutene-2 (1:8210) with Cl₂ + NaHCO₃ at 0° (70-80% yield (9)) or with ter-butyl hypochlorite (3:7165) (47.5% yield (5)), or from 2-methylbutanol-2 (1:6160) with Cl₂ (10) see indic. refs.]

 \ddot{C} with Cl₂ + NaHCO₃ at 0° gives (9) 80% 3,3-dichloro-2-methylbutene-1 (3:7690) + 10% addn. prod. 2,3,3-trichloro-2-methylbutane (3:4755).

 \bar{C} in cold ether adds Br₂ giving (1) (2) 2,3-dibromo-3-chloro-2-methylbutane, cryst. m.p. 197° (1), 197-198° (2).

3:7335 (1) Krassuskii, J. Russ. Phys.-Chem. Soc. 33, 15-17 (1901); Cent. 1901, I 995. (2) Gutner, Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1062-1067 (1938); Cent. 1939, II 4221; C.A. 33, 3755 (1939). (3) Gredy, Bull. soc. chim. (5) 2, 1951 (1935). (4) Béhal, Ann. chim. (6) 15, 284-285

(1888). (5) Irwin, Hennion, J. Am. Chem. Soc. 63, 859 (1941). (6) Detoeuf, Bull. soc. chim. (4)
31, 170 (1922). (7) Groll, Burgin (to Shell Development Co.), U.S. 2,042,223, May 26, 1936;
Cent. 1937, I 1274; C.A. 30, 4875 (1936). (8) Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1116–1132 (1936);
Cent. 1937, I 573; C.A 31, 1003 (1937). (9) Tishchenko, J. Gen. Chem. (U.S.S.R.)
8, 1232–1246 (1938);
Cent. 1939, II 4222, C.A. 33, 4190 (1939). (10) Brochet, Ann. chim. (7)
10, 381 (1897).

[For prepn. of \tilde{C} from ter-butyl methyl ketone (pinacolone) (1:5425) with PCl₅ on htg. (1) (50% yield (3)) or from 3,3-dichloro-2,2-dimethylbutane (3.4325) on htg. with alc. KOH at 150° (1) (3) or with KOAc + phenol (4) sec indic. refs.

Č with alc. KOH (3) or htd. at 160-200° for 5 hrs. with powdered KOH (or NaOH (5)) moistened with alc. (2) gives (80.5% yield (2)) ter-butylacetylene [Beil. 1-256], b.p. 36.4-37.8° at 768.3 mm. (2).

3:7340 (1) Delacre, Bull. acad. roy Belo. 1906, 7-41; Cent 1906, I 1233. (2) Bartlett, Rosen, J. Am. Chem. Soc. 64, 544 (1942). (3) Delacre, Bull. soc. chrm. (3) 35, 343-344 (1906). (4) Meerwein, Wortmann, Ann. 435, 194, Note 1 (1924). (5) de Graef, Bull. soc. chim. Belg. 34, 429 (1925).

3: 7345
$$d$$
, l -1-CHLORO-2-METHYLBUTANE CH₃ C₅H₁₁Cl Beil. I - 134 $(d$, l -sec.-Butylcarbinyl chloride) CH₃.CH₂-C-CH₂Cl H I₁- (46) I₂-(100)

B.P.
$$99.9^{\circ}$$
 at 760 mm. (1) (2) D_4^{20} unrecorded n_D^{20} unrecorded $99.8-100^{\circ}$ at 760 mm. (2) (See note below.) (See note below.) $99.5-100.5^{\circ}$ (3) 99° (4) 52.5° at 150 mm. (1)

[Note: for active d stereoisomer: b.p. 100.45° at 760 mm. (5), 99.5° at 750 mm. (11), 86.8° at 500 mm. (5), 80.0° at 400 mm. (5), 71.5° at 300 mm. (5), 60.4° at 200 mm. (5), 43.0° at 100 mm. (5), 27.7° at 50 mm. (5), D_4^{20} 0.8857 (5), 0.8852 (6); n_D^{20} = 1.4124 (5), 1.4125 (6), 1.4126 (11).]

The sepn. of Č from 4-chloro-2-methylbutane (isoamyl chloride) (3:7365) by fractional distillation cannot be effected (1) (2).

[For prepn. of \tilde{C} from the corresponding alc., d,l-sec.-butylcarbinol (cf. 1:6195) with HCl gas at 90° for 6 hrs. (49% yield) see (2); with SOCl₂ see (3); for prepn. of d-form from corresp. alc. (1:6195) by satn. at 0° with HCl gas and htg. in s.t. 5 hrs. at 100° (20% yield) see (5), by use of SOCl₂ + pyridine (yield: 87% (11), 82% (7), 77% (6)) see (6) (7).]—
[For formn. by chlorination of crude pentane see (4).]

Č is not hydrolyzed by aq. either at 80° or at 180° (4). — For rate of loss of HCl at 180° to yield 2-methylbutene-1, b.p. 31° (1:8210), see (4).

For anal. of mixts. of C with 1-chloro-3-methylbutane (3:7365) via rate of reactn. with KI in acetone see (2).

Č with Mg in dry ether does not react (8). [However, from corresp. d,l-sec.-butyl-carbinyl bromide the R.Mg.Br cpd. was obtd. (9) in 66% yield and with phenyl isocyanate yielded N-(sec.-butylacet)anilide, m.p. 88° cor. (9), 87° (10).]

3:7345 (1) Hass, McBee, Weber, Ind. Eng. Chem. 27, 1192-1195 (1935). (2) Hass, Weber, Ind. Eng. Chem., Anal. Ed. 7, 231-233 (1935). (3) Kohlrausch, Köppl, Monatsh. 65, 195 (1935).
(4) Ayres, Ind. Eng. Chem. 21, 900 (1929). (5) Brauns, J. Research Natl. Bur. Standards 18, 323-324, 327-328 (1937). (6) Whitmore, Olewine, J. Am. Chem. Soc. 60, 2570-2571 (1938).
(7) Brown, Kharasch, Chao, J. Am. Chem. Soc. 62, 3439 (1940). (8) Underwood, Gale, J. Am. Chem. Soc. 56, 2117 (1934). (9) Schwartz, Johnson, J. Am. Chem. Soc. 53, 1063-1068 (1931).
(10) Hommelen, Bull. soc. chim. Belg. 42, 249 (1933).

(11) Brown, Groot, J. Am. Chem. Soc. 64, 2566 (1942).

3: 7350 d, '-4-CHLOROPENTENE-1 Cl C₅H₉Cl Beil. I —
$$I_{1-}(86)$$
 CH₃—C-CH₂—CH=CH₂ I_{2-}

B.P. 97-100° (1)
$$D_{-}^{15} = 0.934$$
 (1) $n_{D}^{15} = 1.417$ (1)

The levorotatory form of \tilde{C} has $D_{\bullet}^{25}=0.8794$ (2), $n_{D}^{25}=1.4218$ (2), but no b.p. or method of prepn. is recorded.

[For prepn. of C from penten-1-ol-4 (allyl-methyl-carbinol) [Beil. I-443] with PCl₅ at 0° see {1}.]

3:7350 (1) Pariselle, Compt. rend. 154, 712 (1912). (2) Levene, Rothen, J. Chem. Phys. 5, 982 (1937).

3: 7355 1-CHLORO-3-METHYLBUTADIENE-1,3
$$C_5H_7Cl$$
 Beil. S.N. 12 (4-Chloro-2-methylbutadiene-1,3) CH_3 Cl CH_2 — C — CH — CH

B.P. 99-100° (1)
$$D_4^{20} = 0.9543$$
 (1) (2) $n_{\alpha}^- = 1.47189$ (1) 97.5-98° (2)

[For prepn. of \bar{C} from 1-chloro-3-methylbutadiene-1,2 (3:7390) by stdg. several days with HCl + Cu₂Cl₂ + NH₄Cl see (2).]

Č without solvent on htg. with maleic anhydride (1:0625) evolves HCl and gives (1) a mixt. of 4 acids: 2 dicarboxylic acids, m.p. 210-211° (1) (2) and m.p. 239-241° (1), and 2 tetracarboxylic acids, m.p. 298-299° (1) and m.p. 352-353° (1) (2); with solvent only the acids of m.p. 210-211° and 352-353° are formed (2).

3:7355 (1) Favorskii, Favorskaya, Compt. rend. 200, 839-840 (1935); Cent. 1935, II 1340; C.A. 20, 3651 (1935). (2) Favorskii, Favorskaya, J. Gen. Chem. (U.S.S.R.) 9, 386-395 (1939); C.A. 33, 9281 (1939).

3:7358 ISOPROPENYL CHLOROFORMATE CH₃ C₄H₅O₂Cl Beil. S.N. 19 (Isopropenyl chlorocarbonate) O=C.O.C=CH₂

B.P. 100° at 760 mm. (estimated) (1)
$$D_{20}^{20} = 1.103$$
 (1) 93° at 746 mm. (1)

98.5-101°

Colorless lachrymatory liq. with sharp and unpleasant odor.

[For prepn. of \tilde{C} from acetone (1:5400) with liq. phospene (3:5000) for $\frac{1}{2}$ hr. at room temp. see (1).

3:7358 (1) Matuszak, J. Am. Chem. Soc. 56, 2007 (1934).

3: 7360 3-CHLOROPENTADIENE-1,3 Cl
$$C_8H_7Cl$$
 Beil. S.N. 12 ("Methylchloroprene"; pirylene monohydrochloride)

B.P. 99.5-101.5° at 759 mm. (1) (2) $D_4^{20} = 0.9576$ (1) (2) $n_D^{25} = 1.4745$ (3) $n_D^{20} = 1.4785$ (1) (2)

Colorless liq. with characteristic odor; after addition of hydroquinone (as antioxidant) can be distilled (1). — [For polymerization of C see (1) (2).]

[For prepn. of \tilde{C} from penten-1-yne-3 (α -methyl- β -vinylacetylene = pirylene (3)) by shaking with conc. HCl contg. CuCl + NH₄Cl see (1) (2) (3).]

C on htg. with 1,4-naphthoquinone (1:9040) at 100° for 2 hrs. then treated with alc. NaOH, and aerated (to oxidize the intermediate addn. prod.), gives (1) (3) 2-chloro-1methylanthraquinone, yel. ndls. from AcOH, m.p. 181° (1), 180.7-181.0° (3). [Dif. from 1-chloro-2-methylbutadiene-1,3 (3:9200) q.v.]

3:7360 (1) Jacobson, Carothers, J. Am. Chem. Soc. 55, 1624-1627 (1933). (2) Jacobson (to du Pont), U.S. 1,950,440, March 13, 1934; Cent. 1934, II 1037; C.A. 28, 3270 (1934). (3) Sargent, Buchman, Farquhar, J. Am. Chem. Soc. 64, 2693 (1942).

B.P. F.P. (1)
$$-104.4^{\circ}$$
 (6) $D_4^{20} = 0.8927$ (7) $n_D^{20} = 1.4096$ (7) $100-101^{\circ}$ (2) 0.8732 (25) 1.40909 (25) 99.15° at 760 mm. (3) 1.4087 (6) 99° at 777 mm. (25) 98.8° at 760 mm. (4) (5) 98.1° (6)

C forms many azeotropes: e.g., C with EtOH (1:6130), b.p. 78.3°, gives a const.-boilg. mixt., b.p. 74.8° at 760 mm., contg. 59 wt. % C (8); with n-propyl alc. (1:6150), b.p. 97.2°. a const.-boilg. mixt., b.p. 89.4° at 760 mm., contg. 69 wt. % C (8); with isopropyl alc. (1:6135), b.p. 82.45°, a const.-boilg. mixt., b.p. 79.2° at 760 mm., contg. 57 wt. % C (8) with isobutyl alc. (1:6165), b.p. 107.85°, a const.-boilg. mixt., b.p. 94.5° at 760 mm., contg. 78 wt. % C (8). [For still others see Beil. I₂-(101).]

[For prepn. of C from isoamyl alc. (1.6200) with conc. HCl (5) (9) (10) (11), with conc. HCl + ZnCl₂ (60% yield (12) (13)), with PCl₃ + ZnCl₂ (13) (14), with PCl₅ (15) or PCl₅ + ZnCl₂ (71% yield (13)), with SOCl₂ (70-83% yield (13) (16)) or SOCl₂ + dimethylaniline (100% yield (13)) see indic. refs.]

[For study of hydrolysis by aq. at 80° and 180°, loss of HCl at 180°, and esterification with NaOAc at 180° see (1).]

[For study of rate of reactn. with KI in acetone at 60° see (2); for use in anal. of mixts. of C with 1-chloro-2-methylbutane (3:7345) see (5).

 \bar{C} with Mg in dry ether + trace I₂ gives RMgCl (yield in 5 hrs. 96.3% (26)); this upon oxidation with O₂ yields (17) isoamyl alc. (1:6200) q.v. [Note: for m.p./compn. data for mixts. of N-phenylcarbamates of isoamyl alc. (1:6200) and d,l-sec.-butylcarbinol (1:6195) see orig. ref. (17).]

- © Isocaproanilide: m.p. 112.0° (18) (19); 111.5° (20); 110.5° u.c. (21); 108° cor. (22). [From RMgCl (21) or RMgBr (22) with phenyl isocyanate.]
- **D** Isocapro-p-toluidide: m.p. 63.0° (18); 61.5-62.5° u.c. (21). [From RMgCl + p-tolyl isocyanate (21).]
- ① Isocapro- α -naphthalide: m.p. 110-111° u.c. (21). [From RMgCl + α -naphthyl isocyanate (21).]
- D Isoamyl mercuric chloride (RHgCl): m.p. 86° (23).
- **⑤** S-Isoamylisothiourea picrate: m.p. 173° (24). [In poor yield from Č in alc. on refluxing 2 hrs. with thiourea, followed by addn. of PkOH (24).]
- --- N-(Isoamyl)tetrachlorophthalimide: lfts. from EtOH, m.p. 170-171° (27).

3:7365 (1) Ayres, Ind. Eng. Chem. 21, 900 (1929). (2) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925). (3) Timmermans, Bull. soc. chrm. Belg. 30, 66 (1921). (4) Hass, McBee, Weber, Ind. Eng. Chem. 27, 1192 (1938). (5) Hass, Weber, Ind. Eng. Chem., Anal. Ed., 7, 231-233 (1935). (6) Turkevich, Smyth, J. Am. Chem. Soc. 64, 737 (1942). (7) Washburn, Keim, J. Am. Chem. Soc. 62, 1747 (1940). (8) Lecat, Rec. trav. chim. 46, 242 (1927). (9) Mouneyrat, Ann. chim. (7) 20, 538 (1900). (10) Malbot, Bull. soc. chim. (3) 1, 603 (1889).

(11) Gleditsch, Bull. soc. chim. (3) 35, 1094-1095 (1906). (12) Norris, Taylor, J. An. Chem. Soc. 48, 756 (1924). (13) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929). (14) Dehn, Davis, J. Am. Chem. Soc. 29, 1332 (1907). (15) Cahours, Ann. 37, 164 (1841). (16) Ross, Bibbins, Ind. Eng. Chem. 31, 255-256 (1939). (17) Davydova, Papkina, Tischenko, J. Gen. Chem. (U.S.S.R.) 6, 1615-1623 (1936); Cent. 1937, I 3786. (18) Hommelen, Bull. soc. chim. Belg. 42, 249 (1933). (19) Brunner, Farmer, J. Chem. Soc. 1937, 1044. (20) Dragendorff, Ann. 487, 76 (1931).

(21) Underwood, Gale, J. Am. Chem. Soc. **56**, 2119 (1934). (22) Schwartz, Johnson, J. Am. Chem. Soc. **53**, 1065 (1931). (23) Marvel, Gauerke, Hill, J. Am. Chem. Soc. **47**, 3010 (1925). (24) Levy, Campbell, J. Chem. Soc. **1939**, 1443. (25) Vogel, J. Chem. Soc. **1943**, 638,640. (26) Houben, Boedler, Fischer, Ber. **69**, 1769, 1782 (1936). (27) Allen, Nicholls, J. Am. Chem. Soc. **56**, 1409-1410 (1934).

						(
B.P.			F.P.			
101.8°	at 760 mm.	(1)	-89.0° (12)	$D_{-}^{25} = 1.0154 ($	2)	
102°		(2)	-89.3° (1)		$\eta_{\mathrm{D}}^{25} = 1.4115$	(2)
101.5°	at 768 mm.	(3)		$D_4^{20} = 1.0277 (1$	3)	
101.4-102°		(4)			3)	
101.1-101.5	•	(5)		1	$\eta_{\rm D}^{20} = 1.4130$	(11)
101-101.5°	at 730 mm.	(6)	(7)		1.4126	(3)
101-102.5°		(8)			1.41209	(13)
100-101.5°		(9)			1.4117 (6) (7)
100-101°		(10)			•	
100.5°	at 733 mm.	(11)				

Comml. C may contain unsatd. and P cpds. (14).

[For prepn. of \tilde{C} from *n*-butyric acid (1:1035) with PCl₅ (83% yield (15)), with PCl₃ (yield 69-77% (16)) (9) (17) or PCl₃ + ZnCl₂ (77% yield (15)), with SOCl₂ (yield: 97.4% (18), 90% (19), 85% (10), 80% (6) (7), 50% (15)) (20), with benzoyl chloride (80-87%

yield (8) (21), with phthalyl dichloride (3:6900) (91.5% yield (22)), with benzotrichloride (3:6540) + ZnCl₂ at 70-80° (23), or with SiCl₄ in xylene (49% yield (24)) see indic. refs.; for prepn. of \tilde{C} from α -chloroethyl n-butyrate on warming with a trace of ZnCl₂ see (25); for prepn. of \tilde{C} from n-butyric acid (1:1035) by use of methyl chlorosulfonate, benzene-sulfonyl chloride, etc., see (26).]

[\bar{C} on htg. with *n*-butyric acid (9) or with sodium *n*-butyrate yields *n*-butyric anhydride (1:1126), b.p. 198.2° at 760 mm. (12), f.p. -75.0° (12), $D_4^{21} = 0.9687$ (27), $n_D^{19.73} = 1.4124$ (28).]

 \tilde{C} with Cl_2 in CCl_4 gives (17) a mixt. of α -, β - and γ -chloro-n-butyryl chlorides, some α -chloro-n-butyric acid anhydride also being formed (29); \tilde{C} with SO_2Cl_2 in pres. of dibenzoyl peroxide gives (30) 15% α -chloro-n-butyryl chloride (3:5570), 55% β -chloro-n-butyryl chloride (3:5970). — For study of mech. of chlorination see (31). — [For action of PCl_5 on \tilde{C} see (32).]

[\tilde{C} with Br₂ in light yields (17) (33) (14) (34) α -bromo-*n*-butyryl chloride, b.p. 151-153° (34), and β -bromo-*n*-butyryl chloride.]

[\tilde{C} on cat. hydrogenation with H_2 + Pd-BaSO₄ cat. in ether (35) or in vapor phase (36) gives n-butyraldehyde (1:0130), b.p. 74.7°; \tilde{C} on reduction with Na/Hg or Na in moist ether yields (37) (38) (39) octene-4-diol-4,5 di-n-butyrate.]

[C̄ added to large excess of certain RMgX cpds. in ether is in part reduced and in part undergoes normal form. of corresp. ketone: e.g., C̄ with ter-BuMgCl gives 9% reduction and 71% ketone form. (6) (7) (11); products include n-butyl n-butyrate, ter-butyl n-propyl ketone (2,2-dimethylhexanone-3), and ter-butyl-n-propyl-carbinyl n-butyrate. — C̄ with excess C₆H₆MgBr gives (84% yield (40)) 1,1-diphenylbutene-1 [Beil. V-648, V₁-(313)].]

[C with chlorosulfonic acid at room temp. {41} or with AlCl₃ in CHCl₃ followed by aq. (42) gives di-n-propyl ketone (butyrone) (1:5447), b.p. 144°. — Note, however, that C on htg. with AlCl₃ at 60° without CHCl₃, then poured into aq., yields (42) (43) 2,4,6-triethylphloroglucinol [Beil. VI-1129], m.p. 107°.]

[$\bar{\rm C}$ with ethylene + AlCl₃ at 20° gives (70% yield (44)) (45) β -chloroethyl n-propyl ketone (1-chlorohexanone-3) [Beil. 1-690]; $\bar{\rm C}$ with cyclohexene + SnCl₄ yields (46) 1-cyclohexenyl n-propyl ketone, b.p. 100–102° at 8 mm., $D_4^{14} = 0.950$, $n_D^{14} = 1.4885$ (oxime, m.p. 67°, semicarbazone, m.p. 175°) (46); $\bar{\rm C}$ with cyclohexane + AlCl₃ yields (47) α -methyl-cyclopentyl n-propyl ketone.]

[\bar{C} with C_6H_6 + AlCl₃ gives (89% yield (48)) (16) phenyl *n*-propyl ketone (butyrophenone) (1:5535), b.p. 230°; \bar{C} with toluene + AlCl₃ gives (49) *n*-propyl *p*-tolyl ketone Beil. VII-330, VII₁-(175)], b.p. 250°.]

[\bar{C} with AlCl₃ + phenol yields (50) (51) (20) 45% o-(n-butyryl)phenol, b.p. 124-126° at 14 mm. (51), 119° at 9 mm. (50), m.p. 10.5-10.6° (50), 8° (51), D_{-}^{24} = 1.0683 (50), $n_{D}^{25.5}$ = 1.5375 (50) (semicarbazone, m.p. 192-193° (50), phenylhydrazone, m.p. 85-87° (51)), and 30% p-(n-butyryl)phenol, b.p. 200° at 15 mm. (51), 187-189° at 9 mm. (50), m.p. 91-91.5° (50) (benzoate, m.p. 107-107.5° (50), 106-107° (51)); for reactn. of \bar{C} with carvacrol (1:1760) + AlCl₃ in nitrobenzene see (52), similarly with thymol (1:1430) see (53).]

 \bar{C} on hydrolysis yields *n*-butyric acid (1:1035), b.p. 164°; for the amide, anilide, *p*-toluidide, and other derivs. corresp. to \bar{C} see *n*-butyric acid (1:1035).

3:7370 (1) Timmermans, Bull. soc. chim. Belg. 36, 507 (1927). (2) Koehl, Wenzke, J. Am. Chem. Soc. 59, 1418 (1937). (3) Martin, Partington, J. Chem. Soc. 1936, 162. (4) Reitter, Z. physik. Chem. 36, 137 (1901). (5) Kohlrausch, Pongratz, Z. physik Chem. B-22, 381 (1933). (6) Greenwood, Whitmore, Crooks, J. Am. Chem. Soc. 60, 2028-2030 (1938). (7) Whitmore, Rec. trav. chim. 57, 565 (1938) (8) Brown, J. Am. Chem. Soc. 60, 1325-1328 (1938). (9)

Linnemann, Ann. 161, 179 (1872). (10) Helferich, Schaefer, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 147-149 (1941); (1st ed.), 142 (1932); 9, 32-33 (1929).

(11) Whitmore, Whitaker et al., J. Am. Chem. Soc. 63, 647-653 (1941). (12) Timmermans, Mattaar, Bull. soc. chim. Belg. 30, 216 (1921). (13) Brühl, Ann. 203, 19 (1880). (14) Kharasch, Hobbs, J. Orp. Chem. 6, 706, 709-712 (1941). (15) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (16) Burcker, Ann. chim. (5) 26, 466-469 (1892). (17) Michael, Ber. 34, 4051, 4057 (1901). (18) Fierz-David, Küster, Helv. Chim. Acta 22, 89 (1939). (19) Read, Orp. Syntheses 14, 90 (1934). (20) Rice, Harden, J. Am. Pharm. Assoc. 25, 7-9 (1936); Cent.

1936, II 70.

(21) Chem. Fabrik vorm. Weiler-ter-Meer, Ger. 350,050, March 11, 1922; Cent. 1972, IV 155. (22) Kyrides, J. Am. Chem. Soc. 59, 208 (1937). (23) Rabcewicz-Zubkowski, Roczniki Chem. 9, 523-531 (1929); Cent. 1979, II 2767; C.A. 24, 61 (1930). (24) Montonna, J. Am. Chem. Soc. 49, 2114-2116 (1927). (25) Soc. Usines Chim. Rhone-Poulenc, Brit. 329,721, June 19, 1930; Cent. 1930, II 1611. (26) Henle, Schirm (to Farbwerke Meister, Lucius & Brunng), Ger. 397,311, July 1, 1924; French 568,331, March 22, 1924; Cent. 1924, II 1402. (27) Tromp, Rec. trav. chim. 41, 299 (1921). (28) Whitby, J. Chem. Soc. 1926, 1463. (29) de Boosere, Bull. soc. chim. Belg. 32, 44, Note (1923). (30) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940).

32, 44, Note (1923). (30) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940). (31) Hertel, Becker, Clever, Z. physik. Chem. B-27, 303-315 (1934). (32) von Braun, Jostes, Munch, Ann. 453, 147 (1927). (33) Michael, Scharf, Ber. 46, 137-138 (1913). (34) Bardan, Bull. soc. chim. (4) 49, 1428 (1931). (35) Rosenmund, Ber. 51, 591-592 (1918). (36) Fröschl, Danoff, J. prakt. Chem. (2) 144, 220-221 (1936). (37) Freund, Ann. 118, 35-43 (1861). (38) Munchmeyer, Ber. 19, 1846 (1886). (39) Klinger, Schmitz, Ber. 24, 1271-1272 (1891). (40)

Gilman, Fothergill, Parker, Rec. trav. chim. 48, 750 (1929).

(41) Krajcinovic, Ber. 63, 2276-2278 (1930). (42) Combes, Bull. soc. chim. (3) 11, 710-712 (1894). (43) Combes, Ann. chim. (6) 12, 263-265 (1887). (44) Kenner, Statham, Ber. 63, 17 (1936). (45) Schering-Kahlbaum Akt. Ges., Brit. 282,412, Feb. 15, 1928; Cent. 1929, I 143. (46) Colonge, Duroux, Bull. soc. chim. (5) 7, 459-468 (1940); C.A. 36, 2842 (1942). (47) Nenitzescu, Ionescu, Ann. 491, 208 (1931). (48) Sorge, Ber. 35, 1073 (1902). (49) Willgerodt, Hambrecht, J. prakt. Chem. (2) 81, 78 (1910). (50) Sandulesco, Girard, Bull. soc. chim. (4) 47, 1305-1310 (1930).

(51) Coulthard, Marshall, Pyman, J. Chem. Soc. 1930, 286. (52) John, Beetz, J. prakt. Chem. (2) 143, 345 (1935). (53) Rosenmund, Schulz, Arch. Pharm. 265, 311 (1927).

3: 7390 1-CHLORO-3-METHYLBUTADIENE-1,2
$$C_5H_7Cl$$
 Beil. S.N. 12 (4-Chloro-2-methylbutadiene-2,3) CH_3 Cl CH_3 CH_4 CH_5 $CH_$

B.P. 102-103° (1)
$$D_4^{20} = 0.9515$$
 (1) (2) $n_\alpha^{20} = 1.46697$ (2) $101-104^\circ$ (2)

[For prepn. of \bar{C} from 2-methylbutyne-3-ol-2 (dimethyl-ethynyl-carbinol) on shaking as specified (1) (2) with HCl + CuCl₂ + NH₄Cl; the initial reactn. prod. is 2-chloro-2-methylbutyne-3 (3:7155) which may be obtd. in 63% yield if reactn. time is short (1) (2); on stdg. with the reactn. mixt. for 18 days, however, this is isomerized to \bar{C} (40-65% yield (2)) cf. (4).]

Č on stdg. several days with HCl/Cu₂Cl₂/NH₄Cl mixt. is isomerized (2) to 1-chloro-3-methylbutadiene-1,3 (3:7355) q.v.

 \tilde{C} on htg. with aq. + CaCO₃ yields (1) (3) not only its precursors, 2-chloro-2-methylbutyne-3 (3:7155) and 2-methylbutyne-3-ol-2, but also vinyl chloride (3:7010), methylacetylene, and 4-chloro-2-methylbutadiene-1,3 (3:7355) q.v.

 \tilde{C} gives no ppt. with NH₄OH/AgNO₈ (1). [Dif. from 2-chloro-2-methylbutyne-3 (3:7155).]

C on oxidn. with KMnO₄ yields (1) α -hydroxyisobutyric acid (1:0431).

3:7300 (1) Favorskii, Favorskaya, Compt. rend. 200, 839-840 (1935); Cent. 1935, II 1340; C.A. 29, 3651 (1935). (2) Favorskaya, J. Gen. Chem. (U.S.S.R.) 9, 386-395 (1939); C.A. 33, 9281

(1939). (3) Favorskaya, J. Gen. Chem. (U.S.S.R.) 9, 1237-1242 (1939); C.A. 34, 1303 (1940).
(4) Hurd (to Commercial Solvents Corp.), U.S. 2,274,611, Feb. 24, 1942; C.A. 36, 4138 (1942).

3: 7395 trans-2,3-DICHLOROBUTENE-2 Cl
$$C_4H_6Cl_2$$
 Beil. S.N. 11 CH_3 — C — C — CH_3 Cl B.P. 101–103° at 758 mm. (1) $D_4^{20} = 1.1416$ (1)

[See also cis stereoisomer (3:5500).]

[For prepn. of \bar{C} (accompanied by its cis stereoisomer (3:5500)) from 2,2,3-trichloro-butane (3:5680) with solid KOH (1 mole) at 135-140° see (1).]

C on oxidn. with 3% aq. KMnO4 yields (1) acetic acid (1:1010).

 \bar{C} in CCl₄ at -20° treated with 7% O₃, then hydrolyzed, yields (1) acetic acid (1:1010) + acetaldehyde (1:0100).

3:7395 (1) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 6, 1553-1558 (1936); Cent. 1937, I 3785; C.A. 31, 2165 (1937).

3: 7400 d,I-4-CHLOROPENTENE-2 Cl
$$C_5H_9Cl$$
 Beil. I - 210 (2-Chloropentene-3; α, γ -dimethylallyl chloride, α -methylcrotyl chloride, piperylene hydrochloride)

B.P.
$$103^{\circ}$$
 dec. at 760 mm. (1) $n_{\rm D}^{25}=1.4311$ (5) $103-106^{\circ}$ (2) 100.5° at 771.6 mm. (3) $D_4^{20}=0.9004$ (3) (10) $n_{\rm D}^{20}=1.4322$ (3) 68° at 200 mm. (4) 1.4328 (10) 65° at 200 mm. (3) 57° at 200 mm. (10) 58° at 155 mm. (5) $18-20^{\circ}$ at 12-13 mm. (1)

Two geom. stereoisomers of \tilde{C} are possible but as yet unrecognized. — [A levorotatory form of \tilde{C} has been obtd. (6) (7) cf. (11). — \tilde{C} does not undergo allylic transposition.]

[For prepn. of C from penten-2-ol-4 with HCl gas in the cold (3) (5), with PCl₃ in dry ether (37% yield (8)) or with pyridine (4), with PCl₅ (2) see indic. refs.]

C is readily hydrolyzed even by cold aq. (3); with KOH gives Sap. Eq. 106.2 (calcd. 104.6) (4). [For study of mech. of hydrolysis of C see (4).]

 $[\bar{C}$ with HBr gives (3) 4-bromopentene-2; with phenol as specified (8) gives phenyl α, γ -dimethylallyl ether, with diethyl sodiomalonate gives the substituted ester (5); for reactn. of \bar{C} with various aliphatic and aromatic amines see (9).]

[Č with *n*-propyl MgCl yields (10) 4-methylheptene-2, b.p. 113.5° at 760 mm., $D_4^{20} = 0.7206$, $n_D^{20} = 1.4123$ (10).]

- $d-(\alpha,\gamma-\text{Dimethylallyl})$ acetate: b.p. 136-137° (11). [From the corresp. d-alcohol with Ac₂O + pyridine (11).]
- $d_{i}l^{2}-(\alpha,\gamma$ -Dimethylallyl) benzoate: b.p. 140° at 21 mm.; $n_{D}^{23}=1.5075$ (11). [From the corresp. d-alcohol with BzCl + pyridine (11).]

- $d_{s}l_{-}(\alpha, \gamma-\text{Dimethylallyl})$ p-nitrobenzoate: m.p. 56° (11). [From the d- or $d_{s}l_{-}$ forms of corresp. alcohol (11).]
- d_i -(α, γ -Dimethylallyl) N-(α -naphthyl)carbamate: m.p. 105° (11). [For important details regarding this see (11).]
- 3:7400 (1) Böttcher (to I.G.), Ger. 512,232, Nov. 7, 1930; Cent. 1931, I 1007; C.A. 25, 1037 (1931). (2) Reif, Ber. 41, 2741 (1908). (3) Baudrenghien, Bull. sci. acad. roy. Belg. (5) 15, 56 (1929); Cent. 1929, I 2966; C.A. 23, 4196 (1929). (4) Arcus, Smith, J. Chem. Soc. 1939, 1748–1749. (5) Shonle, Waldo, J. Am. Chem. Soc. 55, 4650 (1933). (6) Levene, Haller, J. Biol. Chem. 81, 706 (1929). (7) Hills, Kenyon, Phillips, J. Chem. Soc. 1936, 583. (8) Hurd, Cohen, J. Am. Chem. Soc. 53, 1920 (1931). (9) Böttcher (to I. G.), Ger. 473,215, March 14, 1929; Cent. 1929, I 3037, C.A. 23, 3052 (1929). (10) Henne, Chanan, Turk, J. Am. Chem. Soc. 63, 3474–3476 (1941).
 - (11) Balfe, Hills, Kenyon, Phillips, Platt, J. Chem. Soc. 1943, 348-351.

3:7405 ISOPROPYL CHLOROFORMATE
$$C_4H_7O_2Cl$$
 Beil. III - 12 (Isopropyl chlorocarbonate) (CH₃)₂CH.O.CO.Cl III₁— III₂-(10)

B.P. 103-104° (1) (2) at 723 mm. (3)

Colorless liq. insol. cold aq.

[For prepn. (40% yield (2)) from isopropyl alc. (1:6135) + phosgene (3:5000) see (2) (3); using diphosgene (3:5515) see (1).]

 \tilde{C} on htg. with quinoline dec. at 62° (4) into isopropyl chloride (3:7025) + CO₂. [At higher temp. some propylene is also formed: for study see (5).]

- ① Isopropyl carbamate [Beil. III-29]: from \bar{C} in C_6H_6 by treatment with NH₃ gas, filtration of pptd. NH₄Cl, and evapn. of solvent; long ndls., m.p. 92-93° (3).
- ➡ Isopropyl N-phenylcarbamate (isopropyl carbanilate) [Beil. XII-321]: from C + aniline; cryst. from pet. ether, m.p. 75–76° (6). [Previous recorded values are erroneous.]
- 3:7495 (1) Nekrassow, Melnikow, J. prakt. Chem. (2) 127, 215 (1930). (2) Hamilton, Sly, J. Am. Chem. Soc. 47, 436-437 (1925). (3) Thiele, Dent, Ann. 302, 269-270 (1898). (4) Carré, Bull. soc. chim. (5) 3, 1072 (1936). (5) Compere, Proc. Louisiana Acad. Sci. 6, 93-98 (1942); C.A. 38, 2779 (1942). (6) Weizmann, Garrard, J. Chem. Soc. 117, 328 (1920).

B.P. $D_4^{20} = 0.9125$ (1) $D_D^{20} = 1.42973$ (1) $D_D^{20} = 1.43055$ (2) $D_D^{20} = 1.43055$ (2)

Colorless limpid liq. with odor like allyl chloride but weaker; alm. insol. aq. (1). [For prepn. of C from penten-1-ol-5 with PCl₃ + pyridine (1) or with SOCl₂ + dimethylaniline (2) see indic. refs.]

[For study of rate of reactn. of C with KI in acetone see (1).]

- 5-Phthalimidopentene-1: m.p. 40°, b.p. 155-157° at 12 mm. (3). [Not reported from C but obtd. in 90% yield (3) from 5-bromopentene-1 with K phthalimide in xylene at 150-160° for 6 hrs.]
- 3:7410 (1) Juvala, Ber. 63, 1994-1997 (1930). (2) Paul, Compt. rend. 193, 599 (1931). (3) Kharasch, Fuchs, J. Org. Chem. 9, 370 (1944).

3: 7415 2,2-DICHLOROBUTANE Cl
$$C_4H_8Cl_2$$
 Beil. I - 119 I_1 — $CH_3.CH_2.C.CH_3$ I_2 — I_2 —

B.P. M.P.
$$104-104.5^{\circ}$$
 (1) -74° (3) $D_4^{20} = 1.0665$ (2) $n_D^{20} = 1.4306$ (2) $102-104^{\circ}$ (2) (3) $D_4^{21.8} = 1.069$ (5) $n_D^{22} = 1.4270$ (4)

[For prepn. from butanone (ethyl methyl ketone) (1:5405) with PCl₅ see (8) (5) (4) (6) (1); for formn. (together with other isomers and 2-chlorobutene-1 (1)) from 2-chlorobutane (3:7125) by chlorination see (2).]

Č with alc. KOH splits off HCl and gives mixt. of both stereoisomeric 2-chlorobutene-2's (2) (9) (3:7105). [Cleavage of HCl in the other sense to yield mainly 2-chlorobutene-1 (3:7075) is also claimed (7).]

3:7415 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4223. (2) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 663-666 (1937); Cent. 1937, II 372; C.A. 31, 5754 (1937). (3) Dupont, Compt. rend. 148, 1522 (1909). (4) Kahovec, Kohlrausch, Z. physik. Chem. B-48, 10 (1941). (5) Stoll, Rouvé, Helv. Chim. Acta 21, 1544 (1938). (6) Bruylants, Ber. 8, 412 (1875). (7) Schjanberg, Ber. 71, 573 (1938). (8) Henne, Renoll, Leicester, J. Am. Chem. Soc. 61, 940 (1939). (9) Charpentier, Bull. soc. chim. (5) 1, 1407-1411 (1934).

3: 7420 1-CHLOROPENTENE-1 Cl
$$C_6H_9Cl$$
 Beil. S.N. 11 CH $_3$ CH $_2$.CH $_2$.CH $_2$.CH $_3$.CH $_4$.CH

Two geom. stereoisomers of \bar{C} are possible but as yet unrecognized. [For prepr. of \bar{C} from 1.2-dichloropentane (3:8140) with alc. KOH see (1).]

3:7420 (1) Lemke, Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 1995-1998 (1937); Cent. 1939, I 2398; C.A. 32, 482 (1938).

B.P.
$$105-106^{\circ}$$
 (1) $D_{12}^{12} = 1.0111$ (5) $104.3-105.7^{\circ}$ (2) 108° (3) $103-105^{\circ}$ (5)

Colorless liq. with agreeable odor.

[For prepn. from isobutyraldehyde (1:0120) + PCl₅ see (5) (2); for formn. (with other products) during chlorination of isobutane see (1) (3).]

C htd. in s.t. with Ag₂O + H₂O yields Ag isobutyrate (4).

3:7425 (1) Hass, McBee, Weber, Ind. Eng. Chem. 27, 1191 (1935). (2) Kohlrausch, Köppl, Monatsh. 65, 197 (1935). (3) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,072, June 4, 1935; Cent. 1936, I 3012. (4) Spring, Lecrenier, Bull. soc. chim. (2) 48, 626 (1887). (5) Oeconomides, Bull. soc. chim. (2) 45, 497-498 (1881).

3:7430 1,2-DICHLORO-2-METHYLPROPANE CH₃ C₄H₈Cl₂ Beil. I - 126 (Isobutylene dichloride)
$$CH_3$$
— C — CH_2 I_{1-} (88)

B.P.
$$106.5^{\circ}$$
 cor. at 760 mm. (1) $D_4^{20} = 1.089$ (4) $n_D^{20} = 1.4370$ (1) $107-108^{\circ}$ (3) (4) (5) (6) (7) 1.4360 (4) $59-60^{\circ}$ at 150 mm. (1) $D_{20}^{20} = 1.093$ (1) $n_D^{17} = 1.4373$ (3) $38.6-39.2^{\circ}$ at 70 mm. (1)

Liq. with mild clean sweetish odor; stable on stdg. and develops no HCl even in 6 months (1).

[For prepn. from *ter*-butyl chloride (3:7045) by chlorination see (1) (2) (8); from 2-methylpropene (isobutylene) by addn. of Cl_2 at 0° see (4); from 1-chloro-2-methylpropanol-2 (3:7752) with conc. HCl see (2) (9); from isobutane by chlorination see (10).]

Upon hydrolysis the tertiary chlorine atom shows great reactivity, the primary chlorine atom little. Thus $\bar{\mathbb{C}}$ on boiling with aq. for 18 hrs. gives (48% yield (2)) 1-chloro-2-methylpropanol-2 (3:7752). [The addn. of bases (NaOH or NaHCO₃) or antiacids (CaCO₃) results in lower yields (2).] [In addn. to the above 1-chloro-2-methylpropanol-2 the presence of NaHCO₃ or Na₂CO₃ leads (11) to formn. of 2-methylpropanediol-1,2 (isobutylene glycol) [Beil. I-480], 1-chloro-2-methylpropene-1 ("isocrotyl chloride") (3:7120), and isobutyraldehyde (1:0120).] [For study of methods of conversion of $\bar{\mathbb{C}}$ to isobutyraldehyde see (1).]

3:7430 (1) Hersh, Nelson, J. Am. Chem. Soc. 58, 1631-1633 (1936). (2) Sparks, Nelson, J. Am. Chem. Soc. 58, 1010-1011 (1936). (3) Kahovoc, Kohirausch, Z. physik. Chem. B-48, 10 (1941).
(4) Burgin, Engs, Groll, Hearne, Ind. Eng. Chem. 31, 1414 (1939). (5) Hass, McBee, Weber, Ind. Eng. Chem. 27, 1191 (1935). (6) Mouneyrat, Ann. chim. (7) 20, 533-534 (1900). (7) Pogorshelski, J. Russ. Phys.-Chem. Soc. 36, 1129-1184 (1904); Cent. 1905, I 668. (8) Rogers, Nelson, J. Am. Chem. Soc. 58, 1027-1029 (1936). (9) Henry, Compt. rend. 142, 496 (1906). (10) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,072, June 4, 1935; Cent. 1936, I 3012.

(11) Dobryanskii, Gutner, Shchigel'skaya, J. Gen. Chem. (U.S.S.R.) 7, 1315-1320 (1937); Cent. 1938, I 561; C.A. 31, 6189 (1937).

3: 7450
$$\alpha, \alpha$$
-DIMETHYLPROPIONYL CHLORIDE C_5H_9OCl Beil. II - 320 (Trimethylacetyl chloride; CH_3 $II_{1^-}(139)$ pivalyl chloride) CH_3 C $C=O$ $II_{2^-}(280)$ B.P. B.P. B.P. 107° (1) 70.5°-71.0° at 250 mm. (5) (6) $n_D^{20} = 1.4126$ (7) 105–106° (2) 58° at 150 mm. (7) 1.4125 (9)

104.3-105.4° (3) 57.6° at 150 mm. (8) 1.4123 (9) 103-104° (4) 56° at 150 mm. (9) 1.4122 (8) 48° at 100 mm. (9) 1.4118 (5) (6) [For prepn. of \tilde{C} from trimethylacetic acid (pivalic acid) (1:0410) with PCl₅ (2), with

PCl₈ (10), with SOCl₂ (11) (yield 80% (5) (6) (8), 86% (7)), or with benzoyl chloride (1 mole 79% yield, 2 moles 92% yield (4) cf. (16)) see indic. refs.; for form. of C (together with other prods.) from isobutane + CO + AlCl₈ at 20° and 120 atm. see (12).]

[C with MeOH gives (50% yield (8)) methyl trimethylacetate (1:3072), b.p. 99.5° at

731 mm., $n_D^{20} = 1.3895$ (8); \bar{C} with sodium trimethylacetate yields (2) pivalic anhydride, b.p. 124° at 93 mm., $n_D^{20} = 1.4093$ (6).]

[C with large excess of most Grignard reagents is reduced to ter-butyl carbinol (neopentyl alcohol) (1:5812), other products also being formed; for reactn. of C with EtMgBr (8) (13), with n-PrMgBr (13), with iso-PrMgBr (13), with n-BuMgBr (5) (7) (13), with iso-BuMgBr (13) or iso-BuMgI (9), with ter-BuMgCl (5) (6) (9), with n-AmMgBr (13), with iso-AmMgBr (13), with ter-AmMgCl (9), with neopentyl MgCl (9) see indic. refs.]

[For study of rate of reactn. of C with various alcs. see (14).]

C on hydrolysis yields trimethylacetic acid (1:0410) q.v. (for the amide, m.p. 132.0-132.6° cor. (15), anilide, m.p. 132° cor. (16), p-toluidide, m.p. 119.5° cor. (16), and other derivatives (16) corresp. to C see 1:0410 and indic. refs.).

3:7450 (1) Böeseken, Rec. trav. chim. 29, 99 (1910). (2) Butlerow, Ann. 173, 373-374 (1874). (3) Kohlrausch, Pongratz, Z. physik. Chem. B-22, 382 (1933). (4) Brown, J. Am. Chem. Soc. 66, 1325-1328 (1938). (5) Whitmore, Rec. trav. chim. 57, 562-568 (1938). (6) Greenwood, Whitmore, Crooks, J. Am. Chem. Soc. 60, 2028-2030 (1938). (7) Whitmore, Popkin, Whitaker, Mattil, Zech, J. Am. Chem. Soc. 60, 2458-2462 (1938). (8) Whitmore, Foster, J. Am. Chem. Soc. 64, 2966-2968 (1942). (9) Whitmore, Whitaker, Mosher, Breivik, Wheeler, Miner, Sutherland, Wagner, Clapper, Lewis, Lux, Popkin, J. Am. Chem. Soc. 63, 643-654 (1941). (10) Whitmore, Langlois, J. Am. Chem. Soc. 54, 3439 (1932).

(11) Meyer, Monatsh. 27, 36 (1906).
(12) Hopff, Nenitzescu, Iascescu, Cantuniari, Ber. 69, 2250 (1936).
(13) Whitmore, Meyer, Pedlow, Popkin, J. Am. Chem. Soc. 60, 2788-2789 (1938).
(14) Leimu, Ber. 70, 1040-1053 (1937).
(15) Cavalieri, Pattison, Carmack, J. Am. Chem. Soc. 67, 1785 (1945).
(16) Degnan, Shoemaker, J. Am. Chem. Soc. 68, 105 (1946).

3:7455 5-CHLOROPENTENE-2

C₅H₉Cl Beil. S.N. 11

(1-Chloropentene-3) CH₃.CH=CH.CH₂CH₂Cl

B.P. 107.0-107.6° at 755 mm. (1)

$$D_4^{20} = 0.9043 (1) \quad n_D^{20} = 1.4310 (1)$$

Two geom, stereoisomers of C are possible but as yet unrecognized.

[For prepn. of \bar{C} in 75% yield from penten-3-ol-1 with SOCl₂ in CH₂Cl₂ see (1).]

 \bar{C} with NaI in acetone gives (1) after 11 hrs. reflux 74% yield 1-iodopentene-3, b.p. 53.6° at 20 mm., $D_{14}^{20} = 1.5579$, $n_{D}^{20} = 1.5153$ (1).

Č with Mg in dry ether yields RMgCl (used in reactn. with acrolein (1:0115) to give (50% yield (1)) penten-3-yl-vinyl-carbinol).

3:7455 (1) Goethals, Bull. soc. chim. Belg. 46, 417-419 (1937).

3:7460 1-CHLOROPENTANE C₅H₁₁Cl Beil. I - 130 (n-Amyl chloride, CH₃.CH₂.CH₂.CH₂.CH₂.CH₂.Cl I₁-(42) n-butylcarbinyl chloride) I₂-(95)

B.P.		F.P.	
108.35° cor.	at 760 mm.	(1) (2) -99°	
107.74-107.78	° at 760 mm.	(3)	$n_{\rm D}^{25} = 1.41026 (2)$
107-108°		(4)	$D_4^{20} = 0.8828 \qquad (8)$
105.7-105.8°	at 759.3 mm.	(5)	0.8821 (30)
105°	at 764 mm.	(30)	0.8816 (2)
107.8-108.4°	at 749.7 mm.	(6)	$n_{\rm D}^{20} = 1.41280 (8)$
106.6°	at 739.8 mm.	(7)	1.41253 (2)
106°	at 725 mm.	(8)	1.41177 (30)
			$D_4^{15} = 0.88657 (2)$
			$n_{\rm D}^{15} = 1.41481 (2)$

Note that most samples of \bar{C} reported prior to 1938 undoubtedly contained a small amount of mixed 2-chloropentane (3:7325) and 3-chloropentane (3:7330). This previously unrecognized fact may be the cause of much variation in reported physical constants, especially the refractive index.

[For prepn. of \bar{C} (or its mixt. with 2-chloro- and 3-choropentane) from pentanol-1 (1:6205) with conc. HCl (7) (4) in s.t. at 120° for 12-15 hrs. (94% yield (2)) see indic. refs.; with HCl + ZnCl₂ (yield: 67% (30), 57% (8), 72% (9)) see (8) (9) (30); with PCl₃ + ZnCl₂ (70% yield (9)) or PCl₅ + ZnCl₂ (76% yield (9)) see (9); with SOCl₂ + pyridine (gives no rearrangement (8)) (yield: 80% (8), 87% (9)) see (8) (9); for prepn. (23% yield (10)) from γ -chloropropyl p-toluenesulfonate by reactn. with EtMgBr see (10).]

[For formn. of C (together with other products) during chlorination of pentane see (11) (12) (13) (14).]

Č with EtOH forms const.-boilg. mixt., b.p. 72.5°, but forms no azeotrope with MeOH. Č forms with aq. a const.-boilg. mixt., b.p. 82°.

 \ddot{C} on htg. with conc. HCl + ZnCl₂ at 126-134° for 12 hrs. undergoes partial isomerization forming 3% of a mixt. of 2-chloropentane (3:7325) and 3-chloropentane (3:7330) (8).

[For study of rate of hydrolysis by aq. at 80° and 180°, and rate of cleavage of HCl at 180°, see (11); for rate of reactn. with KI in acetone see (4) (15) (16); for reactn. with Na—C=CH see (17) (18); with KCN see (19); with Cl₂ see (6); for extensive study of reactn. with Na see (19) (20) (21) (22) (23) (24) (25).]

- n-Caproanilide: C with Mg in dry ether yields RMgCl which upon reactn. with phenyl isocyanate and subsequent hydrolysis yields (26) n-caproanilide, m.p. 96° cor. (27), 94-95° u.c. (26), 92° (28).
- n-Capro-p-toluidide: m.p. 74-75° u.c. (26), 73° (28). [From RMgCl + p-tolyl isocyanate as above (26).]
- S-n-Amylisothiourea picrate: m.p. 154° (29). [From C
 in alc. on refluxing 2 hrs. with thiourea, followed by addn. of PkOH (29).]
- —— N-(n-Amyl)tetrachlorophthalimide: ndls. from CHCl₃, poured into 2 vols. MeOH, m.p. 145-146° (31).
- 3:7460 (1) Hass, J. Chem. Education 13, 492-493 (1936). (2) Simon, Bull. soc. chim Belg. 38, 48, 56, 58 (1929). (3) Rintelen, Saylor, Gross, J. Am. Chem. Soc. 59, 1129 (1937). (4) Conant, Kirner, J. Am. Chem. Soc. 46, 245 (1924). (5) Karvonen, Ann. Acad Sci. Fennicae 3-A, 1-103; Cent. 1912, II 1271. (6) Hass, Huffman, J. Am. Chem. Soc. 63, 1233-1235 (1941). (7) Lieben, Rossi, Ann. 159, 72 (1871). (8) Whitmore, Karnatz, Popkin, J. Am. Chem. Soc. 60, 2540-2542 (1938). (9) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929). (10) Rossander, Marvel, J. Am. Chem. Soc. 50, 1495 (1928).
- (11) Ayres, Ind. Eng. Chem. 21, 899-904 (1929). (12) Clerk, Ind. Eng. Chem. 22, 439-443 (1930). (13) Ayres (to B.A.S. Co.), U.S. 1,741,393, Dec. 31, 1929; Cent. 1930, I 3353. (14) Sharples Solv. Corp., Ger. 610,660; March 18, 1935; Cent. 1935, II 920. (15) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925). (16) Conant, Kirner, Hussey, J. Am. Chem. Soc. 47, 587-589 (1925). (17) Hurd, Christ, J. Org. Chem. 1, 143-144 (1936). (18) Vaughn, Hennion, Vogt, Nieuwland, J. Org. Chem. 2, 1-22 (1937). (19) Hass, Marshall, Ind. Eng. Chem. 23, 352-353 (1931). (20) Morton, LeFevre, Hechenbleikner, J. Am. Chem. Soc. 58, 757 (1936).
- (21) Morton, Hechenbleikner, J. Am. Chem. Soc. 58, 1700 (1936). (22) Morton, Hechenbleikner, J. Am. Chem. Soc. 58, 2599-2605 (1936). (23) Morton, Richardson, J. Am. Chem. Soc. 62, 123-126 (1940). (24) Morton, Richardson, J. Am. Chem. Soc. 62, 129-131 (1940). (25) Gilman, Pacevitz, J. Am. Chem. Soc. 62, 1301-1302 (1940). (26) Underwood, Gale, J. Am. Chem. Soc. 56, 2119 (1934). (27) Schwartz, Johnson, J. Am. Chem. Soc. 53, 1065 (1931). (28) Robertson, J. Chem. Soc. 115, 1220-1221 (1919). (29) Levy, Campbell, J. Chem. Soc. 1339, 1443. (30) Vogel, J. Chem. Soc. 1943, 638, 640.

(31) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934).

[For prepn. of \bar{C} from β -ethoxyethyl alc. ("Cellosolve") (1:6410) with PCl₃ (7) (8) or with SOCl₂ + pyridine (20% yield (10)) (11) in CHCl₃ (58.3% yield (9)) see indic. refs.; from ethylene chlorohydrin (3:5552) + ethyl alc. (1:6130) + conc. H₂SO₄ at 145° see (1); from ethylene with ethyl hypochlorite (3:7022) (12) or with mixtures yielding the latter, such as EtOH + Cl₂ (85% yield \bar{C} (2)) or alc. N,N-dichlorobenzenesulfonamide (5), see indic. refs.; from β -iodoethyl ethyl ether with Cl₂, SbCl₅, or ICl see (3).]

 \bar{C} with NaI in acctone refluxed 15 hrs. gives (10) (11) β -ethoxyethyl iodide, b.p. 151-154° (10) (11).

[$\bar{\rm C}$ with KSH in s.t. at 65° for 24 hrs. (1) cf. (13) gives (74% yield (1)) β -ethoxyethyl mercaptan, b.p. 125.5–125.8° u.c., $D_{20}^{20}=0.9479$ (1) (corresp. EtOCH₂CH₂SHgCl, m.p. 152.0–153.5° dec. (1)) accompanied by (13% yield (1)) of bis-(β -ethoxyethyl) sulfide, b.p. 229° cor., also obtd. (51% yield (1)) from $\bar{\rm C}$ + alc. Na₂S.]

[\bar{C} with excess NaOC₆H₅ in alc. htd. 10 days gives (1) β -phenoxyethyl ethyl ether (β -ethoxyphenetole), b.p. 230°. — \bar{C} with disodium salt of hydroquinone (1:1590) gives (14) hydroquinone bis-(β -ethoxyethyl ether), m.p. 34-35°, b.p. 210-212° at 25 mm. (14).]

[Č with diethyl malonate + alc. NaOEt gives (14% yield (1)) cf. (15) diethyl β -ethoxy-ethylmalonate, b.p. 134–138° at 15 mm. (1), 118–119° at 6 mm. (15); $D_{\perp}^{20} = 1.0199$ (15).]

[\bar{C} with aniline refluxed 2 hrs. gives (1) N-(β -ethoxyethyl)aniline, b.p. 262-263° cor.] [For reactn. of \bar{C} + NaNH₂ with α -picoline, with γ -picoline, and with β -collidine see (16).]

3:7463 (1) Swallen, Boord, J. Am. Chem. Soc. 52, 653-659 (1930). (2) Ernst (to A. Wacker Soc. Elektrochem. Ind.), Ger. 537,696, Nov. 5, 1931; Cent. 1932, I 1153; C.A. 26, 1297 (1932). (3) Henry, Bull. soc. chim. (2) 44, 459 (1885); Compt. rend. 100, 1007 (1885). (4) Karvonen, Ann. Acad. Sci. Fennicae 5-A, 1-139 (1914); Cent. 1919, III 807; C.A. 14, 2176 (1920). (5) Sklyarov, J. Gen. Chem. (U.S.S.R.) 9, 2121-2125 (1939); Cent. 1940, II 199-200; C.A. 34, 4055 (1940). (6) Mohler, Sorge, Helv. Chim. Acta 23, 1208 (1940). (7) Karvonen, Ann. Acad. Sci. Fennicae 3-A, No. 7, 1-103 (1912); Cent. 1912, II 1270. (8) Chalmers, Can. J. Research 7, 464-471 (1932); Cent. 1933, I 1759; C.A. 27, 701 (1933). (9) Hurd, Fowler, J. Am. Chem. Soc. 61, 251 (1939). (10) Smith, Ungnade, Austin, Prichard, Opie, J. Org. Chem. 4, 339 (1939).

(11) Dutta, J. Indian Chem. Soc. 17, 652 (1940). (12) Suknevich, Chilingaryan, J. Gen. Chem. 2, 783-789 (1932); Cent. 1933, II 1170; C.A. 27, 2670 (1933). (13) Rojahn, Lemme, Arch. Pharm. 263, 623 (1925). (14) Sexton (to Imperial Chem. Ind., Ltd.), U.S. 2,056,299, Oct. 6, 1936; Cent. 1937, I 1798; C.A. 30, 8641 (1936). (15) Palomaa, Kenetti, Ber. 64, 800-801 (1931).

(16) Chichibabine, Bull. soc. chim. (5) 5, 439-441 (1938).

3:7464
$$\beta$$
-CHLOROETHYL VINYL ETHER C₄H₇OCl Beil. I — CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—(473) B.P. 109° cor. at 740 mm. (1) $D_{15}^{15} = 1.0525$ (1)

[For prepn. of \tilde{C} from β,β' -dichlorodiethyl ether (3:6025) with solid N2OH at 200° (1) or with triethanolamine + solid NaOH (70% yield (2)) see indic. refs.]

 $\ddot{\mathbf{C}}$ is stable toward alkalies but with dil. acids even in cold is readily and quant. hydrolyzed (1) to β -chloroethanol (3:5552) and acetaldehyde (1:0100).

[\bar{C} with diethyl sodiomalonate gives (73% yield (1)) diethyl β -(vinyloxy)ethyl malonate, b.p. 130-135° at 9 mm., $D_{15}^{16} = 1.0575$ (1); this prod. condenses (1) with urea to give 5-(β -(vinyloxy)ethyl)barbituric acid (whose properties appear to be subsequently unreported) which itself with dil. minl. acid hydrolyzes to give 5-(β -hydroxyethyl)barbituric acid, m.p. above 300° (3). — For analogous reactions of \bar{C} with various diethyl alkylmalonates and reaction of the products with urea to give the corresp. 5-alkyl-5-(β -(vinyloxy)ethyl)barbituric acids see (3). — \bar{C} with diethyl phenyl-sodio-malonate in s.t. at 140-145° for 14 hrs. gives (52% yield (4)) diethyl 5-phenyl-5-(β -(vinyloxy)ethylmalonate, b.p. 196-197° at 17 mm., $D_4^{20} = 1.098$; this prod. with urea gives (4), 5-phenyl-5-(β -(vinyloxy)ethyl)barbituric acid which upon hydrolysis with dil. acid gives (10% yield (4)) 5-phenyl-5-(β -hydroxyethyl)barbituric acid ("hydroxyluminal").]

[\bar{C} with phenylacetonitrile gives (50% yield (4)) phenyl-(β -vinyloxyethyl)acetonitrile, b.p. 147° at 8 mm., $D_4^{20} = 1.029$ (4).]

[For use of C in prepn. of cellulose ethers see (5).]

3:7464 (1) Cretcher, Koch, Pittenger, J. Am. Chem. Soc. 47, 1175-1176 (1925). (2) Chitwood, Perkins (to Carbide and Carbon Chem. Corp.), U.S. 2,104,717, Jan. 4, 1938; Cent. 1938, I 4236; [C.A. 32, 1712 (1938)]: French 815,148, July 6, 1937; Cent. 1937, II 4238; C.A. 32, 1278 (1938). (3) Cretcher, Koch, Pittenger, J. Am. Chem. Soc. 47, 3083-3085 (1925). (4) Nolson, Cretcher, J. Am. Chem. Soc. 50, 2761-2762 (1928). (5) Hahn (to du Pont Co.), U.S. 2,082,797, June 8, 1937; Cent. 1937. II 3838; C.A. 31, 5577 (1937).

3: 7465 4-CHLORO-2-METHYLBUTENE-2
$$C_5H_9Cl$$
 Beil. I - 214 $(\gamma,\gamma$ -Dimethylallyl chloride; Cl CH_3 I_1 -(88) isoprene hydrochloride) CH_2 -CH=C-CH₃ I_2 -(191)

B.P.
$$109^{\circ}$$
 (1) $D_{4}^{20} = 0.9335$ (1) $n_{D}^{20} = 1.43975$ (4) $30-33^{\circ}$ at 40 mm. (4)

Colorless liq. with odor like allyl chloride. — $\bar{\mathbf{C}}$ darkens on stdg. and loses HCl on distn. (1).

[For prepn. of C from 2-methylbutadiene-1,3 (isoprene) (1:8020) by 1,4-addn. of dry HCl gas see (1) (4).]

 \overline{C} on htg. in s.t. with KOAc + AcOH (1) or passed over TiO_2 at 425–450° at reduced press. (3) loses HCl yielding isoprene (1:8020), b.p. 34°.

Č reduces alk. KMnO₄ (1).

Č in conc. HCl satd. with HCl gas gives (94% yield (1)) 2,4-dichloro-2-methylbutane (3:8105), b.p. 145-146° (1) cf. (4).

C in CHCl₃ adds 1 Br₂, yields (1) 2,3-dibromo-4-chloro-2-methylbutane, oil decomposing on distn. even under reduced press. (1).

[For behavior of C with AlCl₃ see (2).]

3:7465 (1) Aschan, Ber. 51, 1303-1307 (1918). (2) Thomas, Carmody, J. Am. Chem. Soc. 55, 3855 (1933). (3) Müller-Cunradi (to I.G.), Ger. 565,160, Nov. 26, 1932. (4) Soday (to United Gas Improvement Co.), U.S. 2,376,396, May 22, 1945; C.A. 39, 3548 (1945).

3: 7470 1-CHLOROPENTENE-2
$$C_5H_9Cl$$
 Beil. I — $(\gamma$ -Ethylallyl chloride) CH₃.CH₂.CH=CH.CH₂Cl I₁— I₂-(184) B.P. 109–110° (1) (2) $D_-^{23} = 0.9095$ (3) $n_D^{23} = 1.4347$ (3)

Note. Č by virtue of facile allylic transposition is readily converted to an equilibrium mixt. with its synionic isomer 3-chloropentene-1 (3:7260) q.v.; reactns. of Č may therefore frequently yield also the corresponding derivatives of the isomer.

[For prepn. of \bar{C} (or its mixt. with 3-chloropentene-1 (3:7260)) from penten-2-ol-1 with dry HCl gas at 0° (5) (7), with PCl₃ + pyridine (4) (7), or with SOCl₂ in ether (6) see indic. refs.; for prepn. of \bar{C} from 3-chloropentene-1 (3:7260) by htg. at 225° (60-62% \bar{C}) see (6) (3).] [\bar{C} is separable from the accompanying isomer by careful fractional distn. (7) (5).] [For formn. of \bar{C} (together with other products) from pentene-2 (1:8215) + Cl₂ in CCl₄ see (8).]

 \bar{C} on long shaking with aq. Na₂CO₃ gives (7) in poor yield penten-2-ol-1 (*p*-nitrobenzoate, m.p. 53°) accompanied by much penten-1-ol-3. — \bar{C} on htg. with alc. KOH gives (3) (7) in poor yield the corresp. ethyl ether, viz., 1-ethoxypentene-2, b.p. 123°, $D_{-}^{23} = 0.7930$, $n_{D}^{23} = 1.4099$ (3), accompanied by the isomeric 3-ethoxypentene-1, b.p. 102°, $D_{-}^{23} = 0.7768$, $n_{D}^{23} = 1.3986$ (3).

[For study of reactns. of \bar{C} with KOAc in AcOH, with AgOAc, with N-methylaniline, with diethylamine, etc., see (7); for reactn. of \bar{C} with phenol in pres. of K_2CO_3 + acetone see (5).]

 \bigcirc N-(Penten-2-yl-1)phthalimide [N-(γ-ethylallyl)phthalimide]: colorless rhombic cryst. from alc., m.p. 69-70° (7). [From \bigcirc on htg. with K phthalimide in a s.t. at 190-200° for 2½ hrs.; note that some of the corresp. deriv. from the isomer, viz., N-(α-ethylallyl)phthalimide, m.p. 78-79°, is formed to extent of about 10% (7).]

3:7470 (1) Mumm, Richter, Ber. 73, 858-860 (1940). (2) Mumm, Hornhardt, Diederichsen, Ber. 72, 107 (1939). (3) Prevost, Compt. rend. 187, 1053-1054 (1928). (4) Gredy, Bull. soc. chim. (5) 4, 419 (1937). (5) Lauer, Filbert, J. Am. Chem. Soc. 58, 1388 (1936). (6) Prevost, Bull. soc. chim. (4) 49, 264-267 (1931). (7) Meisenheimer, Link, Ann. 479, 254-277 (1930). (8) Stewart, Weidenbaum, J. Am. Chem. Soc. 58, 98-100 (1936).

3:7475 3-CHLORO-2,2-DIMETHYLBUTANE
$$C_6H_{13}Cl$$
 Beil. S.N. 10 (Pinacolyl chloride; CH_3 H ter-butyl-methyl-carbinyl chloride) CH_3 CH_4 CH_5 CH_5

B.P. 109.9° at 734 mm. (1) $D_4^{20} = 0.8767$ (1) $n_D^{20} = 1.4181$ (1) [For form. of \tilde{C} (11%) from 2,2-dimethylbutane (neohexane) (1:8510) on chlorination

see (1).] [Note that the corresp. alc. (pinacolyl alc.) (1:6186) with HCl does not give C but rather rearr. prods. (2).]

Č with Mg in dry ether gives RMgCl which with oxygen yields (1) pinacolyl alc. (1:6186) q.v.

Pinacolyl mercuric chloride (C₆H₁₃HgCl): cryst. from dil. alc., m.p. 89-90° (3); 89.5-90° (2). [From RMgCl + HgCl₂ in ether.] 3:7475 (1) Whitmore, Bernstein, Mixon, J. Am. Chem. Soc. 60, 2539 (1938). (2) Whitmore, Rothrock, J. Am. Chem. Soc. 55, 1106-1109 (1933). (3) Whitmore, Bernstein, J. Am. Chem. Soc. 60, 2627 (1938).

3: 7480 3,3-DICHLORO-2-METHYLPROPENE-1
$$C_4H_6Cl_2$$
 Beil. S.N. 11 (1,1-Dichloro-2-methylpropene-2) Cl CH_3 HC — C = CH_2 Cl

B.P.
$$108-112^{\circ}$$
 at 762 mm. (1) $D_4^{24} = 1.1363$ (1) $n_C^{24} = 1.4523$ (1) $49-50^{\circ}$ at 120 mm. (1)

Note. \bar{C} by virtue of allylic transposition may yield derivatives of its synionic isomer 1,3-dichloro-2-methylpropene-1 (3:5590) q.v.

[For prepn. of \tilde{C} (68% yield together with 32% yield of 1,1,2-trichloro-2-methylpropane (3:5710)) from 1-chloro-2-methylpropene-1 (β,β -dimethylvinyl chloride) (3:7120) with Cl₂ (1 mole) + NaHCO₃ (1.5 moles) at 0° see (1).]

Č on htg. under reflux gives (by allylic transposition) 1,3-dichloro-2-methylpropene-1 (3:5590), b.p. 132°.

Č with O₃ followed by hydrolysis yields (1) α,α -dichloroacetone (3:5430) + methylglyoxal (propanone-2-al-1) [Beil. I-762; I₁-(395), I₂-(819)].

3:7480 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) **8,** 1232-1246 (1938); Cent. **1939,** II 4223; C.A. **33,** 4190 (1939).

3: 7485 1-CHLORO-2-METHYLBUTENE-2 CH₃
$$C_5H_9Cl$$
 Beil. I — $(\beta,\gamma$ -Dimethylallyl chloride) CH₃—CH=C — CH₂Cl I_1 — I_2 —(189) B.P. 110° at 760 mm. (1) $D_4^{20} = 0.9327$ (1) $n_D^{20} = 1.4481$ (1) 25.9-26.4° at 25 mm. (1) $D_4^{16} = 0.9324$ (2)

Note. \tilde{C} by virtue of facile allylic transposition is in equilibrium with its synionic isomer 3-chloro-2-methylbutene-1 (3:7300); reactns. of \tilde{C} therefore may also yield derivatives related to its isomer.

[For prepn. of \bar{C} (or its mixt. with the synionic 3-chloro-2-methylbutene-1 (3:7300)) by actn. of Cl_2 as specified (1) on "tertiary amylene" (a mixt. consisting mainly of 2-methylbutene-2 (1:8220) with some 2-methylbutene-1 (1:8210)) see (1). — The relative amt. of \bar{C} and its isomer is not constant but usually is about 40% of \bar{C} with 60% of 3-chloro-2-methylbutene-1 (3:7300), the ratio, however, being independent of the proportion of the two olefins in the starting material.]

[For formn. of \bar{C} from 2-methylbutene-2 (1:8220) with Cl_2 see (2); from 2-methylbutene-1 (1:8210) see (3); for prepn. of \bar{C} (together with other prods.) from 1-chloro-2-methylbutanol-2 (3:8175) by distn. with anhyd. oxalic acid (4) or with Ac_2O + conc. H_2SO_4 (5) see (4) (5); for prepn. of \bar{C} from 2-methylbuten-2-ol-1 with PCl_3 + pyridine see (1).]

 $\ddot{\mathbf{C}}$ on hydrolysis gives not only the alc. corresponding to $\ddot{\mathbf{C}}$ but also that corresp. to the isomeric 3-chloro-2-methylbutene-1 (3:7300) together with a little ketone: thus $\ddot{\mathbf{C}}$ on hydrolysis with 12 pts. aq. at 70° for 16 hrs. gives (6) 25% alc. A (2-methylbuten-1-ol-3) [N-(α -naphthyl)carbamate, m.p. 91.5-93° (6)] + 50% alc. B (2-methylbuten-2-ol-1) [N-(α -naphthyl)carbamate, m.p. 103-103.5° (6)] + 5% isopropyl methyl ketone (1:5410);

 \bar{C} on hydrolysis with 2 pts. aq. + 1 mole CaCO₃ for 4 hrs. at 70° gives (6) 60% alc. A + 30% alc. B + 5% isopropyl methyl ketone (1:5410); \bar{C} on hydrolysis with CaO for 1½ hrs. gives (6) 70% alc. A + 25% alc. B + a trace of ketone.

[For study of reactn. of C with NaI (4) and its rate of reactn. with KI in acetone at 20° (7) or with NaOEt in alc. at 35° (7) see indic. refs.; the reactivity of the halogenation of C is greater than that in crotyl chloride (1-chlorobutene-2) (3:7205) and the latter in turn is more reactive than that in methallyl chloride (3-chloro-2-methylpropene-1) (3:7145) or allyl chloride (3:7035), which are about the same (4),

 \bar{C} on treatment with O₃ followed by hydrolysis yields (3) (2) chloroacetone (3:7212) + acetaldehyde (1:0100).

3:7485 (1) Burgin, Engs, Groll, Hearne, Ind. Eng. Chem. 31, 1416 (1939). (2) Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1116-1132 (1936); Cent. 1937, I 572; C.A. 31, 1003 (1937). (3) Gutner, Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1062-1067 (1938); Cent. 1939, II 4221; C.A. 33, 3755 (1939). (4) Chalmers, Trans. Roy Soc Can. (3) 22, III 74-77 (1928). (5) Seyer, Chalmers, Trans. Roy. Soc. Can. (3) 20, III 338 (1926). (6) Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1549-1552 (1936); Cent. 1937, I 3785, C.A. 31, 2165 (1937). (7) Tamele, Ott, Marple, Hearne, Ind. Eng. Chem. 33, 118-119 (1941).

Note that the prod. of b.p. 180°, formerly (3) supposed to have been C, is in fact (2) diallyl carbonate.

[For prepn. of \bar{C} from allyl alc. (1:6145) with phosgene (3:5000) (yield 37% (1)) (4) (2) see indic. refs.; note that some diallyl carbonate, b.p. 166° at 730 mm. (2), is also formed (2).]

 \overline{C} in quinoline begins to decompose at 37° (5) (6) presumably into CO_2 + allyl chloride (3:7035) although this is not specifically stated.

[For reaction of \bar{C} with diethylene glycol (1:6525), triethylene glycol (1:6538), etc., see (7).]

3:7487 (1) Schving, Sabetay, Bull. soc. chim. (4) 43, 858 (1928). (2) Fierz-David, Müller, J. Chem. Soc. 125, 26 (1924). (3) Thiele, Dent. Ann. 302, 262 (1898). (4) Schving, French 34,412, June 18, 1929; Cent. 1929, II 2829. (5) Carré, Bull. soc. chim. (5) 3, 1072 (1936). (6) Carré, Passedouet, Compl. rend. 201, 899 (1935). (7) Muskat, Strain (to Pittsburgh Plate Glass Co.), U.S. 2,370,565, Feb. 27, 1945; C.A. 39, 4526 (1945).

3: 7490 2-CHLORO-2-METHYLPENTANE
$$C_{6}H_{13}Cl$$
 Beil. I - 148 (Dimethyl-n-propyl-carbinyl CH₃ I_{1-} (53) I_{2-} (111) CH₃ I_{1-} (53) I_{2-} (111) CH₃ I_{2-} (111) I_{2-} (111) I_{2-} (112) I_{2-} (112) I_{2-} (113) I_{2-} (114) I_{2-} (114) I_{2-} (115) I_{2-} (116) I_{2-} (116) I_{2-} (116) I_{2-} (117) I_{2-} (117) I_{2-} (118) I_{2-} (119) I_{2-} (119) I_{2-} (119) I_{2-} (119) I_{2-} (111) I_{2-

;

[For density of \ddot{C} at 0°, 15°, 25°, 50°, and 65°, together with parachors at 0°, 25°, 50°, and 75°, see (9).]

[For prepn. of \tilde{C} from corresp. alc., dimethyl-n-propyl-carbinol (2-methylpentanol-2) (1:6190) with PCl₅ (6), with HCl gas (1) (2), or with conc. HCl (4) (5) see indic. refs.; for prepn. (68% yield) from ethyl-isopropyl-carbinol (2-methylpentanol-3) (1:6194) with HCl as the result of rearrangement see (1); for formn. (together with other products) from reaction of 2-ethylbutanol-1 (1:6223) with HCl + ZnCl₂ see (3); for formn. from 2-methylpentene-2 (1:8275) by addn. of HCl see (7) (8).]

[For study of rate of reaction with KI in acetone see (5).]

Č with Mg in dry ether yields RMgCl; upon treatment with oxygen this gives (48% yield (1)) of dimethyl-n-propyl-carbinol (2-methylpentanol-2) (1:6190) q.v.

- Dimethyl-n-propyl-acetanilide: m.p. 70.5-74° (3). [From C via conversion to RMgCl and reaction with phenyl isocyanate (3).]
- **Dimethyl-n-propyl-acet-\alpha-naphthalide:** m.p. 116-118° (3). [From \tilde{C} via conversion to RMgCl and reaction with α -naphthyl isocyanate (3).]
- 3:7490 (1) Whitmore, Johnston, J. Am. Chem. Soc. 60, 2266 (1938). (2) Schreiner, J. prakt. Chem. (2) 82, 292-293 (1910). (3) Whitmore, Karnatz, J. Am. Chem. Soc. 60, 2534 (1938). (4) Deschamps, J. Am. Chem. Soc. 42, 2672 (1920). (5) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925). (6) Butlerow, Bull. soc. chim. (2) 5, 23-24 (1866). (7) Nasarow, Ber. 70, 613 (1937). (8) Nasarow, Ber. 70, 622 (1937). (9) Quayle, Owen, Beavers, J. Am. Chem. Soc. 61, 3107-3111 (1939).

3: 7495 d,l-4-CHLORO-2-METHYLPENTANE
$$C_6H_{13}Cl$$
 Beil. I — $(d,l$ -Isobutyl-methyl-carbinyl CH_3 H I_1 — chloride) CH_2 — C — CH_2 — C — CH_3 H I_2 -(111)

B.P. 111-112° at 773 mm. (1)
$$D_4^{20} = 0.861$$
 (1) $n_D^{20} = 1.4113$ (1)

[For prepn. of \bar{C} from 2-methylpentanol-4 (1:6199) with dry HCl for 18 weeks (82% yield) see (1); for formn. of \bar{C} (together with other products) in reaction of 2-ethylbutanol-1 (1:6223) with HCl + ZnCl₂ see (2).]

 \ddot{C} with Mg in dry ether yields RMgCl which with O₂ gives (62% yield (1)) 2-methylpentanol-4 (1:6199) [N-(α -naphthyl)carbamate, m.p. 93.5-94.5° (2)]; this alc. upon oxidn. with CrO₃/H₂SO₄ yields (2) 4-methylpentanone-2 (1:5430) q.v.

3:7495 (1) Whitmore, Johnston, J. Am. Chem. Soc. 60, 2267 (1938). (2) Whitmore, Karnatz, J. Am. Chem. Soc. 60, 2535 (1938).

CHAPTER XVII

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 2. D_4^{20} less than 1.1500

(3:7500-3:7999)

B.P. 109-114° sl. dec. (1)

[For prepn. of \ddot{C} from 2-methylpenten-4-ol-2 (allyl-dimethyl-carbinol) [Beil. I-445, I₂-(487)] with PCl₅ see (1).]

3:7500 (1) M. Saytzeff, A. Saytzeff, Ann. 185, 156 (1877).

3: 7520 1-CHLORO-2,3-DIMETHYLBUTENE-2
$$C_6H_{11}Cl$$
 Beil. S.N. 11 $(\beta,\gamma,\gamma$ -Trimethylallyl chloride) CH_3 CH_3

B.P. 111-112° at 756 mm. (1)
$$D_4^{19} = 0.8895$$
 (1) $n_C^{19} = 1.4315$ (1)

Note. \bar{C} by virtue of allylic transposition would be expected to be in equilibrium with its synionic isomer 3-chloro-2,3-dimethylbutene-1(α,α,β -trimethylallyl chloride). The material described by (1) was regarded as \bar{C} ; the isomer seems to be unrecorded.

[For prepn. of \tilde{C} (or its mixt. with 3-chloro-2,3-dimethylbutene-1) in 90% yield from 2,3-dimethylbutene-2 (tetramethylethylene) (1:8290) with Cl₂ + NaHCO₃ at 0° see (1).]

 $\ddot{\mathbf{C}}$ on hydrolysis yields (1) a hexenol (regarded (1) as 2,3-dimethylbuten-1-ol-3 derived from the synionic isomer of $\ddot{\mathbf{C}}$), b.p. 116-118°, $D_4^{17}=0.835$, $n_{\ddot{\mathbf{C}}}^{17}=1.4248$ (1).

3:7520 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4222; C.A. 33, 4190 (1939).

3: 7525
$$\alpha$$
-CHLOROETHYL n -PROPYL ETHER $C_5H_{11}OCl$ Beil. I - 607 H_1 I_1 — I_2 — CH_3 . C.O. n -C $_3H_7$ Cl Cl B.P. 112–115° at 731 mm. (1) $D_4^{20} = 0.9322$ (2) $n_D^{20} = 1.4013$ (2)

47.5° cor. at 40 mm. (2)

C decomposes considerably if distd. at ord. press. (3).

[For prepn. (93% yield (2)) from paraldehyde (1:0170) + n-propyl alc. (1:6150) + dry HCl see (2) (3).]

C on stdg. polymerizes to dark tarry residue (2).

 $|\tilde{C}|$ on bromination yields α,β -dibromoethyl n-propyl ether (3).

 \overline{C} on shaking with aq. yields acetaldehyde (1:0100), n-propyl alc. (1:6150) + HCl.

3:7525 (1) Gauthier, Ann. chim. (8) 16, 312 (1909). (2) Henze, Murchison, J. Am. Chem. Soc. 53, 4077-4079 (1931). (3) Dykstra, Lewis, Boord, J. Am. Chem. Soc. 52, 3399-3400 (1930).

3:7530 2-CHLOROHEXENE-1 Cl
$$C_6H_{11}Cl$$
 Beil. S.N. 11 $CH_3.CH_2.CH_2.CH_2-CH_2$

B.P.

113° at 740 mm. (1)
$$D_4^{25} = 0.8886$$
 (1) $n_D^{25} = 1.4278$ (1) $109.5-110.5$ ° at 735 mm. (2) 0.8872 (2) 1.4187 (2)

[For prepn. of \tilde{C} from hexyne-1 (1:8055) with dry HCl + BiCl₃ in C₆H₆ (20% yield {1}) together with 40% yield 2,2-dichlorohexane (3:9342)) or with AcCl + SnCl₄ (15% yield {2}) together with 37% 4-chloro-octen-3-one-2, b.p. 75-95° at 20 mm.) sec {1} (2); for prepn. of \tilde{C} (60.5% yield {1}) from 2,2-dichlorohexane (3:9342) with KOH in *n*-propyl alc. at 95° sec {1}.]

 \tilde{C} in CCl₄ + SbCl₅ treated with Cl₂ at 35-40° gives (1) (3) cis-1,2-dichlorohexene-1 (3:9330) (26.7% yield (1)) together with 25.4% 1,1,2,2-tetrachlorohexene (3:9332).

3:7530 (1) Hennion, Walsh, J. Am. Chem. Soc. 62, 1367-1368 (1940). (2) Kroeger, Sowa, Nieuwland, J. Org. Chem. 1, 163-169 (1936). (3) Norris, Hennion, J. Am. Chem. Soc. 62, 450 (1940).

B.P. 113.0-113.5° at 748 mm. (1)
$$D_4^{25} = 0.8898$$
 (1) $n_D^{25} = 1.4320$ (1)

Two geom. stereoisomers of \ddot{C} are possible, but only this one is as yet recognized. [For prepn. of \ddot{C} from hexyne-3 (diethylacetylene) (1:8065) with AcCl + SnCl₄ see (1); (both *cis* and *trans* stereoisomers of 4-chloro-3-ethylhexen-3-one-2 are also formed).

3:7535 (1) Kroeger, Sowa, Nieuwland, J. Org. Chem. 1, 163-169 (1936).

3:7540
$$n$$
-PROPYL CHLOROFORMATE $C_4H_7O_2Cl$ Beil. III - 11 $(n$ -Propyl chlorocarbonate) n -C $_8H_7$.O.CO Cl III $_2$ -(10)

B.P. 114-115.5° at 768 mm. (1)
$$D_4^{20} = 1.0901$$
 (1) $n_D^{20} = 1.40350$ (4) 115.2 cor. (2) (3)

 \tilde{C} reacts but slowly with cold aq., more rapidly on warming, yielding *n*-propyl alc. $(1:6150) + CO_2 + HCl$.

[For prepn. from n-propyl alc. (1:6150) + phosgene (3:5000) (42% yield (3)) see (2) (3).]

 \overline{C} on htg. with ZnCl₂ yields (5) propylene, CO₂, + HCl; \overline{C} on warming with pyridine or quinoline dec. at 66° into *n*-propyl chloride (3:7040) + CO₂ (6) cf. (7).

- ① n-Propyl N-phenylcarbamate (n-propyl carbanilate) [Beil. XII-321]: from Č + excess aniline in ether, cryst. from alc., m.p. 57-59° (8).
- 3:7540 (1) Karvonen, Ann. Acad. Sci Fennicae A-10, No. 4, 19 (1916); Cent. 1919, III 808. (2) Roese, Ann. 205, 227-230 (1880) (3) Hamilton, Sly, J. Am. Chem. Soc. 47, 436-437 (1925).
- (4) Dobrosserdow, Cent. 1911, I 954. (5) Underwood, Baril, J. Am. Chem. Soc. 53, 2201 (1931).
- (6) Carré, Bull. soc. chim. (5) 3, 1069 (1936). (7) Fry, J. Am. Chem. Soc. 36, 260-261 (1914).
- (8) Roemer, Ber. 6, 1103 (1878).

114°

113-115°

3: 7545 CHLOROCYCLOPENTANE (Cyclopentyl chloride)
$$H_2C - CH_2$$
 $H_2C - CH_2$ $H_3C - CH_3$ $H_3C -$

[For prepn. of \bar{C} from cyclopentanol (1:6412) with boilg. conc. HCl + CaCl₂ (87% yield (5)) (6), or with conc. HCl at 110° (87% yield (2)) (1) (7) (8), or with PCl₃ at 0° (3) (4) see indic. refs.] [Some cyclopentene (1:8037), b.p. 34°, may also be formed but is readily sepd. by distn.] [For prepn. of \bar{C} from cyclopentane (1:8400) with Cl₂ see (13).]

C over BaCl₂ at 300-400° at 15-20 mm. yields (9) cyclopentene (1:8037).

(4)

[\bar{C} with C_6H_6 + AlCl₃ gives (54% yield (10)) phenylcyclopentane (cyclopentylbenzene), b.p. 217°, D_4^{20} = 0.9474, n_D^{10} = 1.5280 (10); for reactn. of \bar{C} with 2-methylpyridine (α -picoline) see (11); for reactn. of \bar{C} with Na₂SO₃ at 200° see (4).]

 \tilde{C} with Mg in dry ether gives (1) (2) (5) (7) cyclopentyl MgCl; this with CO₂ gives (1) (7) cyclopentancearboxylic acid [Beil. IX-6], b.p. 215 5-216° cor., $D_4^{20} = 1.0510$, $n_D^{18} = 1.4534$ (1) (amide, lfts. from MeOH, m.p. 179° cor. (1), 178° (12)).

- © Cyclopentyl mercuric chloride C₅H₉HgCl: m.p. 108.5° (4). [The method of formn. of this deriv. is not stated but is presumably from RMgCl + HgCl₂.]
- 3:7545 (1) Zelinskiĭ, Ber. 41, 2627-2628 (1908). (2) Zelinskiĭ, Mikhlina, Eventova, Ber. 66, 1422-1426 (1933). (3) Kohlrausch, Reitz, Stockman, Z physik. Chem. B-32, 235 (1936). (4) Turkiewicz, Pilat, Ber. 71, 284-285 (1938). (5) Pilat, Turkiewicz, Ber. 72, 1527-1531 (1939). (6) Yarnall, Wallis, J. Org. Chem. 4, 287 (1939). (7) Neunhoffer, Schluter, Ann. 526, 70 (1936). (8) Canals, Mousseron, Granger, Gastaud, Bull. soc. chim. (5) 4, 2048 (1937). (9) Badische Anilin u. Sodafabrik, Ger. 255,538, Jan. 3, 1913, Cent. 1913, I 477. (10) Zelinskiĭ, Titz, Ber. 64, 185 (1931).
- (11) Tschitschibabine, Bull. soc. chim. (5) 5, 435 (1938). (12) Nenitzescu, Cantuniari, Ber. 65, 811 (1932). (13) Bailey, McAllister (to Shell Development Co.), U.S. 2,342,072, Feb. 15, 1944; C.A. 38, 4621 (1944).

3: 7550 1,1-DICHLOROBUTANE (
$$n$$
-Butylidene (n -Butylidene (

[For prepn. (47% yield (4)) from n-butyraldehyde (1:0130) by actn. of PCl₆ (39% yield (9)) see (4) (2) (3) (9); for formn. from butane by chlorination see (5) (6); for formn. from n-butyl chloride (3:7160) on chlorination see (7) (8).]

(3) (7)

[Č on passing over alkali (NaOH, K₂CO₃, soda-lime, etc.) at elevated temperatures (e.g., 700-750°) yields (6) butadiene-1,3.]

[C with boilg. satd. n-BuOH/KOH loses 1 HCl giving (64% yield (9)) 1-chlorobutene-1 (3:7110).]

3:7559 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4223. (2) Kohlrausch, Köppl, Monatsh. 65, 197 (1935). (3) Meyer, Petrenko-Kritschenko, Ber. 25, 3308 (1892). (4) Henne, Renoll, Leicester, J. Am. Chem. Soc. 61, 940 (1939). (5) Muskat (to du Pont), U.S. 2,038,593, April 28, 1936; Cent. 1936, II 3358. (6) Muskat (to du Pont), U.S. 2,070,609, Feb. 16, 1937; Cent. 1937, II 2597. (7) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 893-896 (1937); C.A. 31, 5755 (1937); Cent. 1938, II 2575. (8) Muskat, Northrup, J. Am. Chem. Soc. 52, 4050-4052 (1930). (9) Henne, Hinkamp, J. Am. Chem. Soc. 67, 1197 (1945).

B.P.
$$115^{\circ}$$
 (1) (2) $D_{2}^{20} = 0.8670$ (2) $n_{\rm D}^{20} = 1.4161$ (1) 41° at 50 mm. (2) (3) 1.4160 (2) (3)

[For prepn. of C (60% yield) from corresp. alc. (neopentylcarbinol) (1:6219) with SOCl₂ + pyridine see (1); for prepn. of C from *ter*-butyl chloride (3:7045) + ethylene in presence of AlCl₃ (75% yield), FeCl₃ (57% yield), or BiCl₃ (6-30% yield) see (2).]

 \ddot{C} with Mg + dry ether yields RMgCl which with oxygen yields (1) (2) neopentylcarbinol (1:6219) q.v.

- Neopentylcarbinyl mercuric chloride (C₆H₁₃HgCl): m.p. 133-133.5° (1). [From RMgCl + HgCl₂ (1).]
- Φ γ,γ-Dimethyl-n-valeranilide: ndls. from dil. alc., m.p. 138-139° (2). [From C via conversion to RMgCl and reaction with phenyl isocyanate (2).]
- 3:7555 (1) Whitmore, Bernstein, J. Am. Chem. Soc. 60, 2626-2628 (1938). (2) Schmerling, J. Am. Chem. Soc. 67, 1152-1154 (1945). (3) Schmerling, J. Am. Chem. Soc. 67, 1782-1783 (1945).

C₅H₉OCi

0.9844 (1)

Beil. II - 315

1.41488 (1)

114.3-115.7° (4) 114.5-115.5° (5) 113.5-114.5° at 725.7 mm. (6)

3:7560 ISOVALERYL CHLORIDE

[For prepn. of \tilde{C} from isovaleric acid (1:1050) with PCl₃ (7) (8) (9), with PCl₃ + ZnCl₂ (79% yield (10)), with SOCl₂ (72% yield (10)) (1) (5) see indic. refs.; note that use of PCl₅ is inadvisable since the by-prod., POCl₅, boils too close to \tilde{C} .]

[Č htd. with K isovalerate yields (11) isovaleric anhydride [Beil. II-314, II₁-(137), II₂-(277)], b.p. 215.1-215.3° at 762 mm., 102-103° at 15 mm. (11), $D_{4j}^{20} = 0.9327$, $n_{D}^{20} = 1.4043$ (12).]

[\bar{C} with Cl₂ in CCl₄ yields (8) α -chloroisovaleryl chloride (3:8144), b.p. 148–149° (together with some β -chloroisovaleryl chloride).]

[C on cat. hydrogenation using Pd as specified (13) gives 95% yield isovaleraldehyde (1:0140), b.p. 92° (13) (use of PtO₂ gives (14) only small yield).]

[For reactn. of \bar{C} with acetylene + AlCl₃ in pet. eth. at 0-5°, yielding on treatment with aq. β -chlorovinyl isobutyl ketone, b.p. 63-65°, see (15); with cyclohexene + AlCl₃ in cyclohexane yielding cyclohexyl isobutyl ketone, b.p. 216-219°, $D_4^{20} = 0.8867$, $n_D^{20} = 1.58155$, see (16); with sodium azide in benzene yielding isobutyl isocyanate see (17).]

 \bar{C} on hydrolysis yields isovaleric acid (1:1050), b.p. 176.5°. — For the amide, anilide, p-toluidide, and other derivs. corresp. to \bar{C} see isovaleric acid (1:1050).

3:7560 (1) Leimu, Ber. 70, 1049 (1937). (2) von Auwers, Schmidt, Ber. 46, 474 (1913). (3) Martin, Partington, J. Chem. Soc. 1936, 162. (4) Kohlrausch, Pongratz, Z. physik. Chem. B-22, 382 (1933). (5) Bardan, Cent. 1932, II 354. (6) Bruhl, Ann. 203, 24 (1880). (7) Béchamp, Jahresber. 1856, 429. (8) Michael, Ber. 34, 4055-4056 (1901). (9) Scheuble, Ger. 251,806, Oct. 8, 1912; Cent. 1912, II 1503. (10) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III, 97-103 (1933).

(11) Verkade, Rec. trav. chim. 36, 197 (1916). (12) Tromp, Rec. trav. chim. 41, 299 (1921). (13) Froschl, Danoff, J. prakt. Chem. (2) 144, 221-222 (1935). (14) Grignard, Mingasson, Compt. rend. 185, 1176 (1927). (15) Nelles, Baeyer (to I.G.), Brit. 461,080, March 11, 1937; Ger. 642,147, Feb. 25, 1937; Cent. 1937, II 2597; C.A. 31, 4676 (1937). (16) Nenitzescu, Cioranescu, Ber. 69, 1823 (1936). (17) Naegeli, Grüntuch, Lendorff, Helv. Chim. Acta 12, 247-248 (1929).

3: 7563 ·
$$d$$
, l -1-CHLORO-2-METHYLPENTANE $C_0H_{13}Cl$ Beil. I — CH_3 Cl I_1 — I_2 — CH_3 CH_4 CH_5 CH_5 CH_5 CH_5 CH_6 CH_7 CH_8 CH_8 CH_8 CH_8 CH_8 CH_9 CH_9

B.P. 110-120° (1)

[For prepn. of Č from levorotatory 2-methylpentanol-1 with PCl₅ in CHCl₃ or from dextrorotatory 2-methylamylamine with NOCl see (1).]

3:7563 (1) Levene, Mikesa, J. Biol. Chem. 84, 579-580 (1929).

3:7565 d,l-3-CHLORO-2-METHYLPENTANE
$$C_6H_{13}Cl$$
 Beil. I - 148 (Ethyl-isopropyl-carbinyl chloride) Cl CH_3 I_1 —

$$CH_3.CH_2-C$$
 C CH_3 I_2 -(111)

B.P. 115-116.5° dec. at 752 mm. (1)

[For prepn. of C from 2-methylpentanol-3 (1:6194) with PCl₅ see (1).]

3:7565 (1) Grigorowitsch, Pavlov, J. Russ. Phys.-Chem. Soc. 23, 166 (1891).

3:7585

3: 7580 meso-2,3-DICHLOROBUTANE
$$C_4H_8Cl_2$$
 Beil. I — (meso-\$\beta\$-Butylene dichloride) CH_3 — CH — CH — CH_3 I — I2-(82)

B.P. F.P.

116.0° (1) (2) -80.4 ° (1) $D_4^{25} = 1.1023$ (6)
115.9° at 760 mm. (3) $n_D^{25} = 1.4395$ (6)
115.5-116.5° cor. at 746 mm. (4) 1.4392 (6)
114-116° (5) 1.4386 (6)
113.14° at 746 mm. (6) 1.4385 (6)
49.52° at 80 mm. (6) $D_4^{20} = 1.1134$ (5)
49.0-50.5° at 80 mm. (7) 1.1067 (2)
49.4-49.7° at 80 mm. (6) $n_D^{20} = 1.4413$ (2)
48.5-49.0° at 80 mm. (6) 1.443 (5)

[See also d,l-2,3-dichlorobutane (3:7615).]

[For prepn. of $\bar{\mathbb{C}}$ from trans-butene-2 with Cl₂ in light (63% yield (6)) (7) cf. (5) indic. refs.; for formn of $\bar{\mathbb{C}}$ from d,l-erythro-3-chlorobutanol-2 (3:8004) (16% yield (6)) or from (+) threo-3-chlorobutanol-2 (3:8002) (15% yield (6)) with SOCl₂ see (6) (note that from d,l-erythro-3-chlorobutanol-2 with PCl₅ in CHCl₃ a mixt. of $\bar{\mathbb{C}}$ + its d,l-isomer (3:7615) is obtd. (6)); for formn. of $\bar{\mathbb{C}}$ from d,l-2-chlorobutane (3:7125) with Cl₂ in light (42.7% yield) see (2).]

[\bar{C} with Cl₂ (slight excess) in dark at -17° gives (5) 36.5% 1,2,3-trichlorobutane (3:5935) + 18% 2,2,3-trichlorobutane (3:5680).]

[\bar{C} with alc. KOH gives same results as does the d,l-isomer (3:7615) (3).]

3-CHLORO-3-METHYLPENTANE

(Diethyl-methyl-carbinyl chloride)

Timmermans, Bull. soc. chim. Belg. 36, 504 (1927). (2) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 663-666 (1937); Cent. 1937, II 372, C.A. 31, 5754 (1937). (3) Navez, Bull. soc. chim. Belg. 39, 435-439 (1930). (4) Lucas, Simpson, Carter, J. Am. Chem. Soc. 47, 1467 (1925). (5) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 6, 1553-1558 (1936); Cent. 1937, I 3785; C.A. 31, 2165 (1937). (6) Lucas, Gould, J. Am. Chem. Soc. 63, 2541-2545 (1941).
 Taufen, Murray, Cleveland, J. Am. Chem. Soc. 65, 1131-1132 (1943).

C₆H₁₃Cl

CH₃

Beil. I - 149

 I_{1} -(**54**)

[For density of \bar{C} at 0°, 15°, 25°, 50°, and 65° together with parachors at 0°, 25°, and 50° see (9).]

[For prepn. of C from corresp. alc., diethyl-methyl-carbinol (3-methylpentanol-3) (1:6189), with PCl₅ (8), HCl gas (1) (2) at 0° (5) or 10-15° (59% yield (7)) see indic. refs.;

with diphosgene (3:5515) see (4); for formn. from 3-methylpentene-2 (1:8260) + conc. HCl see (3); for formn. (together with other products) during reaction of 2-ethylbutanol-1 (1:6223) with HCl + ZnCl_2 see (6).]

C with Mg in dry ether yields (7) corresp. RMgCl.

Diethyl-methyl-acetanilide: m.p. 86.5-88.5° (6). [From C via conversion to RMgCl and reaction with phenyl isocyanate (6).]

3:7585 (1) Schreiner, J. prakt. Chem. (2) 82, 295 (1910). (2) Gilman, Schulze, J. Am. Chem. Soc. 49, 2330 (1927). (3) Nasarow, Ber. 70, 621 (1937). (4) Nekrassow, Melnikow, J. prakt. Chem. (2) 127, 217-218 (1930). (5) Favorskii, Zalesskii-Kibardine, Bull. soc. chim. (4) 37, 1230 (1925). (6) Whitmore, Karnatz, J. Am. Chem. Soc. 60, 2535 (1938). (7) Whitmore, Badertscher, J. Am. Chem. Soc. 55, 1561 (1933). (8) Butlerow, Bull. soc. chim. (2) 5, 23-24 (1866).
 (9) Quayle, Owen, Beavers, J. Am. Chem. Soc. 61, 3107-3111 (1939).

3:7590 1-CHLORO-2,2-DIMETHYLBUTANE
$$CH_3$$
 $C_6H_{13}Cl$ Beil. S.N. 10 (ter-Amyl-carbinyl chloride; neohexyl chloride) CH_3 — CH_2 — CH_2 CH_3 Cl

B.P. 116.1° at 735 mm. (1)
$$n_{\rm D}^{20} = 1.4200$$
 (1) $113.5-115^{\circ}$ (2) 1.4190 (2)

[For prepn. of \bar{C} from 2,2-dimethylbutane (neohexane) (1:8510) with Cl_2 in the cold see (2).]

[Č with Na yields (1) a mixt. of 4 compounds: 11.8% 1,1,2-trimethylcyclopropane, b.p. $56.5-57^{\circ}$ at 735 mm., $D_{-}^{20} = 0.6967$, $n_{0}^{20} = 1.3880$; 7.8% 2,2-dimethylbutene-3 (ter-butylethylene) (1:8225); 27.1% 2,2-dimethylbutane (neohexane) (1:8510); and 4.3% normal coupling prod., 3,3,6,6-tetramethyloctane, b.p. 125° at 140 mm., $n_{0}^{20} = 1.423$.]

3:7590 (1) Whitmore, Carney, J. Am. Chem. Soc. **63**, 2633-2635 (1941). (2) Whitmore, Bernstein, Mixon, J. Am. Chem. Soc. **60**, 2539 (1938).

3: 7595
$$\alpha,\alpha'$$
-DICHLORODIETHYL ETHER Cl C₄H₈OCl₂ Beil, I - 607 (bis-(α -Chloroethyl) ether) CH₃—CH CH₃—CH

B.P. 116-147° (1) (2)
$$D_4^{25} = 1.106$$
 (3) $n_D^{25} = 1.4186$ (3) $112.5-114$ ° (3)

Colorless liq. at first immiscible with aq. but grad. hydrolyzing (especially on warming) to acetaldehyde (1:0100) and HCl (1) (2).

[For prepn. of C from acetaldehyde (1:0100) with dry HCl gas see (2) (1).]

For identification hydrolyze \tilde{C} to acetaldehyde (1:0100) (3), derivatize the latter, e.g., via the p-nitro- or 2,4-dinitrophenylhydrazones.

3:7595 (1) Lieben, Ann. 106, 337 (1858). (2) Geuther, Laatsch, Ann. 218, 16-18 (1883). (3) Gebauer-Fuelnegg, Moffett, J. Am. Chem. Soc. 56, 2009 (1934).

B.P. 117.2° (1)
$$D_4^{20} = 1.0083 (1)$$
 $n_D^{20} = 1.42044 (1)$

[For prepn. of \bar{C} from 2-methylbutanone-3 (isopropyl methyl ketone) (1:5410) with SO₂Cl₂ in cold (84% yield (1)) or with Cl₂ by vapor-phase chlorination (2) see indic. refs.] \bar{C} with 20% aq. Na₂CO₃ refluxed for 37 hrs. gives (1) 2-methylbutanon-3-ol-2 [Beil. I-832, I₁-(422), I₂-(873)], b.p. 143° (1).

Č with 40% aq. NaOH refluxed 20 hrs. gives (1) trimethylacetic acid (1:0410), b.p. 163°, m.p. 35° (1) (note structural change during this reaction).

 \bar{C} with aq. KCN in cold for 1 hr. gives (1) 2,3-dimethyl-2,3-epoxy-*n*-butyronitrile, b.p. 157.8° at 747 mm., $D_4^{20} = 0.9314$, $n_D^{20} = 1.41334$ (1).

3:7597 (1) Delbaere, Bull. soc. chim. Belg. 51, 1-10 (1942); Cent. 1942, II 763-764; C.A. 37, 5018 (1943). (2) Justoni, Chimica e industria (Italy) 24, 195-201 (1942); Cent. 1943, I 1659.

3:7598 d,l-3-CHLOROBUTANONE-2 H
$$C_4H_7OCl$$
 Beil. I - 669 (α -Chloroethyl methyl ketone) CH_3 C

B.P.			B.P. (cc	ntd.)		
117-119° (1)	at 760 mm.	(8)	49-50°	at 70 mm.	(6)	$D_{-}^{0} = 1.032 (5) (15)$
114-117°	at 760 mm.	(2)	46°	at 40 mm.	(10)	
116-117°		(3)	32°	at 40 mm.	(4)	
116°	at 770 mm.	(4)	40-41°	at 30 mm.	(2)	
115°	at 758 mm.	(5) (15)	33-34°	at 30 mm.	(7)	
115°		(6)	26°	at 18 mm.	(4)	
114-115°		(7) (16)				
114°		(9)				

[See also 1-chlorobutanone-2 (3:8012).]

Liquid with penetrating odor. - Insol. aq., eas. sol. alc., ether.

[For prepn. of $\bar{\mathbb{C}}$ from ethyl methyl ketone (butanone-2) (1:5405) with $\mathbb{C}l_2$ in pres. of $\mathbb{C}a\mathbb{C}O_3$ + aq. (yields of $\bar{\mathbb{C}}$ about 75% always accompanied by 25% of the isomeric 1-chlorobutanone-2 (3:8012)) see (2) (6) (7) (10) cf. (11); with $\mathbb{C}l_2$ as vapor-phase chlorination see (12) (13) (14); with $\mathbb{C}l_2$ diluted with dry $\mathbb{C}O_2$ see (15) (4); with $\mathbb{C}l_2$ in sunlight see (5) (16); with $\mathbb{S}O_2\mathbb{C}l_2$ in sunlight see (5) (16) (17) cf. (11); with N-chlorourea in dil. AcOH see (1) (8); for prepn. of $\bar{\mathbb{C}}$ from acetyl chloride (3:7065) with ethylene over activated carbon at 100° and 50 atm. see (18) (note that acetyl chloride + ethylene $+ AlCl_3$ at 0° gives 4-chlorobutanone-2 (3:7640) q.v.); for prepn. of $\bar{\mathbb{C}}$ from 2-chlorobutene-2 (3:7105) with $\mathbb{C}l_2$ + aq. + $\mathbb{C}Cl_4$ (65% yield) see (3).]

[\bar{C} on reduction using yeast (20) gives levorotatory 3-chlorobutanol-2, b.p. 139° (cf. 3:8000), but with Zn + HCl (15) \bar{C} yields butanone-2 (1:5405).]

 \bar{C} on oxidn. with conc. HNO₃ (5) (16) (20) yields α -chloropropionic acid (3:6125).

Č on hydrolysis with aq. in s.t. at 150° for 6–8 hrs. (15), or Č with alc. alk. (15) or MeOH/ KOH (21) in cold, gives (84% yield (21)) butanone-2-ol-3 (acetyl-methyl-carbinol) (acetoin) (1:5448) (as consequence of latter reactn. Č reduces Tollens' reagt. or Fehling's soln. in cold).

C with satd. aq. NaHSO3 soln. yields (15) a NaHSO3 addn. cpd.

[\bar{C} with conc. aq. KCN at 0° for 1 hr. gives (80% yield (21)) 2,3-epoxy-2-methyl-n-butyronitrile (α -cyano- α , β -dimethyl-ethylene oxide), b.p. 145°, $D_4^{20}=0.9540$, $n_D^{20}=1.4079$ (21); \bar{C} with alc. KCN gives (21) a mixt. consisting mainly of the above prod. together with a little α -methylacetoacetonitrile [Beil. III₂-(433)], b.p. 182–184° at 745 mm. with slight decompn. (22), b.p. 78° at 19 mm. (22), 68–70° at 12 mm. (23). (Note that the above represents a correction of the earlier views (5) (16) (24).)]

[Č with conc. aq. (NH₄)₂SO₃ at 70° yields (9) butanone-2-sulfonic acid-3.—Č with NaN₃ in aq. contg. AcOH yields (10) 3-azidobutanone-2, oil, b.p. 46° at 2 mm.]

[C with Na in abs. ether gives (15) by bimolecular coupling 3,4-dimethylhexanedione-2,5 [Beil. I-798, I₁-(409), I₂-(847)], b.p. 210° (15), 82° at 11 mm.; note therefore that sodium must not be used for drying C cf. (24).]

[\bar{C} with triethyl orthoformate (1:3241) in abs. alc. in pres. of NH₄Cl as cat. gives (70% yield in 10 days but in absence of NH₄Cl only 39% (24)) α -chloroethyl methyl ketone diethylacetal, b.p. 80–84° at 36 mm., $D_4^{20}=0.9773$ (24).]

[C with ethyl sodio-acetoacetate in abs. ether (4) or abs. alc. (25) (26) (24) gives (yields: 45-60% (24), 27-28% (26)) the expected ethyl α,β -diaceto-n-butyrate [Beil. III-757, III₁-(265), III₂-(468)], b.p. 150° at 28 mm. (25), 121-124° at 11 mm. (26). — C with ethyl acetoacetate (1:1710) + aq. NH40H + NH₃ gas htd. for 1 hr. gives (26% yield (4)) 3-carbethoxy-2,4,5-trimethylpyrrole [Beil. XXII-31, XXII₁-(497)], yel. cryst. from alc. or pet. eth., m.p. 101.5-102.5° (4), 104-105° (27), also obtd. from the above ethyl α,β -diaceto-n-butyrate with conc. aq. NH₄0H on warming (4). — C with methyl acetoacetate (1:1705) + conc. aq. NH₄0H in the cold gives (4) methyl β -aminocorotonate, m.p. 82-84° (4), which only on htg. condenses with the ester to give 3-carbomethoxy-2,4,5-trimethyl-pyrrole [Beil. XXII-31], cryst. from dil. alc., m.p. 124.5-126° (4). — C with methyl acetoacetate (1:1705) + CH₃NH₂ (33% in aq.) refluxed for some hours gives only very small yield (28) of 3-carbomethoxy-1,2,4,5-tetramethylpyrrole, cryst. from lgr., m.p. 101° (28).]

[C with diethyl acetonedicarboxylate (1:1772) in dry ether at -15° treated with NH₃ gas gives (10.7% yield (29)) 2-carbethoxymethyl-3-carbethoxy-4,5-dimethylfuran, b.p. 110-115° at 0.2 mm. (29).]

[For condens. of C with various phenols and phenol ethers see (30).]

[C with alc. NH₃ gives (15) in the cold the difficultly isolatable 3-aminobutanone [Beil. IV-319, IV₁-(452)], but on warming this condenses bimolecularly yielding (15) (8) tetramethylpyrazine [Beil. XXIII-99, XXIII₁-(28)], ndls. with 3H₂O from aq., m.p. 74-77°, but aq. lost in desic. to anhydrous prod., m.p. 86° (8) (corresp. picrate, m.p. 194-195° (31)). — C with aniline (2 moles) gives (15) on refluxing 2,3-dimethylindole [Beil. XX-319, XX₁-(130)], m.p. 107-109° (15).]

[C with thioformamide in abs. alc. for 4 days at 0° gives (22% yield (17)) 4,5-dimethylthiazole, b.p. 81-83° at 59 mm. (17) (corresp. picrate, cryst. from alc., m.p. 186-187° (17)).

— C with NH4 dithiocarbamate in abs. alc. refluxed ½ hr. gives (40% yield (17)) 2-mercapto-4,5-dimethylthiazole, cryst. from EtOAc, m.p. 163.5-163.8° (17). — C with benzamide + powd. CaCO₃ htd. at 110-120° for 10 hrs. gives (24% yield (32)) 4,5-dimethyl-2-phenyl-oxazole [Beil. XXVII₁-(219)], m.p. 50°, b.p. 128-130° at 5 mm. (32). — C with thiobenzamide + NaOAc htd. in abs. alc. gives (65% yield (32)) 4,5-dimethyl-2-phenylthiazole, b.p. 126-128° at 6 mm. (32).]

³⁻Chlorobutanone-2 semicarbazone: m.p. 148°, or on slow htg. 143-145° dec. (33), 127° (1).

3:7598 (1) Béhal, Detoeuf, Compt. rend. 153, 1230 (1911). (2) Kling, Bull. soc. chim. (3) 33, 325-326 (1905); Ann. chim. (8) 5, 537-539 (1905). (3) Groll, Hearne (to Shell Development Corp.), U.S. 2,060,303, Nov. 10, 1936; Cent. 1937, I 4155; C.A. 31, 419 (1937); Brit. 437,573, Nov. 28, 1935; French 787,529, Sept. 24, 1935; Cent. 1936, II 2227. (4) Korschun, Ber. 38, 1125-1129 (1905). (5) van Reymenant, Bull. acad. roy. Belg. 1900, 724-742; Cent. 1901, I 95. (6) Justoni, Chimica e industria (Italy) 24, 89-94 (1942); Cent. 1943, I 383. (7) Blaise, Bull. soc. chim. (4) 15, 733 (1914). (8) Godchot, Mousseron, Bull. soc. chim. (4) 51, 356 (1932). (9) Backer, Strating, Zuithoff, Rec. trav. chim. 55, 761-764 (1936). (10) Forster, Fierz, J. Chem. Soc. 33, 675 (1908).

(11) Kolshorn, Ber. 37, 2474-2475 (1904). (12) Justoni, Chimica e industria (Italy), 24, 195-201 (1942), Cent. 1943, I 1659. (13) Calkins (to B. F. Goodrich Co.), U.S. 2,120,392, June 14, 1938; Cent. 1939, I 251; C.A. 32, 5854 (1938). (14) I.G., French S.I., 131, May 26, 1937; Cent. 1937, II 2071. (15) Démètre-Vladesco, Bull. soc. chim. (3) 6, 404-415, 807-829 (1891). (16) Henry, Bull. acad. roy. Belg. 1900, 57-63, Cent. 1900, I 1123. (17) Buchman, Reims, Sargent, J. Org. Chem. 6, 767-769 (1941). (18) Frolich, Wiezevich (to Standard Oil Dev. Co.), U.S. 2,006,198, June 25, 1935; Cent. 1936, I 2827; C.A. 29, 5457 (1935). (19) Santomauro, Buchem. Z. 151, 49 (1924); Cent. 1924, I 2272. (20) N. V. de Bataafsche Petroleum Maatschappij, French 797,043, May 6, 1936; Cent. 1936, II 865.

(21) Justoni, Gazz. chim. ital. 69, 378-391 (1939); Rend ist. lombardo sci 71, 407-424 (1938); C.A. 34, 3268 (1940). (22) Mohr. J. prakt. Chem. (2) 90, 199-200 (1914). (23) von Braun, Rudolph, Ber. 67, 1770 (1934). (24) Youtz, Perkins, J. Am. Chem. Soc. 51, 3512 (Note 5); 3514 (1929). (25) Korschun, Roll, Gazz. chim. ital. 41, I 188 (1911). (26) Willstatter, Clarke, Ber. 47, 307 (1914). (27) Knorr, Hess, Ber. 44, 2762 (1911). (28) Korschun, Roll, Bull. soc. chim. (4) 33, 1107-1108 (1923). (29) Reichstein, Zschokke, Syz, Helv. Chim. Acta 15, 1115-1116 (1932). (30) Curd, Robinson, J. Chem. Soc. 1933, 714-720, 1178-1179.

(31) Piloty, Ber. 43, 496 (1910). (32) Friedman, Sparks, Adams, J. Am. Chem. Soc. 59, 2263 (1937). (33) Blaise, Bull. soc. chem. (4) 17, 426 (1915).

Note. Much confusion exists in the literature with reference to the relation between Č and 3-chloro-2,2-dimethylbutane (3:7475) q.v. Since the identity of the latter has now been established, it is probable that the chloride obtained from 2,2-dimethylbutanol-3 (ter-butyl-methyl-carbinol) ("pinacolyl alcohol") (1:6186) is Č. In view, however, of modern appreciation of the rearrangements frequently occurring during the formation of alkyl chlorides with HCl, the homogeneity of all recorded samples of Č should be taken with reserve.

[For prepn. of \bar{C} from 2,3-dimethylbutanol-2 (1:6187) with HCl gas (4), with 40% HCl (4), or with AcCl (4), or from 2,3-dimethylbutanol-2 (1:6187) with HCl gas (5), see indic. refs.; for formn. of \bar{C} from 2,3-dimethylbutane (di-isopropyl) (1:8515) with Cl₂ (1) or from 2,3-dimethylbutene-2 (tetramethylethylene) (1:8290) with HCl see (3); for formn. of \bar{C} (23% yield) from ter-butyl chloride (3:7045) + 2,3-dimethylbutane (1.8515) on shaking $\frac{1}{2}$ minute with AlCl₃ see (6).]

Dimethyl-isopropyl-acetamide: m.p. 128° (7), 125-127° (6). [From C via conversion to RMgCl, carbonation to dimethyl-isopropyl-acetic acid, and conversion of latter to amide (6) (7).]

① 2,3-Dibromo-2,3-dimethylbutane: m.p. 173-174° cor. (6), 166-168° (8). [From C with Br2 (6).1

3:7600 (1) Silva, Ber. 7, 953 (1874); Ber. 6, 36 (1873). (2) Aschan, Ber. 31, 1802 (1898). (3) Pavlov, Ann. 196, 124 (1879). (4) Henry, Rec. trav. chim. 25, 147 (1906). (5) Whitmore, Rothrock, J. Am. Chem. Soc. 55, 1107-1108 (1933). (6) Bartlett, Condon, Schneider, J. Am. Chem. Soc. 66, 1533, 1537 (1944). (7) Whitmore, Laughlin, J. Am. Chem. Soc. 55, 3735 (1935) (8) Grosse, Ipatieff, J. Org. Chem. 8, 440-441 (1943)

3: 7603 d,l-
$$\alpha$$
-METHYL- n -BUTYRYL CHLORIDE H C_bH_9OCl Beil. II - 306 (Ethyl-methyl-acetyl chloride) CH_3 -- CH_2 -- C -- C -- C -- C -- U_2 --

B.P. 118.0-118.3° at 761 mm. (1)
$$D_4^{20} = 0.9917$$
 (1) $n_D^{20} = 1.41695$ (1) 115.8-116.6° (2) 115-116° (3)

[The dextrorotatory form of \bar{C} , b.p. 119-120°, $D_4^{24} = 0.990$, $n_D^{17.5} = 1.4177$, has also

[For prepn. of \bar{C} from d,l-2-methylbutanoic acid-1 (1:1105) with SOCl₂ see (1).]

[For actn. of PCl₅ on \bar{C} see (5).]

C with K ethyl-methyl-acetate yields (6) corresp. anhydride, b.p. 103-104° at 17 mm.

 \tilde{C} on hydrolysis yields d,l-ethyl-methyl-acetic acid (1:1105) (for the amide, anilide, p-toluidide, and other derivs, corresp. to \bar{C} see 1:1105).

3:7603 (1) Leimu, Ber. 70, 1049 (1937). (2) Kohlausch, Pongratz, Z. physik. Chem. B-22, 382 (1933). (3) Rupe, Ann. **369**, 338 (1909). (4) Kenyon, Philips, Pittman, J. Chem. Soc. **1935**, 1080. (5) von Braun, Jostes, Munch, Ann. **453**, 146-147 (1927). (6) Verkade, Rec. trav. chim. 36, 203 (1916).

3: 7605 3-CHLORO-2,4-DIMETHYLPENTENE-2
$$C_{7}H_{13}Cl$$
 Beil. I - 221 CH_{3} CH_{4} CH_{5} $CH_{$

B.P. 118-120° (1)
$$D_9^0 = 0.9513$$
 (1)

For prepn. of C from 2.4-dimethylpentanone-3 (di-isopropyl ketone) (isobutyrone) (1:5433) with PCls see (1).

Č with alc. KOH gives (1) 2,4-dimethylpentadiene-2,3 (tetramethylallene) [Beil. I-258, I_{1} -(121)], b.p. 70° (1), 86.5° at 763 mm. [Beil. I_{1} -(121)].

3:7605 (1) Henry, Ber. 8, 400 (1875).

B.P. 118-120° sl. dec. (1)

[For prepn. of C from 2,4-dimethylpentanone-3 (di-isopropyl ketone) (1:5433) with PCl₅ see (1).]

C on distillation loses 1 HCl yielding (1) a chloroolefin C7H13Cl of undetermined structure, but presumably 3-chloro-2,4-dimethylpentene-2.

C on htg. with alc. KOH loses 2 HCl yielding (1) a hydrocarbon C_7H_{12} , b.p. 70°, regarded (1) as 2.4-dimethylpentadiene-2,3 [Beil. I-258, I₁-(121)].

3:7610 (1) Henry, Ber. 8, 400 (1875).

3: 7615
$$d$$
, l -2,3-DICHLOROBUTANE $C_4H_8Cl_2$ $(d$, l - θ -Butylene dichloride) CH_3 — CH — CH — CH_3 I_1 -(38) I_2 -(82) B.P. 119-120° at 760 mm. (1) $D_4^{25} = 1.1063$ (4) $n_D^{25} = 1.4411$ (4) 119.5° at 760 mm. (2) (3) 1.1051 (2) 1.4410 (4) 117.10° at 746 mm. (4) 1.4409 (4) 53.0-53.5° at 81 mm. (5) 1.4405 (4) 53.1-53.4° at 80 mm. (4) 1.4404 (4) 53.16° at 80 mm. (4) 1.4402 (4) 53.0-53.2° at 80 mm. (4) $D_4^{15} = 1.1183$ (2) $D_4^{15} = 1.1183$ (2) $D_D^{15} = 1.4458$ (2)

[See also meso-2,3-dichlorobutane (3:7580).]

52.7-53.5° at 80 mm. (4)

Note that constants on the products of other workers (6) (7) (8) (9) (since they were almost certainly mixts. of C with its meso isomer) are not included above.

[For prepn. of C from cis-butene-2 with Cl₂ in light (80.5% yield (4)) (5) cf. (7) see indic. refs.; for formn. of C from d,l-erythro-3-chlorobutanol-2 (3:8004) or from (+) 3-chlorobutanol-2 with PCl₃ or with SOCl₂ + pyridine see (4); for formn. of C from (+) three-3chlorobutanol-2 (3:8002) with SOCl₂ see (4).]

[For prepn. of ordinary samples of C (probably contg. more or less meso-2,3-dichlorobutane (3:7580)) see the following: for prepn. of ord. C from butene-2 with Cl₂ (8) (9) (10) (11) at -10° (60% yield (12)), at -17° in dark (13), or at 0-5° in dark (89-92% yield (14)), or with $Cl_2 + aq$. (15) see indic. refs.; for form. of \bar{C} from 1-chlorobutane (3:7160) with SbCl₅ on warming see (6) (7); from 2-chlorobutane (3:7125) with Cl₂ in light see (3).]

[For equilibrium consts. of system \bar{C} + aq., 3-chlorobutanol-2 (3:8000) + aq., and ternary system \ddot{C} + 3-chlorobutanol-2 + aq. see (16); for uses of \ddot{C} as industrial solvent see (14).]

[C with Cl₂ (slight excess) in dark at -17° gives (13) 36.5% 1,2,3-trichlorobutane (3:5935) + 18% 2,2,3-trichlorobutane (3:5680).

 $|\bar{C}|$ with alc. KOH (1 mole + 25% excess) refluxed for 3 days loses 1 HCl giving (2) (3) a mixt. of cis + trans 2-chlorobutene-2 (3:7105); note, however, that under certain conditions C with NaOEt not only loses 1 HCl but involves a reaction of the second halogen atom with a second mole of NaOEt thus yielding (17) ethyl α,β -dimethylvinyl ether (2ethoxybutene-2) (accompanied by some butyne-2 (dimethylacetylene)). — \tilde{C} with excess alc. KOH, soda-lime, or diethylaniline (18), or C with aq. vapor at 200-500° over silica gel]+ cat. (19) (20), loses 2 moles HCl yielding (35-38% (20)) butadiene-1,3 (accompanied by 21-25% 2-chlorobutene-2 (3:7105) (20) and 6-8% ethyl methyl ketone (1:5405) (20)); note that in absence of water vapor in this last process \bar{C} yields 2-chlorobutene-2 (3:7105) + butene-2 (20). — \bar{C} over BaCl₂ at 200-300° (24) or with aq. alk. or alk.-earth hydroxides at 118-250° (25) loses 1 HCl giving 2-chlorobutene-2 (3:7105).]

[Č is not (3) hydrolyzed by boilg. aq. K₂CO₃, but Č with aq. Ca (OH)₂ at 75° (21) or with aq. Na₂CO₃ + NaHCO₃ under press. (22) cf. (23) yields butanediol-2,3 (some 2-chlorobutene-2 (3:7105) and ethyl methyl ketone (1:5405) also being formed (22)).]

[Č with p-toluidine (6 moles) at 130-140° for 30 hrs. gives (10) d,l-bis-2,3-(di-p-toluidino)-butane, m.p. 62-63°, + meso-bis-2,3-(di-p-tolylamino) butane, m.p. 57-58°, + 2,7,9-trimethylacridine, m.p. 133-134°; on more protracted htg. or at higher temperature the prods. are mainly or even exclusively 2,7,9-trimethylacridine and di-p-tolylamine, m.p. 79° (from the reagent) (10).]

3:7615 (1) Timmermans, Bull. soc. chim. Belg. 36, 504 (1927). (2) Navez, Bull. soc. chim. 39, 435-443 (1930). (3) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 663-666 (1937); Cent. 1937, II 372; C.A. 31, 5754 (1937). (4) Lucas, Gould, J. Am. Chem. Soc. 63, 2541-2545 (1941). (5) Taufen, Murray, Cleveland, J. Am. Chem. Soc. 65, 1131-1132 (1943). (6) Meyer, Müller, J. prakt. Chem. (2) 46, 186 (1892). (7) Kahovec, Kohlrausch, Z. physik. Chem. B-48, 11 (1940). (8) Sheshukov, J. Russ. Phys.-Chem. Soc. 17, 509 (1885). (9) Briner, Hausser, deLuserna, Helv. Chim. Acta 7, 374-376 (1924). (10) Morgan, Hickinbottom, J. Chem. Soc. 123, 97-105 (1923).

(11) Ruys, Edwards (to Shell Development Co.), U.S. 2,099,231, Nov. 16, 1937; Cent. 1938, I 3387; C.A. 32, 190 (1938). (12) Batalin, Ugryumov, Sintet. Kauchuk 5, No. 6, 8-16 (1936); Cent. 1936, II 3357; C.A. 39, 6701 (1936). (13) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 6, 1553-1558 (1936); Cent. 1937, I 3785; C.A. 31, 2165 (1937). (14) Likhosherstov, Alekseev, Shalaeva, J. Chem. Ind. (Moscow) 12, 705-709 (1935); Cent. 1936, I 3377; C.A. 29, 8174 (1935). (15) Batalin, Ugryumov, J. Gen. Chem. (U.S.S.R.) 4, 871-874 (1935); C.A. 29, 2147 (1935). (16) Bushmakin, Gol'dman, Kuchinskaya, Sintet. Kauchuk 4, No. 1, 33-35 (1935); Cent. 1936, I 1131; C.A. 29, 4248 (1935). (17) I.G., Brit. 332,605, Aug. 21, 1930; Cent. 1936, II 2572; French 684,722, June 30, 1930; Cent. 1930, II 2841; French 38,910, Aug. 10, 1931; Cent. 1933, I 1438. (18) Matthews, Strange, Bliss, Austrian 82,804, Feb. 25, 1921; Cent. 1921, IV 517. (19) Tishchenko, Churbakov, Russ. 52,023, Oct. 31, 1937; Cent. 1938, II 1127; C.A. 34, 1336 (1940). (20) Gutner, Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1729-1735 (1936); Cent. 1937, I 3786; C.A. 31, 4265 (1937).

(21) Chem. Fabrik Schering, Ger. 246,572, May 6, 1912; Cent. 1912, I 1874. (22) Gutner, Shchigel'skaya, J. Gen. Chem. (U.S.S.R.) 7, 1315-1320 (1937); Cent. 1938, I 561; C.A. 31, 6189 (1937). (23) Tishchenko, J. Gen. Chem. (U.S.S.R.) 9, 1380-1388 (1939); C.A. 34, 1611 (1940). (24) Cass, Levine (to du Pont Co.), U.S. 2,323,226, June 29, 1943; C.A. 38, 119 (1944). (25) Cass, Levine (to du Pont Co.), Brit. 549,799, Dec. 8, 1942; C.A. 38, 756 (1944).

3: 7620 1-CHLOROHEXENE-2 $C_6H_{11}Cl$ Beil. S.N. 11 $(\gamma-(n-\text{Propyl})\text{allyl chloride})$

CH₃.CH₂.CH₂.CH=CH.CH₂

B.P. 120-122° at 751 mm. (1) 42-44° at 40 mm. (1)

Two geom. stereoisomers of \bar{C} are possible, but only one is yet recognized. Furthermore \bar{C} by virtue of allylic transposition would be expected to be in equilibrium with its synionic isomer 3-chlorohexene-1 (α -(α -propyl)allyl chloride). The material reported by (1) was regarded as \bar{C} ; the isomer appears to be as yet unrecorded; however, see 3:9334.

[For prepn. of C from hexen-1-ol-3 [Beil. I₂-(485)] with PCl₃ in C₆H₆ see (1).]

[For reactn. of C with sodium phenate in alc. see (1).]

C on cat. hydrogenation gives 1-chlorohexane (3:7955), b.p. 126-127° (1).

Č on hydrolysis with hot aqueous 10 N NaOH for $2\frac{1}{2}$ hrs. yields (1) hexen-1-ol-3, b.p. $54-57^{\circ}$ at 20 mm., $n_D^{25} = 1.4485$ (1).

3:7630 (1) Hurd, McNamee, J. Am. Chem. Soc. 54, 1648-1649 (1932).

B.P.
$$121.5^{\circ}$$
 at 746 mm. (sl. dec.) (1) $D_{15}^{15} = 1.114$ (1) $119-120^{\circ}$ at 740 mm. (2) $119-121^{\circ}$ at 740 mm. (3) $113-116^{\circ}$ at 740 mm. (3) (4)

Note that the same observers have noted (3) two dif. b.p.'s, viz., 119-121° and 113-116° both at 740 mm., on dif. prepns.; this anomaly is still unexplained.

[For prepn. of \bar{C} (75% yield (5)) from paraldehyde (1:0170) + AcCl (3:7065) + trace ZnCl₂ see (5) (1); from acetaldehyde (1:0100) + AcCl (3:7065) at 100° see (6); from vinyl acetate + liq. (3) or gas (7) HCl see (3) (7).]

 $\ddot{\mathbf{C}}$ on htg. with 0.02% ZnCl₂ at 80° yields acetaldehyde (1:0100) + AcCl (3:7065) + paraldehyde (1:0170) (8); $\ddot{\mathbf{C}}$ passed through a tube at 360-380° or over pumice at 250-300° yields acetaldehyde + acetyl chloride (9).

 \bar{C} with aq. slowly hydrolyzes in cold, more rapidly on warming, yielding acetaldehyde (1:0100), AcOH (1:1010), and HCl. [This hydrolysis is accelerated by trace of acid, e.g., N/10 HCl (10).]

3:7625 (1) Franchimont, Rec. trav. chim. 1, 245-246 (1882). (2) Descudé, Compt. rend. 132, 1568 (1901). (3) Gebauer-Fuelnegg, Moffett, J. Am. Chem. Soc. 56, 2009 (1934). (4) Ulich, Adams, J. Am. Chem. Soc. 43, 663 (1921). (5) Colonge, Mostafavi, Bull. soc. chim. (5) 5, 1485-1486 (1938). (6) Simpson, Ann. 109, 156-157 (1859). (7) Ger. 313,696, July 19, 1919; Cent. 1919, IV 664. (8) Brit. 329,721, June 17, 1930; Cent. 1930, II 1611. (9) Brit. 330,511, July 10, 1930; Cent. 1930, II 2184. (10) Drushel, Bancroft, Am. J. Sci. (4) 44, 376 (1917).

3:7630 1-CHLOROHEXENE-1

Cl C₆H₁₁Cl Beil. S.N. 11

B.P. 121-121.5° (1)
$$D_{-}^{22} = 0.8872$$
 (1) $n_{D}^{22} = 1.4300$ (1)

[For formn. of \bar{C} (together with other prods.) from either 3,3-dichloropropene-1 (3:5140) or 1,3-dichloropropene-1 (3:5280) with n-propyl MgBr see (1).]

C does not react with NaOEt at 130° (1).

C readily reacts with Na yielding (1) hexene-1 (1:8255), b.p. 64°.

 \tilde{C} adds \tilde{B}_{12} yielding (1) 1,2-dibromo-1-chlorohexane, b.p. 107° at 13 mm., $D_-^{24}=1.664$, $n_D^{24}=1.515$ (1).

3:7630 (1) Kirrmann, Grard, Compt. rend. 190, 876-877 (1930); Bull. soc. chim. (4) 47, 843-847 (1930).

3:7640 4-CHLOROBUTANONE-2

' (β-Chloroethyl methyl ketone; 1-chlorobutanone-3)

[See also 3-chlorobutanone-2 (3:7598).]

Liquid with faint and not disagreeable odor.

[For prepn. of \tilde{C} from methyl vinyl ketone [Beil. I-728, I₁-(379), I₂-(786)] satd. at 0° with HCl gas directly (67% yield (4)) or in C₆H₆ soln. (5); from acetyl chloride (3:7065) with ethylene + AlCl₃ at 0° (yields: 33% (3), 53% (6)) of. (2) or at 100° and 50 atm. press. (22); from 4-chlorobutadiene-1,2 (3:7225) by cat. hydration with conc. H₂SO₄ at -5° (yield 54% crude \tilde{C} (1)); from β -chloropropionyl chloride (3:5690) with Zn(CH₃)₂ (60% yield (7)); from butanol-1-one-3 (γ -keto-n-butyl alcohol) by saturation with HCl gas at 0° espec. in pres. of 5-10% AlCl₃ (63% yield (8)) see indic. refs.] — [Note that \tilde{C} is not formed by chlorination of ethyl methyl ketone (butanone-2) (21).]

 \tilde{C} with hot aq. alk. or alk. carbonates gives only resins, but \tilde{C} on boilg. with dimethylaniline or better diethylaniline loses HCl giving (yields: 30% and 80%, respectively (7)) methyl vinyl ketone (see above), b.p. 79–80°; note, however, that \tilde{C} on warming with alc. KOH or quinoline loses both HCl and H₂O yielding (4) a mixt. of dienes, b.p. 65–75°.

[For behavior of potential \tilde{C} (mixt. of methyl vinyl ketone + HCl gas in C_6H_6) with ethylene glycol (1:6465) see (5); for reactn. of \tilde{C} with trimethylene glycol (1:6490) + K yielding γ -hydroxypropyl γ -keto-n-butyl ethel see (3).]

[$\ddot{\mathbf{C}}$ with β -naphthol (1:1540) in EtOH/KOEt at 0° for 3 days gives (59% yield (9)) 1-(γ -keto-n-butyl)naphthol-2, cryst. from aq. alc., m.p. 88-89° (corresp. semicarbazone, pale yel. pr. from MeOH, m.p. 179-180° (9)).]

[Č with 2-methylcyclohexanone (1:5470) in EtOH/NaOEt (or sodium isopropylate/isopropyl alc.) at 0° for 18 hrs. gives (yields: 15% (10), 10% (20)) 2-keto-10-methyl-2,3,4,5,6,7,8,10-octahydronaphthalene, b.p. 129-133° at 12 mm., $n_{\rm p}^{12} = 1.5250$ (10).]

[$\bar{\mathbf{C}}$ with diethyl sodio-methylmalonate in ether gives (11) diethyl (methyl)-(γ -keto-n-butyl)malonate, b.p. 114-116° at 0.4 mm.; $\bar{\mathbf{C}}$ with ethyl α -isopropylacetoacetate in EtOH/NaOEt as directed yields (13) ethyl Δ -(1)p-menthenone-3-carboxylate-4.]

[C with aniline + conc. HCl or 40% H₂SO₄ htd. with nitrobenzene or H₃AsO₄ yields (14) (6) lepidine (4-methylquinoline) [Beil. XX-395, XXI₁-(150)]; for corresp. reactn. with other amines see (14) (6).]

[\bar{C} with 1-aminoanthraquinone [Beil. XIV-177, XIV₁-(436)] in pyridine yields (15) 1-(γ -keto-n-butylamino)anthraquinone, dark red cryst. which dye cellulose acetate.]

[\bar{C} with hydrazine hydrate in MeOH gives (80% yield (16)) (17) (19) by ring closure 3-methyl- Δ^2 -pyrazoline [Beil. XXIII-30], lıq., b.p. 56° at 15 mm. (16), sol. aq. but forming the corresp. picrate, \bar{B} .PkOH, yel. ndls. from alc., m.p. 153° (16) (17) (19). — \bar{C} in AcOH with methylhydrazine sulfate + NaOAc in aq. stood 2 nrs. gives (18) 1,3-dimethyl- Δ^2 -pyrazoline, oil, which with ethereal picric acid gives the corresp. picrate, \bar{B} .PkOH, m.p. 131.5-132.5° (18). — \bar{C} with phenylhydrazine in ether gives (16) by ring closure 3-methyl-phenyl- Δ^2 -pyrazoline, ndls. from ether by addn. of pet. ether, m.p. 76-77° (16).]

[\bar{C} with NH₂OH.HCl + K₂CO₃ in aq. MeOH htd. for a few minutes gives (20% yield (16)) by ring closure 3-methyl- Δ^2 -isoxazoline [Beil. XXVII-12], oil, b.p. 60° at 15 mm. (16).]

- ① 1-Carbamido-3-methyl-Δ²-pyrazoline: ndls. from EtOAc, m.p. 167-168° (18), 167° (16). [Note that C̄ with 1 equiv. semicarbazide HCl + NaOAc in aq. immediately ppts. the corresp. semicarbazone; this on htg. for 10 min. with strong aq. NaOAc (or C̄ + semicarbazide HCl + strong NaOAc soln. htd. directly in dil. alc. (19)) loses HCl and ring-closes to the indicated deriv.]
- ① 1-Phenyl-3-methyl-Δ²-pyrazoline: ndls. from ether on addn. of pet. eth., m.p. 76-77° (16), 77° (1). [From C in ether with phenylhydrazine, followed by neutralization and drying with anhyd. K₂CO₃ (16) (1); note that the presumably intermediate phenylhydrazone loses HCl and by ring closure gives the indicated deriv.]

3:7640 (1) Carothers, Berchet, Collins, J. Am. Chem. Soc. 54, 4070 (1932). (2) Schoeller, Zöllner (to Schering-Kahlbaum, A.G.), U.S. 1,737,203, Nov. 26, 1929; Cent. 1930, II 1133; Brit.

282,412, Feb. 15, 1928; Cent. 1929, I 143. (3) McGinnis, Robinson, J. Chem. Soc. 1941, 405-408. (4) Smith, Sprung, J. Am. Chem. Soc. 65, 1279-1280 (1932). (5) Kühn, J. prakt. Chem. (2) 156, 125 (1940). (6) Kenner, Statham, Ber. 69, 17 (1936). (7) Blaise, Maire, Bull. soc. chim. (4) 3, 268-270 (1908). (8) Décombe, Compt. rend. 202, 1685-1687 (1936). (9) McQuillin, Robinson, J. Chem. Soc. 1941, 588-589. (10) du Feu, McQuillin, Robinson, J. Chem. Soc. 1937, 53, 58-59.

(11) Lin, Robinson, J. Chem. Soc. 1938, 2006. (12) This reference deleted. (13) Walker, J. Chem. Soc. 1935, 1585. (14) Schering-Kahlbaum, A.G., Brit. 283,577, March 7, 1928; Cent. 1929, I 3148. (15) I.G., Brit. 485,175, June 9, 1938; French 828,581, May 20, 1938; Cent. 1938, II 3465. (16) Maire, Bull. soc. chim. (4) 3, 274-279 (1908). (17) Freudenberg, Stoll. Ann. 440, 44 (1924). (18) von Auwers, Heimke, Ann. 458, 205 (1927). (19) von Auwers, Ludewig, Ber. 69, 2348-2349 (1936). (20) Décombe, Compt. rend. 213, 579-581 (1941); Cent. 1942, II 1568.

(21) Forster, Fierz, J. Chem. Soc. 93, 669 (1908). (22) Frolich, Wiezevich (to Standard Oil Development Co.), U.S. 2,006,198, June 25, 1935; Cent. 1936, I 2827; C.A. 29, 5457 (1935).

B.P. 120-123° (1)

$$D_{20}^{20} = 1.130 (1)$$
 $n_{\rm D}^{20} = 1.464 (1)$

Note. Č by virtue of facile allyllic transposition easily isomerizes to 1,1-dichlorobutene-2 (3:7685) q.v.

[For prepn. of \bar{C} from crotonaldehyde (1:0150) with PCl₅ see (1) (2); the resulting mixt. of \bar{C} with its synionic isomer (1,1-dichlorobutene-2) (supposed by (2) to have been only the latter) has been separated by very precise fractnl. distn. (1).]

C with NaOEt yields (1) 1-chloro-3-ethoxybutene-1, b.p. 132-133° at 760 mm., 54-55° at 46 mm., $D_{16}^{16} = 0.960$, $n_{10}^{16} = 1.432$ (1).

C with NaOAc yields (1) 1-chloro-3-acetoxybutene-1, b.p. 57-58° at 16 mm., $D_{17}^{17} = 1.090$, $n_D^{17} = 1.443$ (1). [Note that crotylidene diacetate (1,1-diacetoxybutene-2), prepd. (95% yield (3)) from crotonaldehyde (1:1050) with Ac₂O, gives (3) with dry HCl the isomeric 3-chloro-1-acetoxybutene-1, b.p. 64° at 13 mm., $D_{20}^{20} = 1.083$, $n_{-}^{20} = 1.451$ (3).]

3:7650 (1) Kirrmann, Compt. rend. **199**, 1228–1229 (1934). (2) Kekulé, Ann. **162**, 98–100 (1872). (3) Kirrmann, Bull. soc. chim. (5) **5**, 917–918 (1938).

B.P. 120-123° dec. (1)

[For prepn. of Č from hexen-1-ol-4 (allyl-ethyl-carbinol) [Beil. I-444] with PCl₅ see (1).] Č with alc. KOH yields (1) hexadiene-1,3 [Beil. I-253], b.p. 72-74°.

3:7655 (1) Fournier, Bull. soc. chim. (3) 15, 402, 886 (1896).

3:7657 3-CHLORO-2-METHYL-1,2-EPOXYPROPANE C₄H₇OCl Bell. S.N. 2362 ("β-Methylepichlorohydrin") CH₆Cl

B.P. 122.0° (1)
$$D_4^{20} = 1.1025$$
 (1) $n_D^{20} = 1.4340$ (1)

Colorless liq.; \tilde{C} is sol. aq. to extent of 3 g. in 100 g. aq. at 20° (1). — \tilde{C} with aq. forms a const.-boilg. mixt. (b.p. 89.8°) contg. 74.4% \tilde{C} + 25.6% aq. (1).

[For prepn. of C from 1,3-dichloropropanol-2 (dichloro-ter-butyl alcohol) (3:5985) with aq. Ca(OH)₂ (93% yield (1)) see (1) (2); from chloroacetone (3:5425) with diagomethane in ether see (3).]

 \bar{C} with aq. especially at elevated temps., or \bar{C} stirred for 3 hrs. at 90-95° with aq. contg. 0.1% H₂SO₄ until mixt. becomes homogeneous, gives (1) (4) (by hydration through ring opening) 95% yield (1) 3-chloro-2-methylpropanediol-1,2 (β -methylglycerol monochloro-hydrin) (3:9190). [Note that alk. also catalyzes this hydration but reacts with the prod.] [Note also that HCl may not be used since it adds to the epoxy ring yielding (3) 1,3-dichloro-2-methylpropanol-2 (3:5977).]

 \ddot{C} on distn. with 12% H₂SO₄ at ord. press. yields (1) (5) quant. α -methylacrolein (" methacrolein") [Beil. I-731].

 \ddot{C} with conc. aq. NH₄OH + alk. yields (1) 1,3-diamino-2-methylpropanol-2 [Beil. IV₂-(739)].

3:7657 (1) Hearne, DeJong, Ind. Eng. Chem. 33, 940-943 (1941). (2) Groll, Hearne (to Shell Development Co.), U.S. 2,061,377, Nov. 17, 1936; Cent. 1937, I 4862; C.A. 31, 704 (1937). (3) Arndt, Amende. Ender, Monatch. 59, 213 (1932). (4) Groll, Hearne (to Shell Development Co.), U.S. 2,086,077, July 6, 1937; Cent. 1937, II 2433; C.A. 31, 5813 (1937). (5) Groll, Hearne (to Shell Development Co.), U.S. 2,106,347, Jan. 25, 1938; Cent. 1938, II 1676; C.A. 32, 2542-2543 (1938).

3: 7660
$$d$$
, l -3-CHLORO-2-METHYLPENTENE-1 $C_0H_{11}Cl$ Beil. S.N. 11 $(\alpha$ -Ethyl- β -methylallyl chloride) Cl CH_3 CH_3 - CH_2 CH_3 - CH_2

B.P. 120-124° (1)

Note. \bar{C} by virtue of allylic transposition would be expected to be in equilibrium with its synionic isomer 1-chloro-2-methylpentene-2 (γ -ethyl- β -methylallyl chloride). The material reported by (1) was regarded as \bar{C} ; the isomer appears to be as yet unrecorded.

[For prepn. of Č from 2-methylpenten-1-ol-3 by htg. with SOCl₂ + pyridine at 65° for 4 hrs. see (1).]

Č in MeOH refluxed 4 hrs. with NaSCN gives (1) α -ethyl- β -methylallyl isothiocyanate, b.p. 190-200° at 760 mm., 75-90° at 10 mm. (1). [This prod. with conc. H₂SO₄ at 0° vields 4-ethyl-5.5-dimethyl-2-mercaptothiazoline, color cryst. from alc., m.p. 115-118° (1).]

3:7660 (1) Bruson, Eastes, J. Am. Chem. Soc. 59, 2013 (1937).

3: 7665
$$d$$
, 1-5-CHLOROHEXENE-1 (Biallyl hydrochloride) (Biallyl hydrochloride) (CH₃—C—CH₂.CH₂.CH=CH₂ I_1 — I_{2-} (192) (H)

B.P. 121–125° at 760 mm. (1) $D_4^{25} = 0.8891$ (1) $n_D^{25} = 1.4279$ (1)

B.P. 121-125° at 760 mm. (1)
$$D_4^{25} = 0.8891$$
 (1) $n_D^{25} = 1.4279$ (1) $120-124^\circ$ (2) $64-66^\circ$ at 103 mm. (1) $D_4^{20} = 0.9141$ (1) $n_D^{20} = 1.4305$ (1) $43-45^\circ$ at 45 mm. (1) $n_D^{12} = 1.4332$ (1) $28-30^\circ$ at 13 mm. (1) $D_4^{12} = 0.9105$ (2) $n_D^{12} = 1.4350$ (2)

[The levorotatory isomeride of \tilde{C} has also been reported (3) from dextrorotatory hexen-1-ol-5 with PCl₅ in ether, b.p. 119-122° (3); ozonolysis followed by treatment with Br₂/aq. yields (3) levorotatory γ -chloro-n-valeric acid.]

[For prepn. of \bar{C} from hexadiene-1,5 (biallyl) (1:8045) by shaking at room temp. with 5 vols. conc. HCl for 120 hrs. see (1) (4) (yield of \bar{C} is 23% accompanied by 57% 1,5-dichlorohexane (3:9340) and other products (1)); for prepn. of \bar{C} from hexen-1-ol-5 [Beil. I-444] with PCl₅ in CHCl₃ (30% yield + much resin (2)) see (2) (attempts to obt. \bar{C} from this alc. with HCl gave (2) as a result of ring closure only 2,5-dimethyltetrahydrofuran [Beil. XVII-14], b.p. 93°).]

Č on oxidn. with CrO₃/H₂SO₄ for 2½ hrs. at 90-95° gave (2) formic acid (1.1005) but no allylacetone.

3:7665 (1) Cortese, J. Am. Chem. Soc. 52, 1519-1521 (1930). (2) Courtot, Pierron, Compt. rend. 190, 1057-1059 (1930). (3) Levene, Haller, J. Biol. Chem. 83, 599 (1929). (4) Wurtz, Ann. chim. (4) 3, 171 (1864).

3: 7670 3-CHLOROHEXANE
$$C_6H_{13}Cl$$
 Beil. S.N. 10 (sec.-(3)-Hexyl chloride; ethyl-n-propyl-carbinyl chloride) $CH_3.CH_2.CH_2$ CH_4 CH_5 CH_5 CH_7 CH_8 CH_8

[For prepn. of \tilde{C} from hexene-3 (1:8270) in CHCl₃ by shaking with conc. HCl for 48 hrs. (45% yield) (HCl gas in CHCl₃ fails) see (2) (for study of rate of reaction in various solvents see (4)); from hexanol-3 (1:6203) in ether + HCl gas for 5 days see (1); for formn. of \tilde{C} (together with other products) from reactn. of 2-ethylbutanol-1 (1:6223) with HCl + ZnCl₂ see (3).]

 \tilde{C} with Mg in dry ether gives RMgCl which with O₂ yields (3) hexanol-3 (1:6203); this alc. upon oxidn. with CrO_3/H_2SO_4 yields (3) hexanone-3 (2,4-dinitrophenylhydrazone, m.p. 146.5-148.5° (3); semicarbazone, m.p. 110.5-111.5° (3)).

3:7670 (1) Lagerev, Shadmanov, Trudy Uzbekskego Gosudarst. Univ. 6, 89-91 (1936); C.A. 35, 2120 (1941). (2) Spiegler, Tinker, J. Am. Chem. Soc. 61, 942 (1939). (3) Whitmore, Karnatz, J. Am. Chem. Soc. 60, 2535 (1938). (4) O'Connor, Baldinger, Vogt, Hennion, J. Am. Chem. Soc. 61, 1455 (1939).

3: 7675
$$d$$
, l -4-CHLOROHEXENE-2 (α -Ethyl- γ -methylallyl chloride; α -ethylcrotyl chloride) CH₃-CH₂-C-CH=CH.CH₃ I_1 - I_{2-} (192) H

B.P. 123-124° at 760 mm., sl. dec. (1) $n_D^{20} = 0.9148$ (6) 73-76° at 136 mm. (4) $n_D^{20} = 0.9148$ (6) $n_D^{20} = 1.4400$ (1) 66-67° at 110 mm. (5) $n_D^{20} = 0.9148$ (6) 1.4385 (5) 65-67° at 110 mm. (2) $n_D^{20} = 0.9148$ (6) 38-43° at 30 mm. (6) 30° at 13 mm. (1) 30° at 10 mm. (7)

Note. The possibility that \bar{C} may by virtue of allylic transposition exist or react in the form of its as yet unisolated symonic isomer 2-chlorohexene-3 (γ -ethyl- α -methylallyl chloride) should not be overlooked.

[For prepn. of \bar{C} from hexen-2-ol-4 (α -ethyl- γ -methylallyl alcohol) (1) [Beil. I-445] with dry HCl gas at 0° (5) (81% yield (2)), with conc. aq. HCl (7), with PCl₅ (5) (6) (54% yield (8)), or with SOCl₂ in ether + quinoline at 0° (1) see indic. refs.]

 \bar{C} is readily hydrolyzed: \bar{C} on shaking with aq. at 15° is 81% hydrolyzed in 48 hrs.; 100% in 90 min. at 40° (2). — \bar{C} with $2\frac{1}{2}$ pts. aq. + 1 pt. CaCO3 stood 3 days gives in good yield (1) 4-chlorohexen-2-ol, b.p. 49-50° at 12 mm. (1) [acid phthalate, m.p. 52-53° (1); p-nitrobenzoate, m.p. 35-37° (1); N-(p-xenyl)carbamate, m.p. 102° (1)].

 \bar{C} on htg. in s.t. at 120° with MeOH/KOH gives (3) 4-methoxyhexene-2, b.p. 110-113° (3).

[For reactn. of \bar{C} with phenol + K_2CO_3 in acetone see (8) (5); for extension to many phenols see (6); for reactn. of \bar{C} with diethylsodiomalonate see (4); for reactn. of \bar{C} with NH₃ or amines see (9).]

 \bar{C} on oxidn. with CrO₃/H₂SO₄ at 40° gives (55% yield (2)) hexen-2-one-4, b.p. 137-140° (2) [2,4-dinitrophenylhydrazone, m.p. 100-101° (2).]

3:7675 (1) Airs, Balfe, Kenyon, J. Chem. Soc. 1942, 24-26. (2) Courtot, Pierron, Bull. soc. chim. (4) 45, 290-291 (1929). (3) Reif, Ber. 39, 1603-1604 (1906), 41, 2742 (1908). (4) Shonle, Waldo, J. Am. Chem. Soc. 55, 4649-4652 (1933). (5) Smith, Ungnade, Lauer, Leekley, J. Am. Chem. Soc. 61, 3080 (1939). (6) Hurd, Puterbaugh, J. Org. Chem. 2, 381-386 (1937). (7) Boettcher (to I.G.), Ger. 513,364, Nov. 26, 1930; Cent. 1931, I 1007, C.A. 25, 1260 (1931). (8) Hurd, Cohen, J. Am. Chem. Soc. 53, 1917-1922 (1931). (9) Boettcher (to I.G.), Ger. 487,787, Dec. 16, 1929; Cent. 1930, I 1050

3: 7680
$$d$$
, l -1, l -DICHLOROBUTANE $C_4H_8Cl_2$ I_1 -(α -Butylene dichloride) CH_3 - CH_2 - CH - CH_2 I_1 -(38) I_2 -(81)

B.P. 124.0° (1) (2) (6) $D_4^{25} = 1.1116$ (2) $n_D^{20} = 1.440$ (7) abt. 125° (4) $D_4^{20} = 1.1182$ (6) 123-125° at 758 mm. (7) 121 -122° at 735 mm. (5) $D_4^{15} = 1.1244$ (2) $n_D^{15} = 1.4474$ (2) 31° at 28 mm. (5) 1.4472 (3)

Colorless liq. with not disagreeable odor.

[For prepn. of \bar{C} from butene-1 with Cl_2 in aq. (5), in CCl_4 (2), or at elevated temp. and press. in pres. of $CaCl_2$ + other cat. (8) (some 1,2,3-trichlorobutane (3:5935) is also formed (5)) see indic. refs.; for prepn. of \bar{C} from 1-chlorobutane (3:7160) with Cl_2 in sunlight or u.v. light (other isomers are also formed) see (9) (10) (11) (4) (7) (other isomers are always formed, and yield of \bar{C} is about 17% (7)) see indic. refs.; for formn. of \bar{C} from 2-chlorobutane (3:7125) with Cl_2 in light see (6).]

[$\bar{\mathbb{C}}$ with Cl₂ at -17° in dark gives (12) 1,2,3-trichlorobutane (3:5935) as main product.] [$\bar{\mathbb{C}}$ is not hydrolyzed by boilg. aq. K₂CO₃ (6) but on htg. with excess 7-15% aq. NaHCO₃ + Na₂CO₃ at 135-195° under press. for 1-6 hrs. gives (13) butanediol-1,2 [Beil. I-477, I₂-(545)] + 2-chlorobutene-2 (3:7105) + ethyl methyl ketone (1:5405) + mixt. of buten-1-ol-3 and buten-2-ol-1.]

[\bar{C} passed as vapor over heated soda-lime as directed (9) (4) (10) (11), or \bar{C} + aq. vapor at 200-500° over silica gel + cat. (14), gives (24.8% yield (9)) butadiene-1,3 (divinyl) [Beil. I-249, I₁-(107), I₂-(224)].]

[$\ddot{\mathbf{C}}$ with alc. KOH (1 mole + 25% excess) refluxed 3 days gives a mixt. contg. (2) cf. (18) 2-chlorobutene-1 (3:7075) + cis-1-chlorobutene-1 (3:7110); note that by this method no butyne-1 is formed (15) and can be obtd. from $\ddot{\mathbf{C}}$ + alc. KOH only by very drastic treatment, e.g., htg. in s.t. at 130-135° for 16-20 hrs. (15).]

[For reactn. of \tilde{C} with phenylacetonitrile (benzyl cyanide) + NaNH₂ in liq. NH₃ giving (40% yield (16)) 1-cyano-2-ethyl-1-phenylcyclopropane, b.p. 93-94° at 1 mm., $D_4^{20} = 0.9921$, $n_D^{20} = 1.52457$, see (16); for condens. of \tilde{C} with diphenyl ether (1:7125) + AlCl₃ see (17).]

3:7680 (1) Timmermans, Bull. soc. chim. Belg. 36, 504 (1927). (2) Navez, Bull. soc. chim. Belg. 38, 435-440 (1930). (3) Kahovec, Kohlrausch, Z. physik. Chem. B-48, 9 (1940). (4) Perkin, J. Soc. Chem. Ind. 31, 616-624 (1912); Cent. 1912, II 1210-1212. (5) de Montmollin, Matile, Helv. Chim. Acta 7, 106-108 (1924). (6) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 663-666 (1937); Cent. 1937, II 372; C.A. 31, 5754 (1937). (7) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 893-896 (1937); Cent. 1938, II 2575; C.A. 31, 5755 (1937). (8) Ruys, Edwards (to Shell Development Co.), U.S. 2,099,231, Nov. 16, 1937; Cent. 1938, I 3387; C.A. 32, 190 (1938). (9) Muskat, Northrup, J. Am. Chem. Soc. 52, 4043-4044, 4050-4053 (1930). (10) Muskat (to du Pont Co.), U.S. 2,038,593, April 28, 1936; Cent. 1936, II 3358; C.A. 30, 3912 (1936). (11) Muskat (to du Pont Co.), U.S. 2,070,609, Feb. 16, 1937; Cent. 1937, II 2597; C.A. 31,

(1937). (12) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.), 6, 1553-1558 (1936);
 Cent. 1937, I 3785;
 C.A. 31, 2165 (1937). (13) Dobryanskii, Gutner, Shchigel'skaya, J. Gen. Chem. (U.S.S.R.)
 7, 1315-1320 (1937);
 Cent. 1938, I 561;
 C.A. 31, 6189 (1937). (14) Tishchenko, Churbakov, Ryanantsev, Russ. 52,023, Oct. 31, 1937;
 Cent. 1938, II 1127;
 C.A. 34, 1336 (1940). (15) Schjanberg, Ber. 71, 573 (1938). (16) Murray, Cloke, J. Am. Chem. Soc. 58, 2016 (1936). (17) Coleman, Hadler (to Dow Chem. Co.), U.S. 2,079,279, May 4, 1937;
 Cent. 1937, II 1267.

(18) Henne, Hinkamp, J. Am. Chem. Soc. 67, 1197 (1945).

3: 7685 1,1-DICHLOROBUTENE-2 C₄H₆Cl₂ Beil. I - 205 (Crotylidene (di)chloride) CH₃—CH—CH—CHCl₂ I₁— I₂—

B.P. 124-125° (1) $D_{18}^{18} = 1.140$ (1) $n_{D}^{18} = 1.466$ (1)

Č by virtue of facile allylic transposition easily isomerizes to 1,3-dichlorobutene-1 (3:7650) q.v.

[For prepn. of \bar{C} from crotonaldehyde (1:0150) with PCl₅ see (1) (2); the resulting mixt. of \bar{C} with its synionic isomer (1,3-dichlorobutene-1) (supposed by (2) to have been only \bar{C}) has been separated by very precise fractional distn. (1).]

Crotylidene diacetate (from crotonaldehyde (1:0150) + Ac₂O in 95% yield (3)) gives (3) with dry HCl 3-chloro-1-acetoxybutene-1, b.p. 64° at 13 mm., $D_{20}^{20} = 1.083$, $n_{D}^{20} = 1.451$ (3), derived from the symionic isomer of \tilde{C} .

3:7685 (1) Kirrmann, Compt. rend. **199**, 1228–1229 (1934). (2) Kekulé, Ann. **162**, 98–100 (1872). (3) Kirrmann, Bull. soc. chm. (5) **5**, 917–918 (1938).

3: 7690 3,3-DICHLORO-2-METHYLBUTENE-1
$$C_{\delta}H_{8}Cl_{2}$$
 Beil. S.N. 11 Cl_{3} CH_{3} CH_{3} CH_{3} CH_{4} CH_{5} CH

[For prepn. of \tilde{C} from 3-chloro-2-methylbutene-2 (3:7335) with $Cl_2 + NaHCO_3$ at 0° see (1) (yield 80% together with 10% 2,3,3-trichloro-2-methylbutane (3:4755), m.p. 182-183° (1)).]

C on htg. gives by allylic transposition 1,3-dichloro-2-methylbutene-2 (3:8170) (1).

3:7690 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4223; C.A. 33, 4190 (1939).

The name crotonoyl chloride is employed to avoid possible confusion with 1-chlorobutene-2 (3:7205) often designated as crotonyl chloride because of its relationship to crotonyl alcohol (buten-2-ol-1).

[For prepn. of \bar{C} from α -crotonic acid (1:0425) with SOCl₂ (yield: 95% (5), 86% (11)) (6) (8) (10) in pet. ether (80% yield (2)), or with PCl₃ (84% yield (3)) (7) (4), or with PCl₅ (12), or with benzoyl chloride (3:6240) (yield: 72-80% (13)) see indic. refs.; for prepn. of \bar{C} from Na \bar{A} with PCl₅ + POCl₃ (1), with PCl₅ in ether (26% yield (14)), or with POCl₃ (9) see indic. refs.; for prepn. of \bar{C} by distn. of isocrotonyl chloride see (12).]

 \ddot{C} with EtOH yields (4) (by addn. of the resultant HCl) ethyl β -chloro-n-butyrate (3:8373).

[C on htg. with NaA (3) or with Et₈N + C₆H₆ in the cold (15) gives (81% yield (3)) crotonic anhydride (1:1155), b.p. 248°.]

[For reactn. of C with methyl diazoacetate see (2), with NaN₃ see (6).]

[C with AlCl₃ + C₆H₆ in CS₂ in light gives (61% yield (11)) (1) both phenyl propenyl ketone [Beil. VII-368, VII₁-(194)], b.p. 135-140° at 20 mm. (1), 90-95° at 2 mm. (11), $n_D^{25} = 1.5475$ (11) (corresp. 1,3-diphenyl-5-methylpyrazoline from ketone with phenyl-

hydrazine, m.p. 108° (1)), and β -phenyl-n-butyrophenone (1,3-diphenylbutanone-1) [Beil. VII-453], m.p. 74° (1) (11). — For reactn. of \bar{C} with AlCl₃ + p-xylene (16), mesitylene (11), accnaphthene (17), anisole (18), methyl p-tolyl ether (7), methyl 3,5-dimethylphenyl ether (19) see indic. refs.]

 \bar{C} on hydrolysis with aq. yields α -crotonic acid (1:0425), m.p. 72°; for the amide, anilide, p-toluidide, and other derivs. corresp. to \bar{C} see 1:0425.

3:7693 (1) Kohler, Am. Chem. J. 42, 395-396 (1909). (2) Staudinger, Becker, Hirzel, Ber. 49, 1991 (1916). (3) Luniak, Ber. 42, 915-916 (1909). (4) Henry, Bull. acad. roy. Belg. (3) 36, 42 (1898); Cent. 1898, II 663 (5) Maxim, Bull. Soc. Chim. Românsa, 10, 97-115 (1928); Cent. 1929, I 2161, C.A. 23, 2697 (1929). (6) Jones, Mason, J. Am. Chem. Soc. 49, 2533 (1927). (7) von Auwers, Ann. 421, 30-36 (1921). (8) Kohlrausch, Pongratz, Z. physik. Chem. B-27, 193 (1934). (9) von Auwers, Schmidt, Ber. 46, 474 (1913). (10) Kuhn, F. Kohler, L. Kohler, Z. physiol. Chem. 247, 197-219 (1937); Cent. 1937, II 2391, C.A. 31, 6264 (1937)

(11) Fuson, Christ, Whitman, J. Am. Chem. Soc. 58, 2450-2452 (1936). (12) von Auwers, Spiess, Ber. 34, 191-192 (1901). (13) Brown, J. Am. Chem. Soc. 60, 1325-1328 (1938). (14) Rupe, Schaerer, Helv. Chim. Acta 8, 863 (1925). (15) Wedekind, Ann. 378, 288 (1910). (16) von Auwers, Risse, Ann. 502, 291-292 (1933). (17) Fieser, Hershberg, J. Am. Chem. Soc. 61, 1280 (1939). (18) von Auwers, Ann. 439, 150 (1924) (19) Ref. 7, pp. 97-100.

B.P. 125-126° at 761 mm. (1)

[For prepn. of $\bar{\rm C}$ from N-(benzoyl)isohexylamine with PCl₅ followed by aq. see (1).] $\bar{\rm C}$ on htg. in alc. with diethyl sodiomalonate in a s.t. at 100° for 4 hrs. gives an ester from which 2-methyloctanoic acid-8, b.p. abt. 230°, was obtd. by conventional methods (1).

3:7695 (1) Clarke, J. Chem. Soc 103, 1699 (1913).

B.P. 125-127° (1)
$$D_4^{21} = 0.8694$$
 (3) $n_D^{21.5} = 1.4142$ (3) 123-126° (2) 122.5° at 754 mm. (3) $D_4^{14} = 0.8762$ (3) 61° at 100 mm. (3)

[For prepn. of \bar{C} from corresp. alc. hexanol-2 (1:6210) with conc. HCl at 125° (90% yield (3)) or conc. HCl (1) (2) see indic. refs.; for formn. of \bar{C} (together with other products) from reaction of 2-ethylbutanol-1 (1:6223) with conc. HCl + ZnCl₂ see (4).]

C on passing over Pyrex glass or unglazed porcelain at 150-500° loses HCl (5).

[For study of rate of reaction with KI in acetone see (2).]

Č with Mg in dry ether gives RMgCl; upon treatment with oxygen this gives (4) hexanol-2 (1:6210) q.v.

① n-Butyl-methyl-acet-anilide: m.p. 91-92° u.c. (1). [From \bar{C} via conversion to RMgCl and reaction with phenyl isocyanate (1).]

3:7715 (1) Underwood, Gale, J. Am. Chem. Soc. 50, 2119 (1934). (2) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925). (3) Zelinskii, Przewalskii, J. Russ. Phys.-Chem. Soc. 49, 1105-1123 (1908); Cent. 1908, I 1854. (4) Whitmore, Karnatz, J. Am. Chem. Soc. 60, 2535 (1938). (5) Farragher, Garner, J. Am. Chem. Soc. 43, 1721 (1921).

B.P.
$$125-127^{\circ}$$
 (1) $D_4^{20} = 0.8914$ (2) $n_D^{20} = 1.4230$ (2) 88° at 225 mm, (2)

[For prepn. of \bar{C} from 2-ethylbutanol-1 (1:6223) with SOCl₂ + pyridine (82% yield) see (2); with 45% HCl in s.t. at 100° (11% yield) see (1). [Note that 2-ethylbutanol (1:6223) with conc. HCl + ZnCl₂ gives (2) by rearr. of the carbon chain 7 different chlorohexanes.]

 \overline{C} on shaking at 79-87° for 7 hrs. with conc. HCl + ZnCl₂ rearranges in part to a mixt. of other hexyl halides (2).

C with Mg in dry ether gives RMgCl; upon treatment with oxygen this yields (2) 2-ethylbutanol-1 (1:6223) q.v.

3:7720 (1) Fourneau, Matti, J. pharm. chim. (8) 14, 513-522 (1931); Cent 1932, I 2587. (2) Whitmore, Karnatz, J. Am. Chem. Soc. 60, 2533-2536 (1938).

3: 7725
$$d$$
, l -4-CHLORO-2,4-DIMETHYLPENTENE-1 $C_7H_{13}Cl$ Beil. I - 220 Cl I_1 — CH_3 — C — CH_2 — C — CH_2 — C — CH_2 — C — CH_3

[For prepn. of \bar{C} from ethyl β -chloroisovalerate + MeMgBr in ether see (1).]

3:7725 (1) Lemaire, Bull. acad. roy. Belg. 1969, 83-159; Cent. 1969, I 1982; C.A. 4, 1483-1484 (1910); Rec. trav. chim. 29, 51-52 (1910).

3:7730
$$d$$
, l -4-CHLORO-5-METHYLHEXENE-1 $C_7H_{13}Cl$ Beil. I - 220 d , l -3-Chloro-2-methylhexene-5 Cl CH_3 I₁— (Allyl-isopropyl-carbinyl chloride) CH_2 — CH — CH — CH — CH — CH 3 I_2 — I_3 4 I_4 4 I_4 5 I_4 5 I_4 5 I_4 5 I_4 6 I_4 6 I_4 7 I_4 7 I_4 9 I_4 9

B.P. 125-130° dec. (1)

[For prepn. of \bar{C} from 2-methylhexen-5-ol-3 (allyl-isopropyl-carbinol) [Beil. I-447] with PCl₅ see {1}.]

3:7730 (1) Fournier, Bull. soc. chim. (3) 15, 886 (1896).

3:7735 3-CHLOROHEXATETRAENE-1,3,4,5 Cl C₆H₆Cl Beil. S.N. 14 CH₂=C=C=C-CH=CH₂

B.P. 127° dec. at 760 mm. (1)
$$D_4^{20} = 0.9997$$
 (1) $n_D^{20} = 1.5280$ (1) 82° at 163 mm. (1) 55° at 54 mm. (1)

[For prepn. of C from 1,4-dichlorohexatriene-2,3,5 (3:9304) with MeOH/KOH at 10-15° or with NaOMe in dry MeOH see (1).]

C on cat. hydrogenation yields (1) n-hexane (1:8530).

 \overline{C} on oxidn. with aq. KMnO₄ + Na₂CO₃ soln. for 10 hrs. at 35–45° gives (1) oxalic acid dihydrate (1:0445).

3:7735 (1) Coffman, Carothers, J. Am. Chem. Soc. 55, 2040-2047 (1933).

3: 7740
$$n$$
-VALERYL CHLORIDE C_8H_9OCl $III_1-II_{2-}(266)$ $III_{2-}(266)$ $III_{2-}(266)$

[For prepn. of \tilde{C} from n-valeric acid (1:1060) with PCl₅ (60% yield (8)), with PCl₃ (77% yield (9)) (1) or PCl₃ + ZnCl₂ (75% yield (8)), with SOCl₂ (yield: 92.5% (7), 84% (4), 77% (8)), with benzoyl chloride (3:6240) (84–76% yield (6)), or with oxalyl dichloride (3:5060) (95% yield (10)) see indic. refs.]

Č htd. with sodium n-valerate yields (11) n-valeric anhydride (1:1137), b.p. 218°.

[\bar{C} with EtMgBr gives (66% yield (4)) 3-ethylheptanol-3; \bar{C} + AlCl₃ treated at 0° with ethylene gives (74% yield (12)) (13) n-butyl β -chloroethyl ketone (1-chloro-heptanone-3), but its constants have not been reported.]

[Č with AlCl₃ and phenol yields (14) 56% o-(n-valeroyl)phenol, b.p. 130° at 10 mm., $D_{-}^{24} = 1.0435$, $n_{D}^{25.5} = 1.5309$ (semicarbazone, m.p. 204-204.5°), and 29% p-(n-valeroyl)phenol, cryst. from pet. ether, m.p. 63°, b.p. 197.5-198.5° at 10 mm. (benzoate, m.p. 92°).]

Č on hydrolysis yields n-valeric acid (1:1060), b.p. 186°. — For the amide, anilide, p-toluidide, α-naphthalide, and other derivs. corresp. to Č see n-valeric acid (1:1060).

3:7740 (1) Freundler, Bull. soc. chim. (3) 11, 312 (1894); (3) 13, 833 (1895). (2) Timmermans, Bull. soc. chim. Belg. 36, 507 (1927). (3) Martin, Partington, J. Chem. Soc. 1936, 162. (4) Whitmore, Orem. J. Am. Chem. Soc. 60, 2574 (1938). (5) Kohlrausch, Pongrats, Z. physik. Chem. B-32, 382 (1933). (6) Brown, J. Am. Chem. Soc. 60, 1325-1328 (1938). (7) Fierz-David, Küster, Helv. Chim. Acta 22, 89 (1939). (8) Clark, Bell, Trans. Roy. Soc. Can. III 27, 97-103 (1933). (9) Reitter, Z. physik. Chem. 36, 137 (1901). (10) Uhlich, Adams, J. Am. Chem. Soc. 42, 604 (1920).

Pickard, Kenyon, J. Chem. Soc. 101, 1432 Note (1912).
 Kenner, Statham, Ber. 69, 17 (1936).
 Schering-Kahlbaum Akt. Ges., Brit. 282,412, Feb. 15, 1928; Cent. 1929, I 143.

(14) Sandulesco, Girard, Bull. soc. chim. (4) 47, 1308-1309 (1930).

3:7745-3:7747

E C₄H₇O₂Cl C₂H₅,O.CH₂,CO.Cl Beil. III - 240 III₁-(92)

III₂-(173)

B.P. 127-128° (1) (2)
$$D_4^{20} = 1.1170$$
 (4) $n_D^{20} = 1.42039$ (4) $123-124$ ° (3) .

Colorless limpid liq. with strong odor and lachrymatory character; fumes in moist air. [For prepn. from ethoxyacetic ac. (1:1070) by actn. of PCl₃ (90% yield (2)) see (1) (2); by actn. of thionyl chloride (90% yield (5), 73% yield (3), 45% yield (4)) see (3) (4) (5) (6).

 \ddot{C} in aq. sinks to bottom in oily drops which soon dissolve by hydrolysis to ethoxyacetic acid (1:1070) + HCl.

3:7745 (1) Henry, Ber. 2, 276–277 (1869). (2) Pratt, Robinson, J. Chem. Soc. 123, 752, footnote (1923). (3) Rothstein, Bull. soc. chim. (4) 51, 841–842 (1932). (4) Leimu, Ber. 76, 1050 (1937). (5) Sommelet, Ann. chim. (8) 9, 492–493 (1906); Bull. soc. chim. (4) 1, 368–369 (1907). (6) Jones, Powers, J. Am. Chem. Soc. 46, 2528 (1924).

3: 7747
$$d$$
, l -1-CHLOROPROPANOL-2 H C_3H_7OCl Beil. I - 363 I_1 -(185) β -chloro-isopropyl alcohol; chloromethyl-methyl-carbinol) B.P. 127-128° at 761 mm. (1) (14) $D_{20}^{20} = 1.115$ (5) $n_D^{20} = 1.43924$ (2) 1.111 (2)

126-127° cor. at 762 mm. (2) (3) (21) 126-127° at 760 mm. (4)

126.0-126.5° cor. at 722 mm. (5) 78-81° at 80 mm. (6)

[See also 2-chloropropanol-1 (3:7917).]

Colorless liq. forming with aq. a const.-boilg. mixt., b.p. 96° at 743 mm., contg. 49.1 wt. % = 15.15 mole % $\bar{\text{C}}$ (37).

[For prepn. of \bar{C} from allyl chloride (3:7035) by addn. of H₂O to the unsatd. linkage through the actn. of H₂SO₄ + CuSO₄ as specified (yield: 66-70% (8)) (9) (3) (5) (2) (11) see indic. refs.; an extensive study (10) has shown that this is the only method of prepn. of \bar{C} which does not gives also some 2-chloropropanol-1 (propylene β -chlorohydrin (3:7917).]

[For prepn. of ordinary \tilde{C} (probably containing some of the isomer) from propanediol-1,2 (propylene glycol) (1:6455) with HCl (2) (12) (10), with S_2Cl_2 (14) (10), or with $SiCl_4$ (15) see indic. refs.; from propylene glycol diacetate with an alc. + HCl see (16); from propylene with HOCl (17) (18) (19) (20) (10) (21), with Cl_2 + aq. (22) (23) (30), or with *ter*-butyl hypochlorite (3:7165) (24) see indic. refs.; from 1,2-epoxypropane (propylene oxide) (1:6115) with HCl see (12) (5) (2) (7) (25) (10); note, however, that by these methods there results an inseparable mixt. of much \tilde{C} with a little 2-chloropropanol-1 (3:7917) (10).]

[For formn. of Č from chloroacetone (3:5425) with AlEt₃ etherate (70% yield (6)) or by actn. of yeast (26); from 2-amino-1-chloropropane with nitrous acid (27) or from 1,2-dichloropropane (propylene dichloride) (3:5200) with SO₃ followed by hydrolysis (28) see indic. refs.]

 $\ddot{\mathbf{C}}$ on htg. in s.t. at 140-160° yields (29) 1,2-dichloropropane (3:5200) + acetone (1:5400); $\ddot{\mathbf{C}}$ similarly htd. with aq. yields (29) acetone (1:5400) + propionaldehyde (1:0110). — $\ddot{\mathbf{C}}$ on htg. with P₂O₅ yields (5) allyl chloride (3:7035) + 1-chloropropene-1 (3:7035).

Č with aq. alk. readily gives (30) by loss of HCl and ring closure 1,2-epoxypropane (propylene oxide) (1:6115), b.p. 35°. [For study of rate of reactn. see (10) (31).]

 \tilde{C} on oxidn. with CrO₃ yields (17) (14) (18) (5) (7) chloroacetone (3:5425) + AcOH (1:1010); \tilde{C} treated with Ca(OCl)₂ in cold, then warmed, yields (32) chloroform (3:5050) + AcOH (1:1010); \tilde{C} on oxidn. with HNO₃ yields chloroacetic acid (3:1370) + AcOH (1:1010) + oxalic acid (1:0445).

[For reactn. of \bar{C} with Na₂S yielding (9) (33) β,β' -dihydroxy-di-n-propyl sulfide; with Me₃N in C₆H₆ on htg. in s.t. 8 hrs. at 100° giving (48% yield (34)) β -methylcholine chloride, m.p. 165° (34); with alkyl sulfates + alk. (35) to yield monoalkyl ethers of propylene glycol; with alkyl sulfates to yield (35) (36) β -chloroisopropyl alkyl ethers; with Br₂ + P to yield (8) 1-bromo-2-chloropropane, b.p. 117.5–118° at 756 mm., $D_4^{20} = 1.537$, $n_D^{20} = 1.47447$ (8), see indic. refs.]

- —— β -Chloroisopropyl acetate: b.p. 149–150° (3) (2). [From \bar{C} + AcCl (3).]
- —— β -Chloroisopropyl benzoate: no b.p. recorded; $D_{19}^{19} = 1.172$ (14). [From \bar{C} on htg. with BzCl at 180° (14); is saponified with great ease by alk. yielding propylene oxide (1:6115), b.p. 35°.]
- ---- β-Chloroisopropyl p-nitrobenzoate: unreported.
- **©** β -Chloroisopropyl 3,5-dinitrobenzoate: m.p. 76.5-77.3° (38).
- ① 1-(Phthalimido)propanol-2 [N-(β-hydroxy-n-propyl)phthalimide: m.p. 88-89° (39), 90-91° (40). [From C̄ + K phthalimide in s.t. at 170° for 3 hrs. (39); see also under corresp. deriv. of 2-chloropropanol-1 (3:7917).]

3:7747 (1) Dewael, Bull. soc. chim. Belg. 33, 504 (1924). (2) Henry, Rec. trav. chim. 22, 209-210. 326-329 (1903). (3) Bancroft, J. Am. Chem. Soc. 41, 426-427 (1919). (4) Henry, Bull. acad, roy. Belg. 1902, 535-536; Cent. 1902, II 1093-1094. (5) Michael, Ber. 39, 2786-2789 (1906). (6) Mecrewin, Hinz, Majert, Sonke, J. prakt. Chem. (2) 147, 237 (1936). (7) Henry, Bull. acad. roy. Belg. 1903, 397-431; Cent. 1903, II 486. (8) Dewael, Bull. soc. chim. Belg. 39, 87-90 (1930). (9) Coffey, J. Chem. Soc. 119, 96-97 (1921). (10) Smith, Z. physik. Chem. 93, 59-85 (1919).

(11) Oppenheim, Ann. Suppl. 6, 367-369 (1868). (12) Michael, J. prakt. Chem. (2) 60, 420-423 (1899). (13) Oser, Ann. Suppl. 1, 254 (1861). (14) Morley, Green, J. Chem. Soc. 47, 132-134 (1885); Ber. 18, 24-25 (1885). (15) Taurke, Ber. 38, 1669 (1905). (16) Britton, Coleman, Moore (to Dow Chem. Co.), U.S. 1,987,227, Jan. 8, 1935; Cent. 1935, II 350; C.A. 29,1432 (1935). (17) Markownikow, Ann. 153, 251-252 (1870). (18) Michael, J. prakt. Chem. (2) 69, 454-458 (1899). (19) Finkelstein (to I G.), Canadian 285,920, Dec. 25, 1928; Cent. 1932, I 1153. (20) Tropsch, Kassler, Brit. 377,595, Aug. 18, 1932; Cent. 1932, II 2724.

(21) Henry, Rec. trav. chim. 26, 138 (1907); Bull. acad. roy. Belg. 1906, 523-557; Cent. 1906, II 1550-1551. (22) Britton, Nutting, Huscher (to Dow Chem. Co.), U.S. 2,130,226, Sept. 13, 1938; Cent. 1939, I 1856; C.A. 32, 9096 (1938). (23) Soc. Carbochimique, Brit. 445,011, Apr. 30, 1936; Cent. 1936, II 1244; French 795,804, March 23, 1936, C.A. 30, 5592 (1936). (24) N. V. De Bataafsche Petroleum Maatschappij, French 740,350, Jan. 24, 1933; Cent. 1933, II 2053. (25) Nef. Ann. 335, 204-205 (1904). (26) Sen. J. Indian. Chem. Soc. 1, 7 (1924). (27) Smith, Platon, Ber. 55, 3150-3153 (1922). (28) Isham, Spring (to Doherty Research Co.), U.S. 1,918,967, July 18, 1933; Cent. 1933, II 2053; C.A. 27, 4815 (1933). (29) Krassuski, J. Russ. Phys.-Chem. Soc. 34, 287-315 (1902); Cent. 1902, II 19-21. (30) Moureu, Dodé, Bull. soc. chim. (5) 4, 281-295 (1937).

(31) Smith, Z. physik. Chem. A-152, 153-156 (1931). (32) Ssuknewitsch, Tschilingarjan, Ber. 69, 1542 (1936). (33) Farbwerke Meister, Lucius Bruning, Brit. 185,403, Oct. 25, 1922; Cent. 1923, II 684. (34) Major, Cline, J. Am. Chem. Soc. 54, 246-247 (1932). (35) Davidson (to Carbide and Carbon Chem. Corp.), U.S. 1,730,061, Oct. 1, 1929; Cent. 1930, I 1366; C.A. 23, 5474 (1929). (36) Dewael, Bull. soc. chim. Belg. 39, 395-401 (1930). (37) Kireev, Kaplan, Zlobin, J. Applied Chem (U.S.S.R.) 7, 1333-1338 (1934); Cent. 1936, I 4286; C.A. 29, 5712 (1935). (38) Magrane, Cottle, J. Am. Chem. Soc. 64, 485 (1942). (39) Gabriel, Ohle, Ber. 50, 807 (1917). (40) Gabriel, Ohle, Ber. 50, 820 (1917).

B.P. 127-128° dec. at 733 mm. (1)
$$D_4^{20} = 0.861$$
 (1) $n_D^{20} = 1.4180$ (1) $126-127^{\circ}$ (2) 1.4239 (3) $33-34^{\circ}$ at 20 mm. (3) $D_4^{10} = 0.8650$ (2) $n_D^{16.5} = 1.4202$ (2)

[For prepn. of \bar{C} from 2,4-dimethylpentanol-2 (dimethyl-isobutyl-carbinol) [Beil. I-417, I₁-(207), I₂-(446)] by saturation with HCl (2) or as by-product during its reacts. with AlCl₃ + C₆H₆ (3) see indic. refs.; for prepn. of \bar{C} from 2,4-dimethylpentanol-3 (di-isopropyl-carbinol) (1:6215) in 100% yield by saturation with HCl gas and stdg. 10 weeks at 20° (note rearrangement) (1).]

 \bar{C} with Mg in dry ether gives (1) RMgCl, which upon oxidation with O₂ and subsequent hydrolysis gives 32% yield 2,4-dimethylpentanol-2 (dimethyl-isobutyl-carbinol), b.p. 130-131° at 738 mm., $D_4^{20} = 0.811$, $n_D^{20} = 1.4166$ (1).

[For reactn. of \tilde{C} with AlCl₃ + C₆H₆ yielding 2,4-dimethyl-2-phenylpentane, b.p. 218°, $D_4^{15} = 0.8741$, $n_D^{16.5} = 1.49383$, see (2).]

3:7750 (1) Whitmore, Johnston, J. Am. Chem. Soc. 60, 2267 (1938). (2) Schreiner, J. prakt. Chem. (2) 82, 294 (1910). (3) Huston, Fox, Binder, J. Org. Chem. 3, 252-253 (1939).

3: 7752 1-CHLQRO-2-METHYLPROPANOL-2
$$C_4H_9OCl$$
 Beil. I - 382 (Chloro-ter-butyl alcohol; CH_3 I_1- chloro-trimethylcarbinol; $CH_3 C CH_2$ isobutylene α -chlorohydrin; α,α -dimethylethylene α -chlorohydrin) OH

B.P.		M.P.	
128-129°	(1) (2)	-20° (5)	$D_4^{20} = 1.0628 (9)$
127-129°	(3)		
127-128.5°	(4)		
126-128°	(5) (6) (7)		
126-127° at 736	3.4 mm. (8)		
126.7°	(9)		
126.0-126.5° at 748	3.3 mm. (10)		
71.0-71.5° at 100	mm. (10)		

[See also 2-chloro-2-methylpropanol-1 (3:7905).]

Colorless liq. somewhat sol. aq.; 100 g. aq. at 20° dis. 18.6 g. Č (note also that 100 g. Č at 20° dis. 19 g. H₂O) (9). — Č forms with aq. a const.-boilg. mixt., b.p. 93-94° at 760 mm., contg. 34% aq. (9).

[For prepn. of \bar{C} from 3-chloro-2-methylpropene-1 (methallyl chloride) (3:7145) or from 1-chloro-2-methylpropene-1 (θ,β -dimethylvinyl chloride) (3:7120) by cat. hydration of their unsatd. linkage (63-66% yield) see (9) (11); note that the former with 80% H₂SO₄ at 0° or the latter with 90% H₂SO₄ at -10° to 0° stirred for 2½ hfs., poured onto ice, and distilled gives 63-66% of the initial chloride as \bar{C} ; note that other acids can also be used for this hydration, e.g., 85% H₃PO₄, 70% HNO₃, 60% HClO₄, benzenesulfonic acid, etc., each having its own optimum conditions (9); note also that in this process some 32-18%

respectively of the initial chloride is not hydrated but partially isomerized to a mixt. contg. 90% β , β -dimethylvinyl chloride (3:7120) + 10% methallyl chloride (3:7145) irrespective of whichever one was initially employed (9).]

[For prepn. of Č from 1,2-dichloro-2-methylpropane (isobutylene dichloride) (3:7430) by liq.-phase hydrolysis of the more reactive halogen atom under neutral (or even slightly acidic or basic) conditions (best yield 48% by refluxing 18 hrs. with aq.) see (10).]

[For prepn. of \bar{C} from chloroacetone (3:5425) or ethyl chloroacetate (3:5700) with MeMgBr (yields: 60% (5), 38% (12)) (3) (6) or MeMgI (20% yield (4)) see (3) (5) (6) (12) (note that \bar{C} is accompanied (as a result of reaction of a second MeMgBr (13) (14)) by some 2-methylbutanol-2 (1:6160)); for prepn. of \bar{C} from isobutylene with HOCl (yields: 64% (6), 63% (1), 60% (7), 47% (2)) (5) (15), with $Cl_2 + H_2O$ (16) (17) in pres. of 10% CuCl₂ (80-85% yield (24)), or with ter-butyl-hypochlorite (3:7165) (18) see indic. refs.; for formn. of \bar{C} from 1,2-epoxy-2-methylpropane (isobutylene oxide) (1:6117) with HCl gas in ether see (19) (6) (4) (1) (note, however, that the prod. is a mixt. consisting of about $\frac{1}{2}$ \bar{C} contaminated with about $\frac{1}{2}$ of the isomeric 2-chloro-2-methylpropanol-1 (3:7905)).] [For formn. of \bar{C} from 1-amino-2-methylpropanol-2 hydrochloride with conc. HCl in s.t. at 100° see (12).]

[Č on reduction with Na/Hg in dil. HCl yields (2) (15) 2-methylpropanol-1 (isobutyl alcohol) (1:6165); this unexpected result presumably is due to intermediate formation of isobutylene oxide (1:6117) which on reduction opens the ring to give isobutyl alc. (not ter-butyl alcohol).]

[\overline{C} on protracted oxidation, e.g., with mixt. of 1.5 wt. pts. fumg. HNO₃ + 3.5 wt. pts. conc. HNO₃ at 75° for 20 hrs. (2), gives traces of chloroacetone (3:5425) and a little oxalic acid (1:0445) and α -chloroisobutyric acid (3:0235) (5).]

C on refluxing with aq. is slowly (e.g., 56% in 14 hrs. (2)) (21) converted to isobutyraldehyde (1:0120); note that this reaction carried out above 100° under press. (20) is greatly accelerated.

[C with warm conc. HCl yields (10) (5) 1,2-dichloro-2-methylpropane (3:7430).]

 \ddot{C} on solution in cold 45% H_2SO_4 followed by warming loses H_2O and yields (9) a mixt. consisting of about 90% 1-chloro-2-methylpropene-2 (methallyl chloride (3:7145)) accompanied by about 10% 1-chloro-2-methylpropene-1 (β,β -dimethylvinyl chloride) (3:7120); a mixt. of these two chlorides has also been obtd. by use of P_2O_5 (1) (2) or anhydrous oxalic acid (2) (22).]

[C added dropwise to dry powdered KOH, NaOH, CaO, or Ca(OH)₂ loses HCl and gives (95% yield using NaOH (10), 67% using KOH (6)) 1,2-epoxy-2-methylpropane (isobutylene oxide) (1:6117), b.p. 56.0-56.5° cf. (24).]

 $[\bar{C}$ with aq. alkali ultimately yields 2-methylpropanediol-1,2 (isobutylene glycol) (1:6446) or its polymerization products; for study of kinetics of reaction of \bar{C} with aq. alk. see (4) (8).

[\bar{C} with KCN in 4 vols. 80% alc. refluxed for 15-20 min. gives (45-50% yield (23)) β -hydroxy-isovaleronitrile [Beil. III-328], b.p. 210-212° at 756 mm., 130-132° at 30 mm., f.p. -12° , $D_{-}^{20} = 0.96762$, $n_{D} = 1.42911$ (23).]

[\tilde{C} with aq. 23% EtNH₂ (4 moles) in s.t. at 100° for 8 hrs. gives (70-75% yield (25)) 1-(ethylamino)-2-methylpropanol-2, b.p. 156° (\tilde{B} .HCl, m.p. 151° (25)). — \tilde{C} with aq. Et₂NH refluxed 3-4 hrs. gives (60% yield (26)) 1-(diethylamino)-2-methylpropanol-2, b.p. 164-165° at 761 mm. (26), $D_4^{20}=0.8382$ (27), $n_D^{20}=1.4253$ (27) (\tilde{B} .PkOH, m.p. 99-100° (26)). — For reactn. of \tilde{C} with N-methylaniline, N-ethylaniline, or di-n-butylamine see (27).]

⁻⁻⁻⁻ Chloro-ter-butyl acetate: b.p. 154° at 760 mm. (28), 153-154° (5), $D_4^{15} = 1.0626$ (28), $n_D^{15} = 1.4340$ (28). [From $\bar{C} + AcCl$ (5); also indirectly (28% yield (28)) from

isobutylene + N,N'-dichlorourea in AcOH.] — [For analogous indirect prepn. of the formate, chloroacetate, and trichloroacetate see (28).]

- ---- Chloro-ter-butyl benzoate: unreported.
- ---- Chloro-ter-butyl p-nitrobenzoate: unreported.
- ---- Chloro-ter-butyl 3,5-dinitrobenzoate: unreported.
- **①** 1-(N-Phthalimido)-2-methylpropanol-2 (N-(α -hydroxyisobutyl)phthalimide): ndls. or lfts. from alc., m.p. 106-107° (12). [From \ddot{C} + K phthalimide in s.t. at 150° for 4 hrs. (60% yield (12)).]
- 3:7752 (1) Michael, Leighton, J. prakt. Chem. (2) 64, 103-104 (1901). (2) Michael, Leighton, Ber. 39, 2157-2163 (1906). (3) Tiffeneau, Compt. rend. 134, 775 (1902). (4) Nillson, Smith, Z. physik. Chem. A-166, 143-144 (1933). (5) Henry, Rec. trav. chim. 26, 142-151 (1907); Bull. acad. rpy. Belg. 1906, 523-557; Cent. 1906, II 1550-1551; Compt. rend. 142, 131, 494-496 (1906). (6) Krassusky, J. prakt. Chem. (2) 75, 241-247 (1907). (7) Krassusky, J. Russ. Phys.-Chem. Soc. 33, 1-26 (1901); Cent. 1901, I 995-997. (8) Evans, Z. physik. Chem. 7, 338-357 (1891). (9) Burgin, Hearne, Rust, Ind. Eng. Chem. 33, 385-388 (1941). (10) Sparks, Nelson, J. Am. Chem. Soc. 58, 1010-1011 (1936).
- (11) Groll, Burgin (to Shell Development Co.), U.S. 2,042,222, May 26, 1936; Cent. 1937, I 1546; C.A. 30, 4875 (1936); N. V. de Bataafsche Petroleum Maatschappi, French 791,644, Dec. 14, 1935; Cent. 1936, II 2227. (12) Dersin, Ber. 54, 3158-3160 (1921). (13) Henry, Compt. rend. 145, 24 (1907). (14) Fourneau, Tiffeneau, Compt. rend. 145, 438 (1907). (15) Butlerow, Ann. 114, 25-26 (1867). (16) Kautter, U.S. 2,060,086, Oct. 17, 1936; Cent. 1937, I 3873; N. V. de Bataafsche Petroleum Maatschappij, French 799,805, June 20, 1936; Cent. 1938, II 3468; C.A. 30, 8250 (1936). (17) Britton, Nutting, Huscher (to Dow Chem. Co.), U.S. 2,130,226, Sept. 13, 1938; Cent. 1939, I 1856; C.A. 32, 9096 (1938). (18) N. V. de Bataafsche Petroleum Maatschappij, French 740,350, Jan. 24, 1933; Cent. 1933, I 2870. (19) Michael, Leighton, Ber. 39, 2789-2795 (1906). (20) Groll, Kautter (to Shell Development Co.), U.S. 2,042,225, May 26, 1936; Cent. 1937, I 184; C.A. 39, 4872 (1936); Canadian 363,685, Jan. 26, 1937; Cent. 1937, II 1661.
- (21) Krassusky, Bull. soc. chim. (3) 24, 236 (1900). (22) Krassusky, J. prakt. Chem. (2) 64, 389-390 (1901). (23) Lemaire, Rec. trav. chim. 29, 58-60 (1910); Bull. acad. roy. Belg. 1909, 83-159; Cent. 1909, I 1982. (24) Moureu, Dodé, Bull. soc. chim. (5) 4, 286-289 (1937). (25) Krassuskii, Kutzenos, Ukrain. Khem. Zhur. 4, Sci. Pt., 75-77 (1929); Cent. 1929, II 2174; C.A. 24, 1083 (1930). (26) Krassusky, Stepanoff, J. prakt. Chem. (2) 115, 321-324 (1927). (27) K. N. Campbell, B. K. Campbell, Proc. Induana Acad. Sci. 49, 101-104 (1939); C.A. 35, 5460 (1941). (28) Likhosherstov, Petrov, J. Gen. Chem. (U.S.S.R.) 9, 2000-2008 (1939); C.A. 34, 4381 (1940).

3:7755 2,2-DICHLOROPENTANE Cl
$$C_6H_{10}Cl_2$$
 Beil. I - 131 $I_1 I_2 CH_3.CH_2.CH_2-C-CH_3$ I_2- (95)

B.P. 128-129° cor. (1)
$$D_{-}^{20} = 1.040$$
 (1) $n_{\rm D}^{20} = 1.434$ (1) 44° at 31 mm. (1) $36-37^{\circ}$ at 20 mm. (1)

The prod. upon which the above data are based was admittedly impure, still contg. 20% 2,3-dichloropentane (3:8010) q.v.

[For prepn. of \tilde{C} from methyl n-propyl ketone (1:5415) with PCl₅ see (1) (2) (3); for formn. of \tilde{C} (together with other products) from pentane (1:8505) + Cl₂ see (4).]

Č with alc. KOH gives (2) 2-chloropentene-1 (3:7280) and pentyne-1 (1:8025). — Č on boilg. with NaNH₂ in xylene gives (1) pentyne-1 (1:8025).

[For reactn. of \bar{C} with SbF₅ yielding 2,2-diffuoropentane, b.p. 59.8°, $D_4^{20} = 0.8958$, $n_{20}^{20} = 1.33570$, see (3).]

\$:7755 (1) Bourgeul, Ann. chim. (10) \$, 220, 368-370 (1925); Bull. soc. chim. (4) \$5, 1634 (1924).
 (2) Bruylants, Ber. 8, 411 (1875).
 (3) Henne, Renoll, Leicester, J. Am. Chem. Soc. 61, 938-940

Beil. III - 12

C₅H₉O₂Cl

3:7760 ISOBUTYL CHLOROFORMATE

(1939). (4) Lemke, Tishchenko, J. Gen. Chem. (U.S.S.R.), 7, 1995-1998 (1937); Cent. 1939, I 2397; C.A. 32, 482 (1938).

(Isobutyl chlorocarbonate) (CH₃)₂CH.CH₂.O.CO.Cl
$$III_{1}$$
-(6) III_{2} -(11)

B.P. 128.8° cor. (1) (2) $D_{4}^{17.9} = 1.0425$ (3) $n_{H_{e}}^{17.9} = 1.40711$ (3) $D_{15}^{18.5} = 1.0445$ (4)

Colorless mobile lachrymatory oil. — Insol. in aq. and only slowly hydrolyzed by it even on htg.

[For prepn. of \tilde{C} (35% yield (2)) from isobutyl alc. (1:6165) + phosgene (3:5000) see (1) (2) (5).]

- D Isobutyl carbamate [Beil. III-29]: from C

 in C

 of B

 of by treatment with NH3 gas, filtration of pptd. NH4Cl, and evapn. of solvent; lfts. from aq., m.p. 61° (6); 64.4° (7); 64-65° (8).
- (isobutyl N-phenylcarbamate (isobutyl carbanilate) [Beil. XII-321]: from Č in ether by treatment with ether soln. of aniline (1 mole) + pyridine (1 mole); ndls. from alc., m.p. 86° (9) (10).
- 3:7760 (1) Roese, Ann. 205, 230 (1880).
 (2) Hamilton, Sly, J. Am. Chem. Soc. 47, 436 437 (1925).
 (3) von Auwers, Ber. 60, 2140 (1927).
 (4) Dobrosserdow, Cent. 1911, I 955 (5) Hochstetter, Ger. 254,471, Feb. 16, 1915; Cent. 1915, I 464.
 (6) Thiele, Dent, Ann. 302, 271 (1898).
 (7) Brunel, Ber. 44, 1002 (1911).
 (8) Schmidt, Z. physik. Chem. 58, 514 (1907).
 (9) Michael, Cobb, Ann. 363, 84 (1908).
 (10) Huckel, Ackermann, J prakt. Chem. (2) 136, 23 (1933).

$$CH_3$$
— C — CH_2 — C = O
 CH_3 — C 1

B.P. 128.5–130.3° at 746 mm. (1)

 $D_4^{20} = 0.9696$ (1) $n_D^{20} = 1.4230$

B.P. 128.5-130.3° at 746 mm. (1)
$$D_4^{20} = 0.9696$$
 (1) $n_D^{20} = 1.4230$ (6) 79.5° at 165 mm. (2) 0.968 (3) 1.4226 (5) $79-81^{\circ}$ at 150 mm. (3) 1.422 (1) (3) 79 at 150 mm. (4) 1.4213 (2) 68° at 100 mm. (5) 1.4212 (4) 1.4212 (4) 1.4213 (2) 1.4212 (4) 1.4213 (2) 1.4213 (4)

[For prepn. of Č from ter-butylacetic acid (1:1112) with SOCl₂ (1) (yields: 93% (3), 86% (4) (5), 84% (2)) see indic. refs.]

[For reactn. of \bar{C} with various alcs. to give corresp. alkyl ter-butylacetates see (2) (3) (7): e.g., methyl ter-butylacetate, b.p. 126.5° at 739 mm. (3), 128° at 735 mm. (2), $D_4^{20} = 0.8710$ (3), $n_D^{20} = 1.3997$ (2), 1.3981 (3); ethyl ter-butylacetate, b.p. 144.5-144.7° at 739 mm. (3), $D_4^{20} = 0.8604$ (3), $n_D^{20} = 1.4010$ (3).]

[For behavior of C with a large excess of various Grignard compounds see following refs.: with EtMgBr (5), n-PrMgBr (5), iso-PrMgBr (2), n-BuMgBr (5), iso-BuMgBr (2), ter-BuMgCl (4) (6), n-AmMgBr (5).]

 $\ddot{\mathbf{C}}$ on hydrolysis yields *ter*-butylacetic acid (1:1112) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to $\ddot{\mathbf{C}}$ see 1:1112).

3:7880 (1) Hommelen, Bull. soc. chim. Belg. 42, 243-250 (1933). (2) Whitmore, Foster, J. Am. Chem. Soc. 64, 2966-2968 (1942). (3) Homeyer, Whitmore, Wallingford, J. Am. Chem. Soc. 55, 4211-4212 (1933). (4) Whitmore, Heyd, J. Am. Chem. Soc. 60, 2030-2031 (1938). (5) Whitmore, Popkin, Whitaker, Mattel, Zech, J. Am. Chem. Soc. 60, 2462-2464 (1938). (6) Whitmore, Whitaker, Mosher, Breivik, Wheeler, Miner, Sutherland, Wagner, Clapper, Lewis, Lux, Popkin, J. Am. Chem. Soc. 63, 643-654 (1941). (7) Whitmore, Homeyer (to Mallinckrodt, Chem. Works), U.S. 2,052,995, Sept. 1, 1936; Cent. 1936, II 3846; C.A. 30, 7125 (1936).

3: 7885
$$d$$
, l -4, d -DICHLORO-2-METHYLBUTANE $C_{\delta}H_{10}Cl_{2}$ Beil. I - 135 $I_{1-}($ 47) I_{2-} $I_{1-}($ 47) I_{2-} I_{2-}

Colorless limpid liquid, insol. aq., sol. in alc. or ether.

[For prepn. of C from isovaleraldehyde (1:0140) with PCl₅ see (1) (2) (3); for formn. of \bar{C} by actn. of Cl_2 (+ I_2) on diisoamyl sulfide see (4).]

C with KOH gives (1) (3) 4-chloro-2-methylbutene-3 (3:7215) and ultimately 3-methylbutyne-1 (isopropylacetylene) (1:8010), b.p. 28°.

 \bar{C} htd. with PbO + H₂O gives (4) isovaleraldehyde (1:0140).

3;7885 (1) Ebersach, Ann. 106, 265-266 (1858). (2) Kohlrausch, Monatsh. 65, 197 (1935). (3) Bruylants, Ber. 8, 413-414 (1875). (4) Spring, Lecrenier, Bull. soc. chim. (2) 48, 627 (1887).

For prepn. of C from 2-methylhexen-4-ol-3 [Beil. I-447, I₂-(489)] with conc. HCl at ord. temp. (90% yield (2)) or with SOCl2 in pet. ether (1) see indic. refs.]

[C with quinoline loses HCl on boilg, giving (1) 2-methylhexadienc-2.4 [Beil, I-257. I₂-(235)], b.p. 99° (1).]

[C with diethylamine yields (3) 3-diethylamino-2-methylhexene-4, oil, b.p. abt. 175° (3).]

3:7890 (1) Staudinger, Muntwyler, Ruzicks, Seibt, Helv. Chim. Acta 7, 399 (1924). (2) Böttcher (to I.G.), Ger. 508,891, Oct. 2, 1930; Cent. 1930, II 3637; C.A. 25, 710 (1931). (3) Bottcher (to I.G.), Ger. 487,787, Dec. 16, 1929; Cent. 1930, I 1050.

[For prepn. of \tilde{C} from pentanone-2 (methyl n-propyl ketone) (1:5415) with Cl₂ (yields: 35.5% (3), 85% crude (2)) cf. (6) or with SO₂Cl₂ in C₆H₆ (44% yield (7)) see indic. refs.; from ethyl α -chloro- α -ethylacetoacetate [Beil. III-694, III₁-(241), III₂-(438)] by ketonic cleavage with dil. HCl in s.t. at 180° for 4-6 hrs. see {1} cf. (7).

[\tilde{C} in abs. alc. treated with NH₃ gas yields (2) 2,5-dimethyl-3,6-diethylpyrazine [Beil. XXIII-101], liq., b.p. 215-217°, forming with aq. a sublimable hydrate, m.p. 42.5°. (Note that 2-chloropentanone-3 (3:7935) similarly treated gives same prod.) — \tilde{C} with equiv. amt. ethyl β -aminocrotonate [Beil. III-654, III₁-(228), III₂-(423)] in pres. of excess conc. NH₄OH gives (27.3% yield (4)) ethyl 2,5-dimethyl-4-ethylpyrrolecarboxylate-3 [Beil. XXII-33, XXII₁-(501)], cryst. from dil. MeOH, m.p. 74-75° (4); note, however, m.p. 106-107° (5) reported for this prod. obtd. in a dif. way.]

[\overline{C} with thioformamide gives (29% yield (7)) 4-methyl-5-ethylthiazole, b.p. 169.5-170° at 745 mm., 78-79° at 25 mm. (7).]

3:7893 (1) Conrad, Ann. 186, 241-242 (1877). (2) Démetre-Vladesco, Bull. soc. chim. (3) 6, 832-834 (1891). (3) Korschun, Bull. soc. chim. (4) 3, 595-596 (1908). (4) Korschun, Bull. soc. chim. (4) 3, 594-595 (1908). (5) Vecchi, Gazz. chim. ital. 44, I 477 (1914). (6) Justoni, Chimica e industria (Italy) 24, 195-201 (1942); Cent. 1943, I 1659. (7) Buchman, Richardson, J. Am. Chem. Soc. 67, 397 (1945).

3: 7895 3,3-DICHLOROPENTANE Cl
$$C_5H_{10}Cl_2$$
 Beil. I — I_1 — I_2 — CH_3 . CH_2 — CH_2 . CH_3 I_2 — I_2 — I_3 — I_4

B.P. 131-132° at 750 mm. (1)
$$D_{-}^{20} = 1.053$$
 (1) $n_{D}^{20} = 1.442$ (1) 32° at 14 mm. (1)

 \ddot{C} has never been reported in completely pure form; the above material contains abt. 20% 2,3-dichloropentane (3:8010) q.v. (1).

[For prepn. of \tilde{C} (together with other products) from diethyl ketone (1:5420) with PCl₅ see (1).]

3:7895 (1) Bourgeul, Compt. rend. 178, 1559 (1924); Bull. soc. chim. (4) 35, 1635 (1924); Ann. chim. (10) 3, 371 (1925).

3:7900
$$\alpha,\alpha$$
-DIMETHYL-n-BUTYRYL CHLORIDE C_6H_{11} OCl Beil. II - 336 (Dimethyl-ethyl-acetyl chloride) CH_3 C

B.P.
$$132^{\circ}$$
 at 760 mm. (6) $D_4^{20} = 0.9801$ (1) $n_D^{20} = 1.4245$ (5) $131.8-132.4^{\circ}$ at 748 mm. (1) $131.7-131.9^{\circ}$ (2) 129.8° at 727 mm. (5) $D_4^0 = 0.9973$ (1) 23° at 12 mm. (3) 27° at 11 mm. (4)

[For prepn. of C from 2,2-dimethylbutanoic acid-1 (1:1113) with SOCl₂ (50% yield (5)) see (1) (5); with benzoyl chloride (yield not given) see (6).]

[For reactn. of C with isobutyl zinc iodide yielding (3) 2,5,5-trimethylheptanone-4

(tetrahydroartemisaketone) see (3); for reactn. of \bar{C} with isopropyl MgBr yielding (by reducing actn.) 2,2-dimethylbutanol-1 (1:6204) and 2,4,4-trimethylhexanol-3 (5) see (5).] \bar{C} on hydrolysis yields 2,2-dimethylbutanoic acid-1 (1:1113) q.v. (for the amide, anilide,

p-toluidide, α -naphthalide, and other derivatives corresponding to \tilde{C} see 1:1113).

3:7900 (1) Hommelen, Bull. soc. chim. Belg. 42, 243-250 (1933). (2) Kohlrausch, Pongrats, Z. physik. Chem. B-22, 383 (1933). (3) Ruzicka, Reichstein, Pulver, Helv. Chim. Acta 19, 648-649 (1936). (4) Reichstein, Rosenberg, Eberhardt, Helv. Chim. Acta 18, 723 (1935). (5) Whitmore, Foster, J. Am. Chem. Soc. 64, 2966-2968 (1942). (6) Degnan, Shoemaker, J. Am. Chem. Soc. 68, 104-105 (1946).

3: 7903 CHLOROBENZENE (Phenyl chloride)	CI	C ₆ H ₅ Cl Beil. V - 199	
(I henyl cmorace)	\smile	V ₁ -(109)	
B.P.	F.P.	V ₂ -(148)	,
132.10-132.12° cor. (1)	-44.0° (21) (22)	$D_4^{25} = 1.1016 (14)$	
132.07° at 760 mm. (2)	-45.0° (23) (24)	1.1012 (31)	
132.02° at 761.8 mm. (3)	(7) (25)	1.1011 (32)	
132.0° at 760 mm. (4)	-45.1° (4)	1.10091 (4)	
(5) (6) (7) (8) (9) (10)	-45.2° (26) (27)	$n_{\rm D}^{25} = 1.5222 (14)$,
131.83° at 760 mm. (11)	(28) (29)	1.5221 (28)	
131.7° at 760 mm. (12)	(8)	1.5217 (31)	
131.6° (13)	-45.29° (2)	1.5215 (36)	
131.4-131.6° at 748 mm. (14)	See Note 2.	$D_4^{20} = 1.1066 (38)$	
130.7° at 755 mm. (15)		1.10643 (33)	
130.5° at 755 mm. (16)		1.1064 (12)	
129.6° at 719 mm. (17)		1.10631 (4)	
114.9° at 468.5 mm. (17)		$n_{\rm D}^{20} = 1.5251 (37)$	
99.7° at 292.8 mm. (17)		1.525 (2)	
44.8° at 30 mm. (18)		1.52479 (38)	
See Note 1.		1.52459 (15)	
		$D_4^{15} = 1.11172 (4)$	
		See Note 3.	
		$n_{\rm D}^{15} = 1.52748 (4)$	
		1.5272 (39)	,
		See Note 4.	

Note 1. For further data on b.p. of C at various press. in range 98-758 mm. see (19), between 3-11, 188 mm., see (20).

Note 2. For details on m.p. of C under high pressures see (26) (30).

Note 3. For details on D_4^4 over range 0.3-123.6° see (34), over range -42.7° to + 126° see (35).

Note 4. For details of change of refractive index with pressure see (40).

 \tilde{C} is pract. insol. aq.; for precise data see (11) (225). — \tilde{C} is very eas. sol. alc., ether, C_6H_6 , $CHCl_3$, CS_2 . — For detn. of \tilde{C} in mixt. with C_6H_6 and the dichlorobenzenes see (226) (227). — For use of \tilde{C} as immersion fluid in refractometry see (228). — For toxicity of \tilde{C} see (229). — For brief study of detn. of vapors of \tilde{C} in air using a combustion method see (230).

Selected data and references on physical properties of mixts. of \bar{C} with other cpds. (for additional data and references on many other systems see Beilstein).

Binary systems. \tilde{C} with H_2O forms a const.-boilg. mixt., b.p. 90.2° at 760 mm., contg; 71.6° \tilde{C} (41) (use in sepn. of \tilde{C} from polychlorobenzenes see (69)): \tilde{C} with acetone (1:5400).

vapor/liq. equilibrium see (13): $\bar{\mathbb{C}}$ with acetic acid (1:1010), f.p./compn. data and diagrams (eutectic, m.p. -48.5° , contg. $97\%\bar{\mathbb{C}}$ (28)) see indic. refs.: $\bar{\mathbb{C}}$ with C_6H_6 (1:7400), f.p./compn. diagram see (24): $\bar{\mathbb{C}}$ with aniline, liq./vapor equil., D_{25}^{25} /compn., etc., see (43): $\bar{\mathbb{C}}$ with nitrobenzene, f.p./compn. data + diagram (eutectic, m.p. -50.7° contg. 78.3 wt. $\%\bar{\mathbb{C}}$) see (21): $\bar{\mathbb{C}}$ with pyridine, f.p./compn. data + diagram (eutectic, m.p. -63.5° , contg. $54\%\bar{\mathbb{C}}$) and also n_D^{25} /compn. diag. see (28): $\bar{\mathbb{C}}$ with o-chlorotoluene (3:8245), f.p./compn. diagram (eutectic, m.p. abt. -71° , contg. 39.4 mole $\%\bar{\mathbb{C}}$) see (44); $\bar{\mathbb{C}}$ with m-dichlorobenzene (3:5960), f.p./compn. data, see (23): $\bar{\mathbb{C}}$ with benzoyl chloride (3:6240), f.p./compn. data see (45): $\bar{\mathbb{C}}$ + ethylene dibromide, f.p./compn. dag. (eutectic, m.p. -55° contg. 83 mole $\%\bar{\mathbb{C}}$) see (44); vapor-press. equil. see (46): $\bar{\mathbb{C}}$ + bromobenzene, f.p./compn. diagram (no eutectic) see (22) (24); for use in testing efficiency of distillation columns see (39): $\bar{\mathbb{C}}$ + iodobenzene, f.p./compn. diagram (eutectic, m.p. -51.5° , contg. $57\%\bar{\mathbb{C}}$) see (22) (24): $\bar{\mathbb{C}}$ with fluorobenzene, f.p./compn. diagram (complex system) see (22) (24).

Ternary Systems. \bar{C} with aq. + HCl forms ternary const.-boilg. mixt., b.p. 96.6° at 756 mm., contg. 74.5 wt. $\%\bar{C} + 20.2$ wt. % aq. + 5.3 wt. % HCl (41): \bar{C} with aq. + acetone, solubility diagram see (47): \bar{C} + ethylene glycol (1:6465) + acetone, soly. of system at 23° see (48).

Preparation of \tilde{C} . Because of the magnitude of the literature on this topic only a few selected references can be given here; reference should also be made to Beil. V-199, V_1 -(109) and V_2 -(148).

[For prepn. of \bar{C} from C_6H_6 with Cl_2 in pres. of $SnCl_4$ at 30-40° (49), with NOCl at 425° (50), with $HCl + O_2$ (air) + cat. (51) see indic. refs.; for discussion of prepn. of industrial \bar{C} see (52); for study of photochem. chlorination of C_6H_6 see (53).]

[For prepn. of \bar{C} from aniline via formn. of benzenediazonium chloride/ZnCl₂ cpd. and htg. with molten phenol (40% yield $\bar{C}+26\%$ hydroxybiphenyl + 20% diphenyl ether (54)) or by isolation of solid benzene diazonium chloride and cautious decompn. by warming in various org. solvents see (55); from p-chloroanline via formn. of p-chlorobenzenediazonium chloride/ZnCl₂ cpd. and htg. latter with EtOH (67% yield) or EtOH + Zn dust (60% yield) see (54); from phenylhydrazine by oxidn. with aq. FeCl₃ at 70° (61% yield) or with HClO₃ (30% yield) see (56); from C₆H₅MgBr with ethyl hypochlorite (3:7022) (60% yield (57)), sulfuryl chloride (57), benzenesulfonyl chloride (yields: 52% (58), 25% (57)), other aromatic sulfonyl chlorides (58) (57), N-chloropiperidine and other N-chloroanines (59), or N-chloro-p-chlorobenzaldimine (60), see indic. refs.]

[For formn. of \bar{C} from benzoyl chloride (3:6240) on htg. in porcelain tube at 550-600° see (61); from benzeneazotriphenylmethane on warming in CCl₄ see (62); from bis-(p-chlorophenyl)zinc by reaction with aq. see (63); from phenylboric acid with Cl₂/aq. or refluxed with aq. CuCl₂ (85% yield) see (64); from C₆H₆ + n-butyl chlorosulfonate + AlCl₃ (11% yield) see (65); from C₆H₆ with SeCl₄ + AlCl₃ see (66); from 4-chlorodiphenyl sulfide by htg. with sulfur see (67); from 2-chlorobenzophenone (3:0715) or 4-chlorobenzophenone (3:1914) on fusion with KOH/NaOH see (68).]

Pyrolysis. Č passed over Pt wire at bright red heat (70) or through hot Fe tube (71) yields 4,4'-dichlorobiphenyl (3:4300) accompanied by biphenyl (1:7175), 4-chlorobiphenyl (3:1912), and other products.

Reduction. \tilde{C} in EtOH at 55° with excess H_2 at 3 atm. in pres. of Adams' cat. readily (72) yields cyclohexane (1:8405). $-\tilde{C}$ with H_2 or $NH_2.NH_2$ in MeOH or EtOH in pres. of Pd/CaCO₃ gives (73) cf. (74) small yields of biphenyl (1:7175). $-\tilde{C}$ with Na in boilg. EtOH (75), or Na/Hg in EtOH (76), or Na in AmOH (77), or NaOAm in AmOH (78) is dehalogenated, but extent of reactn. varies with conditions. $-\tilde{C}$ with HI + P is unaffected at 300° but at 375° yields (79) benzene. $-\tilde{C}$ in aq. or dil. alc. alk, with H_2 in pres. of Ni

splits off all (80) its halogen as HCl. — $\bar{\rm C}$ with H₂ + Ni at 270° yields (81) benzene + biphenyl.

Behavior with chlorine. \bar{C} with Cl_2 may add or substitute or both according to conditions. — \bar{C} under dil. aq. NaOH with excess Cl_2 in sunlight (82) or with Cl_2 at 0° in dark as directed (83) (84) gives (90% yield (83)) heptachlorocyclohexane [Beil. V-23, V₂-(12)] (known in 2 stereoisomeric forms, " α ," m.p. 146° (82), " β ," m.p. 260° (82)). [For study of relative amts. addition and substitution with $\bar{C} + Cl_2$ see (85).]

 \bar{C} with Cl₂ in pres. of AlCl₃ (86), Al/Hg (87), or FeCl₃ (86), or \bar{C} with SO₂Cl₂ + S₂Cl₂ + AlCl₃ (88), or \bar{C} htd. with FeCl₃ (89) or PbCl₄.2NH₄Cl (90), gives mainly 1,4-dichlorobenzene (3:0980) accompanied by other products. — \bar{C} with Cl₂ at 400–700° in pres. of cat. yields (91) (92) 1,3-dichlorobenzene (3:5960) + 1,3,5-trichlorobenzene (3:1400) and other products.

Behavior with bromine. \bar{C} with Br₂ (93) under aq. (82) or in pres. of AlCl₃ (94), Al/Hg (95), Al (99), or Fe (99), or \bar{C} htd. with FeBr₃ (96), gives mainly 4-bromochlorobenzene [Beil. V-209, V₁-(116), V₂-(162)], m.p. 66°, together with other products; for study of rate in AcOH see (97). — \bar{C} with Br₂ at elevated temp. gives greatly increased proportion of meta-bromochlorobenzene; e.g., \bar{C} with Br₂ at 475° gives (98) 53% m-, 27% p-, and 20% o-bromochlorobenzenes.

Behavior with metals. \bar{C} with Li in dry ether under dry N₂ gives (35-49% yield (100)) phenyllithium [Beil. XVI₁-(589)]; for reactns, of latter with fluoro, chloro, bromo, or iodobenzene see (101).

 $\bar{\mathbf{C}}$ on boilg, with Na yields (102) $\mathrm{C_6H_6}$, biphenyl, and other products; $\bar{\mathbf{C}}$ with Na in boilg, toluene yields mainly (102) $\mathrm{C_6H_6}$ together with other prods. — $\bar{\mathbf{C}}$ with amylsodium (from amyl chloride + Na) in lgr. gives (103) (104) (105) phenylsodium [Beil. XVI₁-(589)] which with $\mathrm{CO_2}$ gives (105) benzoic acid; $\bar{\mathbf{C}}$ with Na + diethyl carbonate in $\mathrm{C_6H_6}$ gives (79% yield (106)) (for use of other esters such as methyl benzoate, ethyl benzoate, or diethyl oxalate in ether see (107)) or $\bar{\mathbf{C}}$ with Na + benzophenone in $\mathrm{C_6H_6}$ gives (98% yield (106)) (108) triphenylcarbinol (1:5985). — $\bar{\mathbf{C}}$ with Na + AsCl₃ in xylene gives (82% yield (109)) triphenylarsine; $\bar{\mathbf{C}}$ with Na + SbCl₃ in xylene yields (109) triphenylstibine.

 \bar{C} with Mg/Cu alloy in pres. of I_2 (110), or \bar{C} with Mg in s.t. at 150-160° for 3 hrs. (111) (112), or \bar{C} refluxed with Mg + Cu₂Cl₂ (113), gives (yields: 80% (110), 85% (111)) phenyl magnesium chloride.

Behavior with Al halides. \bar{C} does not react with AlCl₃ even on long boilg. (dif. from bromobenzene and iodobenzene which react at once) (114). — \bar{C} with freshly prepared fused AlBr₃ yields (115) bromobenzene.

Behavior with AlCl₃ + other compounds. \tilde{C} (2 moles) with CCl_4 (1 mole) + AlCl₃ (1.75 moles) in CS_2 gives (116) (117) bis-(4-chlorophenyl)dichloromethane [Beil.V -592], m.p. 52-53°, together with other products; \tilde{C} (6 moles) with CCl_4 (1 mole) + AlCl₃ (1 mole) htd. at 60-70° gives mainly (118) 2-chlorophenyl-bis-(4-chlorophenyl)chloromethane [Beil. V-703], m.p. 153°, accompanied by a small amt. tris-(4-chlorophenyl)chloromethane [Beil. V-703], m.p. 113°.

 \tilde{C} with AcCl (3:7065) or Ac₂O + AlCl₃ yields p-chloroacetophenone (3:6735) q.v. for details.

 $\ddot{\mathbf{C}}$ + furoic acid (1:0475) + AlCl₃ gives (18% yield (119)) 6-chloronaphthoic acid-1 (3:4845); $\ddot{\mathbf{C}}$ + methyl furoate (1:3452) + AlCl₃ gives in good yield (120) methyl 6-chloronaphthoate.

 \ddot{C} with phthalic anhydride (1:0725) + AlCl₃ gives (121) (122) (123) (124) o-(4-chlorobenzoyl)benzoic acid [Beil. X-750, X₁-(356)], m.p. 147-148°, which on ring closure with

cone. H₂SO₄ yields 2-chloroanthraquinone (3:4922) q.v. [For corresp. reactns. of Č with 4-bromophthalic anhydride (125), 4-sulfophthalic anhydride (126), naphthalene-1,2-dicarboxylic acid anhydride (127), or naphthalene-2,3-dicarboxylic acid anhydride (128) see indic. refs.]

Miscellaneous condensations. \bar{C} with acetylene + AlCl₃ gives (129) 1,2-bis(4-chlorophenyl)ethane (4,4'-dichlorodibenzyl) + other prods., cf. also (130). — \bar{C} with propylene in pres. of sulfonic acids at 86–130° gives (131) isopropylbenzene (cumene) (1:7440). — \bar{C} + hexene-3 + H₂F₂ gives (25% yield (132)) 4-chloro-(1'-ethylbutyl)benzene. — \bar{C} + cyclohexene + conc. H₂SO₄ gives (50% yield (133)) 4-chlorophenylcyclohexane. — \bar{C} + allyl chloride (3:7035) + conc. H₂SO₄ gives (133) 1-chloro-2-(p-chlorophenyl)propane.

 \tilde{C} + isopropyl alc. with 80% H₂SO₄ at 70° gives (72% yield (134)) 4-chloro-isopropyl-benzene (3:8705). $-\bar{C}$ with ter-butyl alc. + AlCl₃ gives (135) 4-chloro-ter-butylbenzene; \bar{C} with ter-amyl alc. + AlCl₃ gives (135) 4-chloro-ter-amylbenzene.

 $\ddot{\mathbf{C}}$ + CO + AlCl₃ + TiCl₄ at 60 atm. and 30-35° (136) or $\ddot{\mathbf{C}}$ + HCN + AlCl₃ at 100° for 6 hrs. (137) gives p-chlorobenzaldehyde (3:0765). — $\ddot{\mathbf{C}}$ + CO + cat. + steam at 300-400° (138) (139) gives benzoic acid. — $\ddot{\mathbf{C}}$ with paraformaldehyde + ZnCl₂ (140) (142) or $\ddot{\mathbf{C}}$ with formalin + HCl (141) or $\ddot{\mathbf{C}}$ with chloromethyl methyl ether (3:7085) + ZnCl₂ (142) or $\ddot{\mathbf{C}}$ with bis-(chloromethyl) ether (3:5245) + ZnCl₂ (142) yields p-chlorobenzyl chloride (3:0220) q.v. — $\ddot{\mathbf{C}}$ with p-chlorobenzyl chloride (3:0220) + H₂SO₄ yields (142) 4.4'-dichlorodiphenylmethane.

Č with chloral (3:5210) or chloral hydrate (3:1270) + conc. or fumg. H₂SO₄ gives 1,1,1-trichloro-2,2-bis-(p-chlorophenyl)ethane ("DDT") (3:3298) q.v.

Hydrolysis. \bar{C} is unaffected by protracted boilg. with aq. or even alc. alk.; however, by use of increased temp. and press. especially in pres. of catalysts the hydrolysis of \bar{C} constitutes an extremely important industrial process for manufacture of phenol.

For general studies on the catalytic hydrolysis of \bar{C} to phenol with steam at elevated temperatures see (143) (144) (145) (146); for patents employing this method see (147)–(159) incl. — For résumé of prepn. of phenol via Raschig method ($C_6H_6+HCl+O_2$ to \bar{C} with subsequent hydrolysis) see (160); for relevant patents see (161) (162) (163). — For sepn. of products of hydrolysis see (41) (164).

Č may also be hydrolyzed to phenol by means of aq. NaOH, Ca(OH)₂, Na₂CO₃, NaHCO₃, etc., at elevated temp. and press. especially in pres. of catalysts, notably copper: for impt. general review of these methods up to 1927 see (165); for general discussion see (166); for recent patents on this process and its variants see (167)–(182) incl. — For conv. of Č with alk. to 4-hydroxybiphenyl (1:1585) see (183) or to diphenyl ether (1:7125) see (184) (185) (186).

 \tilde{C} htd. with aq. Na₂S, NaSH, or H₂S under press. gives (187) (188) (189) (190) diphenyl sulfide and/or thiophenol. — \tilde{C} + H₂S + cat. at 700° gives (191) thiophenol.

[For use of C in prepn. of sulfur dyes by htg. with sulfur see (192) (193).]

Ammonolysis. \bar{C} with dry NH₃ does not react even in pres. of Cu + I₂ and high temp. and press. (194). — However, \bar{C} with conc. aq. NH₄OH htd. at high temp. and press. especially in pres. of Cu, Cu cpds., or other cat. yields aniline and/or diphenylamine; for general discussion of this reactn. see (195) (196) (197) (198) (199); for illustrative patents see (200)–(208) incl.; for purification of reactn. prod. see (209) (210). — For behavior of \bar{C} with Na in liq. NH₃ (211) and its use in detn. of halogen content of \bar{C} (212) see indic. refs. — For behavior of \bar{C} with KNH₂ in liq. NH₃ see (213) (214).

Nitration. \tilde{C} on mononitration, e.g., with mixt. of 10 ml. HNO₃ (D=1.52) + 50 ml. HNO₃ (D=1.48) for 25 g. \tilde{C} at 0° (215), gives a prod. contg. 69.9% p-chloronitrobenzene [Beil. V-243, V₁-(130), V₂-(183)], m.p. 82°, together with 29.8% o-chloronitrobenzene [Beil. V-241, V₁-(129), V₂-(180)], m.p. 32°; the p/o ratio is but little different at -30°;

for f.p./compn. curve of system p-chloronitrobenzene/o-chloronitrobenzene (eutectic, m.p. 14.7°, contg. 33.1% p-isomer) see (215). — For mononitration using 0.9 g. of 70% HNO₃ + 1.29 g. 94% H₂SO₄ per gram of \bar{C} (216) or using nitrosulfonic acid (from fumg. HNO₃ treated with SO₂) at 30° (217) or using Fe(NO₃)₃ in Ac₂O at 40–45° (218) see indic. refs. — Note that no appreciable amt. of m-chloronitrobenzene is formed by direct nitration of \bar{C} .

Č on dinitration, e.g., with 5 wt. pts. of a mixt. consisting of equal wts. of 92.8% HNO₃, 93.3% H₂SO₄, and fumg. H₂SO₄ (contg. 14.2% SO₃) at 95° for 2 hrs. (219) gives 96.7% yield 2,4-dinitrochlorobenzene [Beil. V-263, V-(137), V₂-(196)], cryst. from alc., m.p. 52-53°. [The other dinitro isomers are known but need not be discussed here.]

Sulfonation. \bar{C} is insol. in cold conc. H_2SO_4 ; however, \bar{C} on warming or on stdg. at room temp. for 48 hrs. (220) with equal wt. conc. H_2SO_4 dissolves and later ppts. p-chlorobenzenesulfonic acid [Beil. XI-54, XI₁-(14)], anhydrous cryst. from CHCl₃, m.p. 92-93° (220), monohydrate from aq., m.p. 67° (221). — \bar{C} with fumg. H_2SO_4 (10% SO_3) below 60° for 1 hr. then poured into 6 vols. satd. aq. NaCl soln. gives (222) (223) sodium salt of p-chlorobenzenesulfonic acid which with PCl₅ yields corresp. sulfonyl chloride (see below). — For reactn. of \bar{C} with ClSO₃H see below. — [The corresp. bis- (4-chlorophenyl) sulfone [Beil. VI-327, VI₁-(149)] which may be formed in small amt. has m.p. 147-148°.] [For study of kinetics of sulfonation of \bar{C} see (231).]

- **p-Bromochlorobenzene:** \bar{C} with 0.25-0.50 mole Br₂ at 60° in pres. of Fe gives (88% yield (99)) p-bromochlorobenzene, cryst. from alc., m.p. 67-68°.
- ② 2,4-Dinitrochlorobenzene: C on htg. with mixt. of HNO₃ + H₂SO₄ (see above under nitration) at 95° for 2 hrs. gives (96.7% yield (219)) 2,4-dinitrochlorobenzene, cryst. from alc., m.p. 52-53°.

3:7903 (1) Brooks, Hobbs, J. Am. Chem. Soc. 62, 2851 (1940). (2) Stull, J. Am. Chem. Soc. 59, 2729 (1937). (3) Feitler, Z. physik. Chem. 4, 68 (1889). (4) Timmermans, Martin, J. chim. phys. 23, 780-782 (1926). (5) Lecat, Rec. trav. chim. 46, 242 (1927). (6) Grimm, Patrick, J. Am. Chem. Soc. 45, 2799 (1923). (7) Timmermans, Bull. soc. chim. Belg. 30, 67 (1921). (8) Timmermans, van der Horst, Onnes, Compt. rend. 174, 366 (1922); Cent. 1923, IV 377. (9) Young, Proc. Roy. Dublin Soc. 12, 424 (1909/10). (10) Timmermans, Bull. soc. chim. Belg. 24, 244-269 (1909); Cent. 1916, II 442.

(11) Gross, Saylor, J. Am. Chem. Soc. 53, 1748 (1931). (12) Matthews, J. Am. Chem. Soc. 48, 570 (1926). (13) Othmer, Ind. Eng. Chem. 35, 619 (1943). (14) Thomson, J. Chem. Soc. 1937, 1055. (15) McAlpine, Smyth, J. Chem. Phys. 3, 56 (1935). (16) Hurdis, Smyth, J. Am. Chem. Soc. 64, 2212 (1942). (17) Ramsay, Steele, Z. physik. Chem. 44, 362-363 (1903). (18) Patterson, McDonald, J. Chem. Soc. 93, 941 (1908). (19) Ramsay, Young, Z. physik. Chem. 1, 248 (1887). (20) Young, J. Chem. Soc. 55, 490, 502 (1889).

(21) Hrynakowski, Szmyt, Z. physik. Chem. A-182, 110-112 (1938). (22) Pascal, Bull. soc. chim. (4) 13, 745-752 (1913). (23) Timmermans, Bull. soc. chim. Belg. 43, 633 (1934). (24) L. Klemm, W. Klemm, G. Schiemann, Z. physik. Chem. A-165, 384-386 (1933). (25) Timmermans, Bull. soc. chim. Belg. 25, 300-327 (1911); Cent. 1911, II 1015. (26) Bridgman, J. Chem. Phys. 9, 794-795 (1941). (27) Skau, J. Phys. Chem. 37, 612-613 (1933). (28) Burnham, Madgin, J. Chem. Soc. 1936, 790-792. (29) Menschutkin, J. Russ. Phys.-Chem. Soc. 43, 402 (1911); Cent. 1910, II 379. (30) Bridgman, Phys. Rev. (2) 6, 7-10 (1915). (31) Curran, J. Am. Chem. Soc. 64, 830 (1942). (32) Sugden, J. Chem. Soc. 1933, 772. (33)

(31) Curran, J. Am. Chem. Soc. **64**, 830 (1942). (32) Sugden, J. Chem. Soc. **1933**, 772. (33) Biron, J. Russ. Phys.-Chem. Soc. **42**, 148 (1910); Cent. **1910**, I 1912. (34) Meyer, Mylius, Z. physik. Chem. **95**, 356 (1920). (35) Smyth, Morgan, J. Am. Chem. Soc. **50**, 1554 (1928). (36) Dobrosserdow, J. Russ. Phys.-Chem. Soc. **44**, 692 (1912); Cent. **1912**, II 789. (37) Margulewa, J. Russ. Phys.-Chem. Soc. **46**, 237 (1914); Cent. **1914**, I 2137. (38) Brühl, Ann. **200**, 187 (1879).

- (39) Miller, Bull. soc. chim. Belg. 48, 447-550 (1939). (40) Himstedt, Wertheimer, Ann. physik. (4) 67, 395-406 (1922).
- (41) Prahl, Mathes, Angew. Chem. 47, 11-13 (1934). (42) Baud, Bull. soc. chim. (4) 13, 436 (1913). (43) Coulter, Lindsay, Baker, Ind. Eng. Chem. 33, 1251-1253 (1941). (44) Linard, Bull. soc. chim. Belg. 34, 392-393 (1925). (45) Menschutkin, J. Russ. Phys.-Chem. Soc. 45, 1706 (1913); Cent. 1914, I 463. (46) Lacher, Hunt, J. Am. Chem. Soc. 63, 1753 (1941). (47) Othmer, White, Trueger, Ind. Eng. Chem. 33, 1242, 1245 (1941). (48) Trimble, Frazer, Ind. Eng. Chem. 21, 1064 (1929). (49) Marcs (to Monsanto Chem. Co.), U.S. 2,111,866, March 22, 1938; Cent. 1938, I 4719. (50) Moyer (to Solvay Process Co.), U.S. 2,152,357, March 28, 1939; Cent. 1938, II 1775.
- (51) Prahl (to F. Raschg), Ger. 539,176, March 7, 1932; Brit. 362,817, Dec. 31, 1931; French 715,009, Nov. 24, 1931; Cent. 1932, II 2642. (52) Bourion, Ann. chim. (9) 14, 215-272, 273-321 (1920). (53) Lane, Noyes, J. Am. Chem. Soc. 54, 161-169 (1932). (54) Hodgson, Foster, J. Chem. Soc. 1942, 582-583. (55) Waters, J. Chem Soc. 1937, 2007-2014. (56) Seide, Scherlin, Bras, J. prakt. Chem. (2) 138, 55, 65, 227 (1933). (57) LeFevre, Markham, J. Chem. Soc. 1934, 703-705. (58) Gilman, Fothergill, J. Am. Chem. Soc. 51, 3501-3508 (1929). (59) LeFevre, J. Chem. Soc. 1932, 1745-1747. (60) LeMaistre, Ramsford, Hauser, J. Org. Chem. 4, 106-110 (1939).
- (61) Erlenmeyer, Leo, Helv. Chim. Acta 16, 897-904 (1933). (62) Wieland, Ann. 514, 155-156 (1934). (63) Kozeschkow, Nesmejanow, Potrosow, Ber. 67, 1140 (1934). (64) Ainley, Challenger, J. Chem. Soc. 1936, 2175-2176. (65) Barkenbus, Hopkins, Allen, J. Am. Chem. Soc. 61, 2452-2453 (1939). (66) Bradt, Green, J. Org. Chem. 1, 540-543 (1937). (67) Billman, Dougherty, J. Am. Chem. Soc. 61, 387-389 (1939). (68) Lock, Rodiger, Ber. 72, 867-868 (1939). (69) Buchheim (to Chem. Fabrik von Heyden), Get. 616,596, Aug. 1, 1935, Cent. 1935, II 3703.
- (71) Kramers, Ann. 189, 135-141 (1877). (72) Brown, Durand, Marvel, J. Am. Chem. Soc. 58, 1594-1596 (1936). (73) Busch, Schmidt, Ber. 62, 2617 (1929). (74) Busch, Weber, J. prakt. Chem. (2) 146, 15, 22 (1936). (75) Stepanov, J. Russ. Phys.-Chem. Soc. 37, 15 (1905); Cent. 1905, I 1273. (76) Jöwenherz, Z. physik. Chem. 40, 414 (1902). (77) Lowenherz, Z. physik. Chem. 32, 486 (1940). (78) Lowenherz, Z. physik. Chem. 29, 413-414 (1899). (79) Klages, Liecke, J. prakt. Chem. (2) 61, 313, 319 (1900). (80) Kelber, Ber. 50, 309 (1917).
- (81) Sabatier, Mailhe, Compt. rend. 138, 246 (1904). (82) Matthews, J. Chem. Soc. 61, 104-111 (1892). (83) Kharasch, Berkman, J. Org. Chem. 6, 810-817 (1941). (84) Bender (to Great Western Electrochem. Co.). U.S. 2,010,841, Aug. 13, 1935; Cent. 1936, I 1112. (85) Hart, Noyes, J. Am. Chem. Soc. 58, 1305-1310 (1934). (86) Holleman, van der Linden, Cent. 1916, II 640-641; Rec. trav. chim. 30, 321-329 (1911). (87) Cohen, Hartley, J. Chem. Soc. 87, 1362-1363 (1905). (88) Silberrad, J. Chem. Soc. 121, 1019 (1922). (89) Thomas, Compt. rend. 126, 1212 (1898). (90) Seyewetz, Trawitz, Compt. rend. 136, 242 (1903).
- (91) Wibaut, van de Lande, Wallagh, Rec. trav. chim. 56, 65-70 (1937). (92) Wibaut, van de Lande, Wallagh (to Dow Chem. Co.), U.S. 2,123,857, July 12, 1938; Cent. 1939, I 250. (93) Korner, Gazz. chim. ital. 4, 342-343 (1874). (94) Mouneyrat, Pouret, Bull. soc. chim. (3) 19, 801-802 (1898). (95) Cohen, Dakin, J. Chem. Soc. 75, 895 (1899). (96) Thomas, Compt. rend. 128, 1577 (1899). (97) Lauer, Oda, Ber. 69, 984 (1936). (98) van Loon, Wibaut, Rec. trav. chim. 56, 826-828 (1937); Nature 139, 151 (1937). (99) Holleman, van der Linden, Rec. trav. chim. 30, 356-361 (1911). (100) Gilman, Zoellner, Selby, J. Am. Chem. Soc. 55, 1253 (1933).
- (101) Wittig, Pieper, Fuhrmann, Ber. 73, 1193 (1940). (102) Bachmann, Clarke, J. Am. Chem. Soc. 49, 2089-2098 (1927). (103) Morton, Fallwell, J. Am. Chem. Soc. 60, 1429-1431 (1938). (104) Morton, Hechenbleikner, J. Am. Chem. Soc. 58, 1697-1701 (1936). (105) Morton, LeFevre, Hechenbleikner, J. Am. Chem. Soc. 58, 754-757 (1936). (106) Morton, Stevens, J. Am. Chem. Soc. 53, 4030 (1931). (107) Morton, Stevens, J. Am. Chem. Soc. 53, 2246 (1931). (108) Imperial Chem Ind., Ltd., French 687,316, Aug. 7, 1930; Cent. 1930, II 3851. (109) Morgan, Vining, J. Chem. Soc. 117, 778-779 (1920). (110) Gilman, N. B. St. John, Rec. trav. chim. 49, 717-723 (1930).
- (111) Gilman, Brown, J. Am. Chem. Soc. 52, 3330-3332 (1930). (112) Schorigin, Issaguljanz, Gussewa, Ossipowa, Poljakowa, Ber. 64, 2584-2588 (1931). (113) I.G., Italian 341,937, May 14, 1936; Cent. 1937, II 2073. (114) von Dumreicher, Ber. 15, 1866-1870 (1882). (115) Harlow, Ross (to Dow Chem. Co.), U.S. 1,891,415, Dec. 20, 1932; Cent. 1933, I 1683. (116) Norris, Green, Am. Chem. J. 26, 492-499 (1901). (117) Norris, Twieg, Am. Chem. J. 30, 392-399 (1903). (118) Gomberg, Cone, Ber. 37, 1635-1636 (1904); 39, 1465, 3280-3282 (1906). (119) Price, Chapin, Goldman, Krebs, Shafer, J. Am. Chem. Soc. 63, 1861 (1941). (120) Price, Huber, J. Am. Chem. Soc. 64, 2136-2139 (1942).
 - (121) Murch (to National Aniline & Chem. Co.), U.S. 1,746,736, Feb. 11, 1930; Cent. 1930,

I 2798. (122) Müller, (to I.G.), Ger. 495,447, April 7, 1930; Cent. 1931, I 1675. (123) Lloyd, Gershon (to W. M. Grosvenor), U.S. 1,826,621, Oct. 6, 1931; Cent. 1931, II 3663. (124) Jacobson (to Calco Chem. Co.), U.S. 1,942,430, Jan. 9, 1934; Cent. 1934, I 2493. (125) Waldmann, J. prakt. Chem. (2) 126, 75 (1930). (126) Schwenk, Waldmann, Angew. Chem. 45, 20 (1932). (127) Waldmann, J. prakt. Chem. 127, 199-200 (1930). (128) Waldmann, Mathiowetz, Ber. 64, 1717-1718 (1931). (129) Cook, Chambers, J. Am. Chem. Soc. 43, 338 (1921). (130) Böeseken, Adler, Rec. trav. chim. 48, 482-483 (1929).

(131) Pine, Isham, U.S. 2,014,766, Sept. 17, 1935; Cent. 1936, I 4990. (132) Spiegler, Tinker, J. Am. Chem. Soc. 61, 1003 (1939). (133) Truffault, Compt. rend. 207, 677 (1938). (134) Meyer, Bernhauer, Monatsh. 53/54, 741 (1929). (135) Zuckerwanik, J. Gen. Chem., (U.S.S.R.) 8, 1512-1515 (1938). (136) I.G., Biit. 334,009, Sept. 18, 1930; Cent. 1930, II 3850. (137) Hinkel, Ayling, Beynon, J. Chem. Soc. 1936, 342. (138) Dieterle, Exchenbach, Ger. 537,610, Nov. 6, 1931; Cent. 1932, I 1155. (139) Marecek, Chem. Obzor 7, 171-173 (1932); Cent. 1933, I

1286; C.A. 27, 1876 (1933). (140) Blanc, Bull. soc. chim. (4) 33, 317-318 (1923).

(141) Tschunkur, Eichler (to I.G.), Ger. 509,149, Oct. 8, 1930; Cent. 1931, I 360. (142) Stephen, Short, Gladding, J. Chem. Soc. 117, 522-523 (1920). (143) Vernon, Thompson, J. Phys. Chem. 44, 727-730 (1940). (144) Tishchenko, Churbakov, J. Applied Chem. (U.S.S.R.) 7, 764-769 (1934); Cent. 1935, II 2358; C.A. 29, 2520 (1935). (145) Tishchenko, Gutner, Faerman, Shchigelskaya, J. Applied Chem. (U.S.S.R.) 8, 685-694 (1935); Cent. 1936, I 3907; C.A. 30, 4155 (1936). (146) Chalkey, J. Am. Chem. Soc. 51, 2489-2495 (1929). (147) Redman (to Bakelite Corp.), U.S. 2,311,777, Feb. 23, 1943, C.A. 37, 4405 (1943). (148) Meyer (to A.O. Smith Corp.), U.S. 2,138,609, Nov. 29, 1938; Cent. 1939, I, 1654. (149) Bertsch (to Monsanto Chem. Co.), U.S. 1,966,281, July 10, 1934; Cent. 1935, I 959. (150) Steingrover, Zellmann (to Chem. Fabrik. von Heyden), U.S. 1,961,834, June 5, 1934; Cent. 1934, II 1845.

(151) Jenkins, Norris (to Swann Research, Inc.), U.S. 1,950,359, March 6, 1934; Cent. 1934, II 1201. (152) Rittler (to Chem. Fabrik von Heyden), U.S. 1,936,567, Nov. 21, 1933; Cent. 1934, I 1711. (153) Jenkins, Norris (to Swann Research, Inc.), U.S. 1,884,710, Oct. 25, 1932; Cent. 1933, I 1998. (154) Kennedy, Lloyd (to Federal Phosphorus Co.), U.S. 1,735,327, Nov. 12, 1929; Cent. 1930, I 2009. (155) Zelnskii, Ushakov, Russ. 30,688, June 30, 1933, Cent. 1934, I 767. (156) Progil, Soc. An., French 720,721, Feb. 23, 1932; Cent. 1932, II 616. (157) Dreyfus, French 709,184, Aug. 4, 1931; Cent. 1931, II 2933. (158) Progil, Soc. An., Italian 302,818, Oct. 26, 1931; Cent. 1938, I 3263. (159) I.G., Brit. 308,220, May 15, 1929; Cent. 1930, II 1772. (160) Mathes, Augew. Chem. 52, 591-592 (1939); Olive, Chem. & Met. Eng. 47, 770-775, 789-792 (1940).

(161) F. Raschig Co., Ger. 700,802, Nov. 28, 1940; C.A. 35, 7421 (1941). (162) F. Raschig Co., Ger. 588,649, Nov. 21, 1933, Cent. 1934, I 767. (163) F. Raschig Co., French 698,341, Jan. 29, 1931; Cent. 1931, II 1491. (164) Progil, Soc. An., French 765,128, June 2, 1934; Cent. 1934, II 1687. (165) Hale, Britton, Ind. Eng. Chem. 20, 114-124 (1928). (166) Ushakov, Zelinskii, J. Applied Chem. (U.S.S.R.) 5, 302-309 (1932), Cent. 1932, I 2242; C.A. 27, 276 (1933). (167) Grebe (to Dow Chem. Co.), U.S. 2,275,044, 2,275,045, March 3, 1942; C.A. 36, 4137 (1942). (168) Poffenberger (to Dow Chem. Co.), U.S. 2,137,587, Nov. 22, 1938; Cent. 1939, I 1254. (169) Raeth, Rittler, Steingroever (to Chem. Fabrik von Heyden), U.S. 2,079,383, May 4, 1937; Cent. 1937, II 858. (170) Grebe, Reilly (to Dow Chem. Co.), U.S. 1,986,194, Jan. 1, 1935; Cent. 1935, II 1257.

(171) Hale, Britton (to Dow Chem. Co.), U.S. 1,925,321, Sept. 5, 1933; Cent. 1934, I 127. (172) Grebe, Dow (to Dow Chem. Co.), U.S. 1,924,313, Aug. 29, 1933; Cent. 1934, I 127. (173) Putnam (to Dow Chem. Co.), U.S. 1,921,373, Aug. 8, 1933; Cent. 1934, I 127. (174) Hale, Britton (to Dow Chem. Co.), U.S. 1,882,824, Oct. 18, 1932; Cent. 1933, I 309. (175) Hale (to Dow Chem. Co.), U.S. 1,868,140, July 19, 1932; Cent. 1933, I 309. (176) Griswold (to Dow Chem. Co.), U.S. 1,833,485, Nov. 24, 1931; Cent. 1932, I 739. (177) Hale, Britton (to Dow Chem. Co.), U.S. 1,806,798, May 26, 1931; Cent. 1931, II 1348. (178) Hale, Britton (to Dow Chem. Co.), U.S. 1,737,841, 1,737,842, Dec. 3, 1929, Cent. 1930, II 803. (179) Williams, Britton (to Dow Chem. Co.), U.S. 1,756,110, April 29, 1930; Cent. 1930, II 803. (180) Rath, Buchheim, Rittler (to Chem. Fabrik von Heyden), Ger. 586,646, Oct. 25, 1933; French 751,158, Aug. 28, 1933; Cent. 1934, I 126.

(181) Vorozhtzov, Oshuev, Russ. 28,219, Nov. 30, 1932; Cent. 1933, II 3195; C.A. 27, 3724 (1933). (182) Chem. Fabrik von Heyden, Brit. 382,969, Dec. 1, 1932; Cent. 1933, I 2315. (183) Hale (to Dow Chem. Co.), U.S. 1,922,695, Aug. 15, 1933; Cent. 1934, I 128. (184) Hale (to Dow Chem. Co.), U.S. 1,744,961, Jan. 28, 1930; Cent. 1936, II 803. (185) I.G., French 755,051, Nov. 18, 1933; Cent. 1934, I 945. (186) Vorozhtzov, Oshuev, Russ. 40,345, Dec. 31, 1934; C.A. 30, 3838 (1936). (187) Vorozhtzov, Mitzengelder, Compt. rend. acad. sci. (U.R.S.S.) 1933, 291-295; Cent. 1935, I 1860; C.A. 28, 2340 (1934). (188) Vorozhtzov, Mützenhandler,

Russ. 34,554, Feb. 28, 1934; Cent. 1935, I 2442; C.A. 29, 2977 (1935). (189) Vorozhtzov-Mladschi Mitzengendler, Russ. 29,168, Feb. 28, 1933; Cent. 1933, II 3195. (190) Hale (to Dow Chem. Co.), U.S. 1,825,662, Oct. 6, 1931; Cent. 1931, II 3264.

(191) Ohse (to Chem. Fabrik von Heyden), Ger. 497,570, May 8, 1930; Cent. 1930, II 622. (192) Palmer, Lloyd, J. Am. Chem. Soc. 52, 3388-3395 (1930). (193) Palmer, Lloyd, McLure, LeMaistre, Waring, Bachman, J. Am. Chem. Soc. 62, 1005-1006 (1940). (194) Stähler, Ber. 47, 912 (1914). (195) Quick, J. Am. Chem. Soc. 42, 1041-1042 (1920). (196) Groggins, Stirton, Ind. Eng. Chem. 28, 1051-1056 (1936). (197) Vorozhtzov, Kobelev, Compt. rend. acad. sci. (U.R.S.S.), 3, 108-114 (1934); Cent. 1935, I 3653; C.A. 28, 6706 (1934). (198) Vorozhtzov, Kobelev, J. Gen. Chem. (U.S.S.R.) 4, 310-323 (1934); Cent. 1935, II 505; C.A. 29, 1787 (1935). (199) Vorozhtzov, Kobelev, J. Gen. Chem. (U.S.S.R.) 8, 1106-1119 (1938); Cent. 1939, II 3397. (200) Calcott, Bake (to du Pont Co.), U.S. 2,062,349, Dec. 1, 1936; Cent. 1937, II 472.

(201) Booth (to Swann Research, Inc.), U.S. 1,954,469, April 10, 1934; Cent. 1934, II 1846. (202) Prahl, Mathes (to Raschig Co.), Ger. 579,229, June 22, 1933; Cent. 1933, II 1430. (203) Williams (to Dow Chem. Co.), U.S. 1,840,760, Jan. 12, 1932; Cent. 1932, I 3498. (204) Hale (to Dow Chem. Co.), U.S. 1,804,466, May 12, 1931; Cent. 1931, II 1195. (205) Federal Phosphorus Co., Brit. 370,774, May 5, 1932; Cent. 1932, II 1237. (206) Hale (to Dow Chem. Co.), U.S. 1,764,869, June 17, 1930; Cent. 1930, II 1442. (207) Britton, Williams (to Dow Chem. Co.), U.S. 1,726,170-1,726,173 incl., Aug. 27, 1929; Cent. 1930, I 2479. (208) A.G.F.A., Ger. 204,951, Dec. 14, 1908; Cent. 1909, I 475. (209) Britton (to Dow Chem. Co.), U.S. 1,823,024, 1,823,025, Sept. 15, 1931; Cent. 1932, II 1237. (210) Britton, Williams, Putnam (to Dow Chem. Co.), U.S. 1,823,026, Sept. 15, 1931; Cent. 1932, II 1237.

(211) White, J. Am. Chem. Soc. 45, 779-784 (1923). (212) Dains, Brewster, J. Am. Chem. Soc. 42, 1573-1579 (1920). (213) Bergstrom, Wright, Chandler, Gilkey, J. Org. Chem. 1, 170-178 (1936). (214) Wright, Bergstrom, J. Org. Chem. 1, 179-188 (1936). (215) Holleman, de Bruyn, Rec. trav. chim. 19, 189-197, 375 (1900). (216) Bashioum, Powers, Ind. Eng. Chem. 15, 407-408 (1923). (217) Varma, Kulkarni, J. Am. Chem. Soc. 47, 143-147 (1925). (218) Menke, Rec. trav. chim. 44, 146 (1925). (219) Hoffman, Dame, J. Am. Chem. Soc. 41, 1015-1016 (1919). (220) Tanasescu, Macarovici, Bull. soc. chim. (5) 5, 1128 (1939).

(221) Meyer, Schmidt, Ann. 433, 333 (1923). (222) Baxter, Chattaway, J. Chem. Soc. 107, 1815 (1915). (223) Davies, Wood, J. Chem. Soc. 1928, 1124-1125. (224) Huntress, Carten, J. Am. Chem. Soc. 62, 512-513 (1940). (225) van Arkel, Vles, Rec. trav. chim. 55, 408 (1936). (226) Coffin, Holt, Analyst 44, 226-229 (1919). (227) Frankland, Carter, Webster, J. Soc. Chem. Ind. 38, 153-155T (1919). (228) Emmons, Am. Mineral. 14, 482-483 (1929). (229) Cameron, Thomas, et al., J. Path. Bact. 44, 281-296 (1937). (230) Smyth, Ind. Eng. Chem., Anal. Ed. 8, 379 (1936).

(231) Wadsworth, Hinshelwood, J. Chem. Soc. 1944, 469-473.

3: 7905 2-CHLORO-2-METHYLPROPANOL-1 Cl C₄H₉OCl Beil. I - 378 (" β -Isobutylene chlorohydrin"; CH₃—C—CH₂OH I₁— I₂— I₂—

B.P. 132-133° sl. dec. (1).

[See also 1-chloro-2-methyl-propanol-2 (3:7752).]

Colorless visc. liq. with disagreeable odor (1). — Does not freeze in mixt. of solid CO_2 + ether (1). — Sol. in cold fumg. HCl (1).

[For prepn. (accompanied by the isomeric 1-chloro-2-methylpropanol-2 (3:7752)) from 2-methyl-1,2-epoxypropane (isobutylene oxide) + HCl see (1) (2) (3).]

Č on stdg. a few days with aq. yields (2) isobutyraldehyde (1:0120) [cf. behavior of 1-chloro-2-methylpropanol-2 (3:7752)].

- —— β-Chloroisobutyl acetate: unreported.
- ---- β-Chloroisobutyl benzoate: unreported.
- ---- β-Chloroisobutyl p-nitrobenzoate: unreported.
- ----- β-Chloroisobutyl 3,5-dinitrobenzoate: unreported.
- ---- 2-(N-Phthalimido)-2-methylpropanol-1: unreported.

127-130°

at 748 mm. (9)

3:7905 (1) Henry, Compt. rend. 142, 495-496 (1906). (2) Michael, Leighton, Ber. 39, 2793-2795 (1906). (3) Krassusky, J. prakt. Chem. (2) 75, 238-247 (1907).

3: 7908 METHYL
$$d$$
, l - α -CHLOROPROPIONATE C₄H₇O₂Cl Beil. II - 249 CH₃-CH—C=O II₁-(111) II₂-(226) B.P. 132.5° (1) $D_4^{20} = 1.1374$ (4) $n_D^{20} = 1.4182$ (4) 130.9–131.5° at 760 mm. (2) 130–132° at 767 mm. (3)

[For prepn. of \tilde{C} from α -chloropropionyl chloride (3:5320) with MeOH see (1); for formn. of \tilde{C} (20% yield) together with other prods. from phosgene (3:5000) + methyl lactate (1:3236) + pyridine see (3); for formn. (90% yield) from methyl α -aminopropionate hydrochloride with HCl + NaNO₂ see (5); for prepn. of \tilde{C} from methyl lactate (1:3236) with SOCl₂ (71% yield) see (9).]

 $[\bar{C} + 1-5\% \text{ FeCl}_3 \text{ at } 100^\circ \text{ or above loses HCl yielding (6) methyl acrylate (1:3025), b.p. 80.3°.]}$

[\overline{C} with MeOH/NaOMe gives (63% yield (9)) methyl α -methoxypropionate [Beil. III-280, III₁-(109)], b.p. 127-129° at 747 mm. (9).]

 \bar{C} on hydrolysis yields MeOH (1:6120) + α -chloropropionic acid (3:6125). [For study of kinetics of hydrolysis see (7).] — For the amide, anilide, p-toluidide, and other derivs. corresp. to \bar{C} see the acid (3:6125).

D Methyl α -(tetrachlorophthalimido)-propionate: pl. from alc., m.p. 165-166° (8). [From \ddot{C} + K tetrachlorophthalimide as directed (8).]

3:7908 (1) Kahlbaum, Ber. 12, 343-344 (1879).
 (2) Burkard, Kahovec, Monatsh. 70, 340 (1938).
 (3) Rıtchie, J. Chem. Soc. 1935, 1059.
 (4) Schjanberg, Z. physik. Chem. A-172, 230 (1935).
 (5) Barker, Skinner, J. Am. Chem. Soc. 46, 409-410 (1924).
 (6) Barrett (to du Pont), U.S. 2,013,648, Sept. 10, 1935; Cent. 1936, I 3217; C.A. 29, 6902 (1935).
 (7) Bürki, Helv. Chim. Acta 1, 243-244 (1918).
 (8) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934).
 (9) Niemann, Benson, Mead, J. Org. Chem. 8, 401 (1943).

3: 7915 d,l-5-CHLORO-2-METHYLPENTENE-2
$$C_6H_{11}Cl$$
 Beil. I — Cl CH_3 I_1 — I_2 —(194)

B.P. 132–133° at 759 mm. (1) $D_2^{20} = 0.92653$ (1) $n_D^{20} = 1.44193$ (1)

[For prepn. of C from dimethyl-cyclopropyl-carbinol [Beil. VI-10] by shaking with conc. HCl see (1) (2.5-dichloro-2-methylpentane (3:8550) is also formed (1)).

 \tilde{C} on prolonged treatment with KOAc + AcOH yields (1) corresp. acetate, b.p. 170-171°, $D_A^{20} = 0.9108$, $n_D^{20} = 1.43107$ (1).

 \bar{C} with NaOEt yields (1) corresp. ethyl ether, 5-ethoxy-2-methylpentene-2, b.p. 142-143°, $D_{4}^{20} = 0.7989$, $n_{1}^{20} = 1.41948$ (1).

 \tilde{C} on protracted boilg. with aq. + CaCO₃, followed by further treatment with alc. KOAc + a little NaI, regenerates (1) dimethyl-cyclopropyl-carbinol, b.p. 124-125° at 762 mm. $D_A^{20} = 0.8800$, $n_D^{20} = 1.43237$ (1).

3:7915 (1) Bruylants, Dewael, Bull. sci. acad. roy. Belg. (5) 14, 140-153 (1928); Cent. 1928, I 2708; C.A. 22, 3883 (1928).

3: 7917
$$d$$
, l -2-CHLOROPROPANOL-1 CH_3 — CH — CH_2 C_3H_7OCl Beil. I - 356 (Propylene β -chlorohydrin; Cl OH I₂-(369) B.P. 133–134° cor. at 762 mm. (1) $D_-^{20} = 1.103$ (1) $n_D^{20} = 1.43623$ (1) 133–134° at 761 mm. (2) 133–134° at 760 mm. (3) $D_4^{15} = 1.4505$ (9) $n_D^{15} = 1.4766$ (9) 133° (10) 94° at 8 mm. (9)

[See also 1-chloropropanol-2 (3:7747).]

[For prepn. of \bar{C} from its acetate (see below) by alcoholysis with excess boilg. dry MeOH for 8 hrs. (83% yield) see (1); note that this prepn. really starts from the isomeric 1-chloropropanol-2, the conversion of which to \bar{C} involves the following steps: reaction with KOAc yielding CH₃.CH(OH).CH₂(OAc), conversion of latter with HCl + ZnCl₂ to CH₃.CH(Cl).-CH₂(OAc), and finally alcoholysis to \bar{C} as mentioned above (1) (4); for formn. of \bar{C} by alk. hydrol. of its trichloroacetate see (9).]

[Note that although \bar{C} is formed in other ways (e.g., from propanediol-1,2 (propylene glycol) (1:6455) with HCl or S₂Cl₂ (5), from 2,3-epoxybutane (propylene oxide) (1:6115) by addn. of HCl (5), from propylene with HOCl (5), or from α -chloro-n-propylamine with HNO₂ (6)) the product of these reactions appears to be (5) (6) an inseparable mixt. of about 40% \bar{C} with 60% of the isomeric 1-chloropropanol-2 (3:7747).]

Reactions of the halogen atom of \tilde{C} . $[\tilde{C}$ when added dropwise to conc. aq. KOH loses HCl yielding (1) 2,3-epoxybutane (propylene oxide) (1:6115), b.p. 35°. — \tilde{C} with KCN in 80% alc. contg. some NaI gives on warming (60% yield (2)) β -hydroxy-n-butyronitrile [Beil. III-309, III₂-(221)], b.p. 214-215° (2); note that this is not the product to be expected from simple replacement of Cl by CN and apparently results from preliminary formation of propylene oxide to which HCN then adds so as to give a straight (rather than forked) carbon chain.]

Reactions of the OH group of C. [C reacts normally as a substituted primary alc. giving ethers, esters, oxidn. products, etc.]

[$\bar{\mathbf{C}}$ readily gives the corresp. ethers; e.g., $\bar{\mathbf{C}}$ with Me₂SO₄ on warming gives $\langle 7 \rangle$ β -chloro-n-propyl methyl ether, b.p. 98–99° at 756 mm., $D_4^{20}=0.9946$, $n_D^{20}=1.40754$ $\langle 7 \rangle$; $\bar{\mathbf{C}}$ with EtOH + conc. H₂SO₄ on htg. gives (54%) yield $\langle 7 \rangle$) β -chloro-n-propyl ethyl ether, b.p. 116–117° at 758 mm., $D_4^{20}=0.9828$, $n_D^{20}=1.41285$ $\langle 7 \rangle$; for corresp. formn. of ethers with n-propyl alc. (1:6150) and with allyl alc. (1:6145) see $\langle 7 \rangle$.]

[\bar{C} (1 mole) with SO₂Cl₂ (2.5 moles) at 130° gives (16% yield {7}) bis-(β -chloro-n-propyl) ether, b.p. 188° at 762 mm., $D_4^{20} = 1.109$, $n_D^{20} = 1.4467$ (7); note that this ether is not obtd. from \bar{C} with cone. H₂SO₄ (7).]

[\bar{C} on oxidn. with 3 wt. pts. conc. HNO₃ as directed (8) (2) gives (85% yield (2)) α -chloropropionic acid (3:6125), accompanied by some acetic acid (1:1010) and oxalic acid (1:0445); note that \bar{C} on oxidn. with chromic acid yields no α -chloropropionic acid but only acetic acid (1:1010) and formic acid (1:1005) (2).]

- β-Chloro-n-propyl acetate [Beil. II-129, II₁-(58), II₂-(139)]: oil, insol. aq., b.p. 151-152° at 768 mm. (11), 152-153° at 750 mm. (1). [Prepd. indirectly; furthermore the prods. reported may be contaminated with some of the isomeric β-chloroisopropyl acetate cf. (10).]
- ---- β-Chloro-n-propyl benzoate: unreported.
- β -Chloro-n-propyl β -nitrobenzoate: unreported.
- ------ β -Chloro-n-propyl 3,5-dinitrobenzoate: unreported.

2-(Phthalimido)propanol-1 (N-(β-hydroxyisopropyl)phthalimide); lfts. from EtOAc m.p. 99-101° (10). [Prepd. indirectly (10); note that the prod. obtd. (10) from C with K phthalimide in s.t. at 200-230° was the isomeric 1-(phthalimido)propanol-2, m.p. 88-89° (10), but whether this result was due to contamination of C with the isomeric 1-chloro-propanol-2 (3:7747) or the rearr, has never been clarified.

3:7917 (1) Henry, Rec. trav. chim. 22, 327-333 (1903). (2) Dewael, Rec. trav. chim. 33, 504-507 (1924). (3) Henry, Rec. trav. chem. 22, 209-210 (1903). (4) Henry, Bull. acad. roy. Belg. 1902, 445-494; Cent. 1902, II 929. (5) Smith, Z. physik. Chem. 93, 59-85 (1919). (6) Smith, Platon, Ber. 55, 3150-3155 (1922). (7) Dewael, Bull. soc. chim. Belg. 34, 343-346 (1925). (8) Henry, Rec. trav. chim. 22, 341-344 (1903). (9) Gayler, Waddle, J. Am. Chem. Soc. 63, 3359 (1941). (10) Gabriel, Ohle, Ber. 50, 807, 812 (1917).

(11) Dewael, Bull. soc. chim. Belg. 39, 400 (1930).

B.P.
$$135^{\circ}$$
 at 760 mm. (7) $D_{15}^{15} = 1.0893$ (3) $n_{\rm D}^{21} = 1.4122$ (7) $133-135^{\circ}$ at 760 mm. (1) (2) $128-129.5^{\circ}$ at 753 mm. (3) $n_{\rm D}^{15} = 1.4019$ (3) $64-65^{\circ}$ at 55 mm. (3) $42-44^{\circ}$ at 17 mm. (7)

[For prepn. of \bar{C} from α -chloroisobutyric acid (3:0235) with MeOH see (3) (4); for formn. of \tilde{C} as by-product of reactn. of methyl α -hydroxyisobutyrate (1:3206) with phospene (3:5000) + pyridine see (1) (2) (6).]

(C on htg. at 500-510° (1), or passed over silica gel at 300° (4), or htd. with anhydrous FeCl₃ for 4 hrs. at 100° (5), or htd. with quinoline in pres. of hydroquinone (3), gives (83% yield (5)) methyl methacrylate, b.p. 100-101°.]

3:7918 (1) Burns, Jones, Ritchie, J. Chem. Soc. 1935, 717. (2) Ritchie, J. Chem. Soc. 1935, 1059. (3) Zal'kind, Markov, J. Applied Chem. (U.S.S.R.) 10, 1042-1044 (1937); Cent. 1938, II 2421; C.A. 32, 1652 (1938).
 (4) du Pont Co. & Loder, Brit. 428,223, June 6, 1935; Cent. 1936, I 179;
 C.A. 29, 6607 (1935).
 (5) Barrett (to du Pont Co.), U.S. 2013,648, Sept. 10, 1935; Cent. 1936, I 3217; C.A 29, 6902 (1935). (6) Imperial Chem. Ind & Ritchie, Jones, Burns, Brit. 424,885, March 4, 1935; Cent. 1936, I 2440; C.A. 29, 5124 (1935) (7) Kahovec, Kohliausch, Monatsh. 74, 116 (1943).

3: 7920 d,I-1,2-DICHLORO-2-METHYLBUTANE
$$C_8H_{10}Cl_2$$
 Beil. I — Cl Cl I_1 — I_2 —(101) CH₃.CH₂—C,CH₂ I_1 — I_2 —(101)

B.P.
$$133-135^{\circ}$$
 (1) $D_4^{20} = 1.0785$ (1) $n_D^{23.5} = 1.4432$ (4) 133.5° at 760 mm. (caled.) (4) 1.0766 (4) 71.5° at 100 mm. (4)

[For prepn. of C from 1,2-epoxy-2-methylbutane (1) with PCl₅ see (1); for formn. of Č (together with other products) from 2-methylbutene-1 (unsym.-ethyl-methyl-ethylene) (1:8210) with Cl_2 at -5 to -17° see (2) (3); for forms. of \bar{C} (together with other products) from dextrorotatory amyl chloride by photochemical chlorination with SO₂Cl₂ in pres. of benzoyl peroxide see (4).]

C on boilg. with aq. K₂CO₃ gives (1) (together with other products) 1-chloro-2-methyl-butene-1 (3:7303), b.p. 96-97°.

C on oxidn. with KMnO₄ gives (2) butanone-2 (ethyl methyl ketone) (1:5405).

3:7920 (1) Chalmers, Trans. Roy. Soc. Can. (3) 22, III 69-78 (1928). (2) Gutner, Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1062-1067 (1938); Cent. 1939, II 4221; C.A. 33, 3755 (1939). (3) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4222; C.A. 33, 4190 (1939). (4) Brown, Kharasch, Chao, J. Am. Chem. Soc. 62, 3437-3439 (1940).

3: 7925 1,3-DICHLOROBUTANE H
$$C_4H_8Cl_2$$
 Beil. I — $I_{1^-}(38)$ I_{2^-} CH₃.C.CH₂.CH₂ I_{2^-} Cl Cl Cl B.P. 134° (1) $D_4^{20} = 1.1158$ (3) $n_D^{20} = 1.445$ 131–133° at 758 mm. (3)

[For prepn. from butanediol-1,3 by htg. in s.t. with conc. HCl (satd. at 0°) see (1); for prepn. from 1-chlorobutane (n-butyl chloride) (3:7160) by actn. of Cl₂ in light (other products also being formed) see (2) (3) (4) (5); for prepn. from 2-chlorobutane (3:7125) by actn. of Cl₂ see (6).]

 \bar{C} on passing over alkali (NaOH, K₂CO₃, soda-lime, etc.) at elevated temperatures (e.g., 700-750°) yields butadiene-1,3. [For studies of this reaction see (2) (4) (5).]

C is readily saponified with aq. K₂CO₃ to butanediol-1,3 (1:6482) (6).

3:7925 (1) Fargher, Perkin, J. Chem. Soc. 105, 1356 (1914). (2) Muskat, Northrup, J. Am. Chem. Soc. 52, 4050-4052 (1930). (3) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 893-896 (1937); Cent. 1938, II 2575; C.A. 31, 5755 (1937). (4) Carothers (to du Pont), U.S. 2,038,593, April 28, 1936; Cent. 1936, II 3358; C.A. 30, 3912 (1936). (5) Muskat (to du Pont), U.S. 2,070,609, Feb. 16, 1937; Cent. 1937, II 2597; C.A. 31, 2236 (1937). (6) Tishchenko, Churbakov, J. Gen. Chem. (U.S.S.R.) 7, 663-666 (1937); Cent. 1937, II 372; C.A. 31, 5754 (1937).

3:7935 2-CHLOROPENTANONE-3
$$(\alpha$$
-Chloroethyl ethyl ketone; α -chlorodiethyl ketone) CH₃.CH₂—C—CH—CH₃ I_1 — I_2 —

B.P. 135° (1) (2) 145° (3)

Oil, insol. aq., sol. alc., ether.

[For prepn. of Č from pentanone-3 (diethyl ketone) (1:5420) with Cl₂ (3) (4), with Cl₂ in pres. of aq. + CaCO₃ (86% yield (1)), or with Cl₂ in vapor-phase chlorination (4) see indic. refs.; from 4-chloro-4-methyl-3-ethylisoxazolone-5 [Beil. XXVII-163] with hydrochloric acid see (2).]

 $\ddot{\mathbf{C}}$ on reduction with \mathbf{H}_2 yields (3) pentanone-3 (1:5420).

C does not (3) form a cpd. with satd. aq. NaHSO3 soln.

Č dis. readily in aq. alk. yielding a soln. (presumably contg. pentanone-3-ol-2) which readily reduces NH₄OH/AgNO₃ and reduces Fehling's soln. on warming (3).

[C in abs. alc. treated with NH₃ gas yields (3) 2,5-dimethyl-3,6-diethylpyrazine [Beil. XXIII-101], liq., b.p. 215-217°, forming with aq. a sublimable hydrate, m.p. 42.5°. (Note that 3-chloropentanone-2 (3:7893) similarly treated gives the same prod.)]

3:7935 (1) Justoni, Chimica e industria (Italy) 24, 89-94 (1942); Cent. 1943, I 383. (2) Hanriot, Reynaud, Bull. soc. chim. (3) 21, 14-15 (1899). (3) Demetre-Vladesco, Bull. soc. chim. (3) 6, 834-835 (1891). (4) Justoni, Chimica e industria (Italy) 24, 195-201 (1942); Cent. 1943, I 1659.

[For prepn. of \bar{C} from 2-methylhexanol-2 (n-butyl-dimethyl-carbinol) [Beil. I-415, I₂-(444)] (5) (6) with dry HCl gas at -10° (65-75% yield (6)) or at $10-15^\circ$ (75% yield (5)) (8), with conc. HCl (1), or with AcCl (1) (2) see indic. refs.; for formn. of \bar{C} as byproduct during reactn. of the above carbinol with $C_6H_6+AlCl_3$ (main prod. 45% yield of 2-methyl-2-phenylhexane, b.p. $106-109^\circ$ at 20 mm.) see (4); for prepn. of \bar{C} from 2-methylhexanol-3 (isopropyl-n-propyl-carbinol) [Beil. I-416, I₁-(206)] (3) with dry HCl at 0° (80% yield (3)) by rearrangement see (3).]

[For data on density and parachor of C at 25°, 50°, and 75° see (7).]

Č with Mg in dry ether as specified (5) gives 74.4% yield corresponding RMgCl.

 \bar{C} converted (as above) to RMgCl and the latter oxidized with O_2 gives (42% yield (3)) 2-methylhexanol-2, b.p. 139.5–140.5° at 741 mm., 110° at 250 mm., $D_4^{20}=0.813, n_D^{20}=1.4173$ (3).

[For reactn. of RMgCl with ethyl chloroformate (3:7295) yielding (5) ethyl n-butyl-dimethyl-acetate, b.p. 66.5– 70.0° at 16 mm., $n_{\rm D}^{20}=1.4148$ (5) (corresp. amide, m.p. 92.8–93.8° (5)) see (5); for reactn. of RMgCl with AcCl (3:7065) giving (9% yield (5)) 3,3-dimethylheptanone-2, b.p. 68– 70.5° at 20 mm., $n_{\rm D}^{20}=1.4206$ (semicarbazone, m.p. 129–130°) (5) see (5).]

Č converted to RMgCl and treated with CO₂ gives (5) n-butyl-dimethylacetic acid (constants not given (5)) (corresp. amide via acid chloride, m.p. 92.8-93.8° u.c. (5)).

3:7945 (1) Henry, de Wael, Bull. acad. roy. Belg. 1908, 957-963; Cent. 1909, I 1854; Rec. trav. chim. 28, 448 (1909). (2) Muset, Bull. acad. roy. Belg. 1906, 775-789; Cent. 1907, I 1313. (3) Whitmore, Johnston, J. Am. Chem. Soc. 60, 2266 (1938). (4) Huston, Fox, Binder, J. Org. Chem. 3, 252 (1939). (5) Whitmore, Badertscher, J. Am. Chem. Soc. 55, 1559-1567 (1933). (6) Whitmore, Woodburn, J. Am. Chem. Soc. 55, 363-364 (1933). (7) Quayle, Owen, Beavers, J. Am. Chem. Soc. 61, 3108 (1939). (8) Petrov, Kurbskii, J. Gen. Chem. (U.S.S.R.) 14, 492-494 (1944); C.A. 39, 4600 (1945).

3:7950 3-CHLORO-3-METHYLHEXANE Cl
$$C_1H_{16}Cl$$
 Beil. I — (Ethyl-methyl-n-propyl-carbinyl chloride) $CH_3.CH_2.CH_2$ — C — $CH_2.CH_3$ I_{1-} (58) I_{2-} (119) CH_3 B.P. abt. 135° (1) $D_4^{20} = 0.8787$ (4) $n_D^{20} = 1.4250$ (2) 1.4283 (3) 18 (4) (2) I_{16} (2) (5)

B.P. abt. 135° (1) $D_{4}^{\circ} = 0.8787$ (2) $n_{D}^{\circ} = 1.4280$ (2) 1.4283 (3) 41° at 20 mm. (3) $n_{D}^{18} = 1.4280$ (5) $n_{D}^{18} = 1.42705$ (4) $n_{D}^{18} = 1.42705$ (4)

[For prepn. of $\bar{\rm C}$ from 3-methylhexanol-3 (ethyl-methyl-n-propyl-carbinol) [Beil. I-416, I₁-(206), I₂-(445)] (2) with dry HCl at 10-15° (90% yield (2)) or with HCl (4) see (2) (4); for formn. of $\bar{\rm C}$ as a by-product of the reactn. of the above carbinol with ${\rm C_6H_6}+{\rm AlCl_3}$ (main prod. 45% yield of 3-methyl-3-phenylhexane, b.p. 106-107° at 20 mm., $n_D^{20}=1.4964$) see (3); for formn. of $\bar{\rm C}$ from 3-methylhexene-2 (1:8322) with conc. HCl see (5); for formn. of $\bar{\rm C}$ from ethyl-methyl-n-propyl-carbinyl isocyanate on htg. with conc. HCl see (1).]

[For data on density and parachor of \bar{C} at 0°, 15°, 25°, 50°, and 65° see (6).]

C with Mg in dry ether as specified (2) gives 67-78% yield corresponding RMgCl.

[\bar{C} converted as above to RMgCl, treated with formaldehyde gas, gives (30% yield (2)) 2-ethyl-2-methylpentanol-1, b.p. 75.5-76.0° at 15 mm., $n_D^{20} = 1.4353$ (2).]

 \bar{C} with C_6H_6 + AlCl₃ yields (4) 3-methyl-3-phenylhexane, b.p. 110-112° at 15 mm., D_4^{20} = 0.8819, n_1^{15} = 1.49951 (4).

3:7950 (1) Montagne, Ann. chim. (10) 13, 125 (1930). (2) Whitmore, Badertscher, J. Am. Chem. Soc. 55, 1561, 1565 (1933). (3) Huston, Fox, Binder, J. Org. Chem. 3, 253 (1939). (4) Halse, J. prakt. Chem. (2) 89, 452-453 (1914). (5) Nasarov, Ber. 70, 622 (1937). (6) Quayle, Owen, Beavers, J. Am. Chem. Soc. 61, 3108 (1939).

B.P.											
135-136°				(1)		$D_4^{20} =$	0.8784	(18)	$n_{\rm D}^{20} =$	1.42364	(1)
134-135° cor.	at	763	mm.	(2)	(3)		0.8765	(7)		1.4200	(4)
134°	at	759	mm.	(18)			0.87551	(8)		1.41991	(18)
134°	at	738	mm.	(4)						1.41944	(6)
133.6-134.4°				(5)							
132.9°	at	764.7	mm.	(6)							
132.7-133.3°				(15)							
132-133°	at	760	mm.	(7)							

Colorless mobile liq., insol. aq.

[For prepn. of \bar{C} from hexanol-1 (1:6230) by htg. with fumg. HCl in s.t. at 100° (100% yield) see (2); by shaking with HCl + ZnCl₂ for 2 days (45% yield), with PCl₃ + ZnCl₂ (61% yield), with PCl₅ + ZnCl₂ (77% yield), or with excess SOCl₂ (yield: 85-87% (1), 63% (18) see (1) (18)); for prepn. from 1-chlorohexene-2 by cat. reducts. see (9).]

[For formation (besides other products) from n-hexanc by chlorination see (10) (11) (12) (13); for formation from heavy metal n-caproates + Cl_2 see (14).]

C on refluxing with 10% aq. NaOH yields (9) n-hexanol (1:6230).

[For study of reaction of \tilde{C} with KI in acetone see (15); with metallic Na see (16); with NaC₂H₅ see (4); with CH₃NH₂ see (17).]

C with Mg in dry ether + trace I₂ gives (97.2% yield (19)) RMgCl.

— N-(n-Hexyl)tetrachlorophthalimide: lfts. from EtOH, m.p. 150-151° (20). [From C (?) or from n-hexyl bromide with K tetrachlorophthalimide (20).]

3:7955 (1) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III, 77-89 (1929). (2) Henry, Bull. acad. roy. Belg. 1905, 158-177; Cent. 1905, II 214 (3) Henry, Rec. trav. chim. 24, 354-355 (1905). (4) Whitmore, Zook, J. Am. Chem. Soc. 64, 1784 (1942). (5) Kohlrausch, Köppl, Monatsh. 63, 268 (1933). (6) Karvonen, Ann. Acad. Scr. Fennicae (A) 5, No. 6, 125 (1914), Cent. 1919, III 807. (7) Olivier, Rec. trav. chim. 55, 1035 (1936). (8) Karvonen, Cent. 1912, II 1271. (9) Hurd, McNamee, J. Am. Chem. Soc. 54, 1648-1651 (1932). (10) Schorlemmer, Ann. 161, 272 (1872). (11) Michael, Turner, Ber. 39, 2154-2156 (1906). (12) Ger. 261,677; June 27, 1913; Cent. 1913, II 325. (13) Wertyporoch, Ber. 66, 732-739 (1933). (14) C. Hunsdiecker, H. Hunsdiecker, Vogt, U.S. 2,176,181, October 17, 1939; C.A. 34, 1686 (1940); Brit. 456,565, Dec. 10, 1936; French 803,941, Oct. 12, 1936; Cent. 1937, I 2258. (15) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925). (16) Morton, Hechenbleikner, J. Am. Chem. Soc. 58, 1697-1701 (1936). (17) Westphal, Jetchel, Ber. 73, 1007 (1940). (18) Vogel, J. Chem. Soc. 1943, 638,640. (19) Houben, Boedler, Fischer, Ber. 69, 1768, 1777 (1936). (20) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934).

B.P.
$$136.0^{\circ}$$
 at 760 mm. (1) (2) (3) $D_{20}^{20} = 1.131$ (3) $n_{\rm D}^{19} = 1.4627$ (4) $135.5^{\circ}-136.5^{\circ}$ (9) $131.5-132.5^{\circ}$ at 721 mm. (4) 24.5° at 10 mm. (1)

[For prepn. by chlorination of isobutane see (3) (5) (6); from 3-chloro-2-(chloromethyl)-propene-1 (3:5633) or from 1,3-dichloro-2-(chloromethyl)propene-1 (3:9066) with H_2 + Pt black in alc. soln. see (10).]

 $\bar{\rm C}$ on htg. in s.t. at 180° with anhyd. NaOAc + AcOH yields corresp. diacetate, and this on alcoholysis by htg. with 3% dry HCl in dry MeOH gave an overall yield of 60% of the glycol, 2-methylpropanediol-1,3 [Beil. I-480], b.p. 213-214°, $D_4^{20}=1.0290, n_D^{20}=1.4445$ (6).

[For study of further chlorination of \bar{C} see (7); note that \bar{C} with Cl_2 or with $SO_2Cl_2 + Bz_2O_2$ gives (73% yield (9)) 1,2,3-trichloro-2-methylpropane (3:5885).]

 \ddot{C} on treatment with Zn dust in 85% alc. gives 38% yield 2-methylpropene-1, (isobutylene) (8).

 $[\bar{C}]$ with aq. alc. NaCN as directed (11) gives 20.4% yield γ -chloro- β -methyl-n-butyronitrile, b.p. 82-83° at 16 mm., $D_4^{20} = 1.042$, $n_D^{20} = 1.44255$, accompanied by 11.5% yield of β -methyl glutaro (di)nitrile, b.p. 133-137° at 16 mm. (11).]

3:7960 (1) Hass, J. Chem. Education 13, 493 (1936). (2) Hass, McBee, Weber, Ind. Eng. Chem. 27, 1191 (1935). (3) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,072, June 4, 1935; Cent. 1936, I 3012. (4) Kahovec, Kohlrausch, Z. physik. Chem. B-48, 11 (1940). (5) Hass, McBee (to Purdue Research Foundation), U.S. 2,147,577, Feb. 14, 1939; Cent. 1939, II 226. (6) Hass, McBee, Weber, Ind. Eng. Chem. 27, 1194 (1935). (7) Rogers, Nelson, J. Am. Chem. Soc. 58, 1027-1029 (1936). (8) Lott, Christiansen, Schakell, J. Am. Pharm. Assoc. 27, 125-130

35-37°

33-35°

(1938). (9) Mooradian, Cloke, J. Am. Chem. Soc. 68, 787 (1946). (10) Kleinfeller, Ber. 62, 1595-1596 (1929).

(11) Cloke, Stehr, Steadman, Westcott, J. Am. Chem. Soc. 67, 1588 (1945).

3: 7965
$$d_{r}$$
 a_{r} b_{r} DIMETHYL- n -BUTYRYL CHLORIDE C_{0} C_{11} $C_{$

[For prepn. of \bar{C} from 2,3-dimethylbutanoic acid-1 (1:1114) with SOCl₂ see (1).] \bar{C} on hydrolysis yields 2,3-dimethylbutanoic acid (1:1114) q.v. (for the amide, anilide, p-toluidide, and other derivatives corresponding to \bar{C} see 1:1114).

3:7965 (1) Hommelen, Bull. soc. chim. Belg. 42, 243-250 (1933). (2) Nenitzescu, Chicos, Ber. 68, 1587 (1935).

3: 7970 3-CHLORO-2,3-DIMETHYLPENTANE
$$C_7H_{16}Cl$$
 Beil. I - 157 (Ethyl-isopropyl-methyl-carbinyl Cl H I_1 — I_2 — CH₃. CH₂— C — C — C H₃ C H₄ C H₅ C H₆ C H₇ C H₈ C H₉ C H₉

[For prepn. of \bar{C} from 2,3-dimethylpentanol-3 (ethyl-isopropyl-methyl-carbinol [Beil. I-417, I₁-(207), I₂-(446)] with HCl (1) or dry HCl at 0° (50% yield (2)) see (1) (2); for formn. of \bar{C} from reactn. of the above carbinol with C₆H₆ + AlCl₃ (14% yield accompanied by 22% yield 2,3-dimethyl-2-phenylpentane) see (3).]

3:7970 (1) Kaschirsky, J. Russ. Phys.-Chem. Soc. **13**, 90 (1881); Ber. **11**, 985 (1878). (2) Whitmore, Evers, J. Am. Chem. Soc. **55**, 813-814 (1933). (3) Huston, Fox, Binder, J. Org. Chem. **3**, 253 (1939).

[For prepn. of C from 2-methylbutene-2 (trimethylethylene) (1:8220) with Cl₂ at low temp. (6) (7) (8) (3) or SO₂Cl₂ at 0° (9) see indic. refs.; for formn. of C from 2-methylbutane

at 18-20 mm. (4)

at

17 mm. (5)

(isopentane) (1:8500) (4) (10) or from 2-chloro-2-methylbutane (ter-amyl chloride) (3:7220) (11) with Cl_2 see indic. refs.; for form. of \bar{C} from 2-methylbutene-1 (unsymethyl-methyl-ethylene (1:8210) + Cl_2 see (12); for form. of \bar{C} from 3-chloro-2-methylbutene-1 (3:7300) + HCl see (3); for form. of \bar{C} from 2-methylbutanol-2 (ter-amyl alcohol) (1:6160) + Cl_2 see (1).]

[C on further chlorination yields (3) 2,3,3-trichloro-2-methylbutane (3:4755) together with other prods.]

Č on htg. with solid KOH (3) or with alc. KOH (3) (4) loses HCl yielding 3-chloro-2-methylbutene-2 (3:7335) and other prods. — [Č on passing over soda-lime or burnt lime at 600° (13) or BaCl₂ at 300−500° at 20−50 mm. (14) yields 2-methylbutadiene-1,3 (isoprene) (1:8020).]

Č on boilg. with aq. or with aq. Na₂HPO₄ for 30 hrs. gave (2) only 10% hydrolysis; Č on boilg. with 1 mole NaOH in aq. soln. for 24 hrs. gave (2) only 17% hydrolysis, accompanied by isopropyl methyl ketone (1:5410).

C on boilg. with 35 pts. aq. for 40 hrs. gave (5) complete decomposition with formn. of isopropyl methyl ketone (2-methylbutanone-3) (1:5410) q.v., b.p. 94°.

3:7975 (1) Brochet, Ann. chim. (7) 10, 385 (1897). (2) Evers, Rothrock, Woodburn, Stahly, Whitmore, J. Am. Chem. Soc. 55, 1137 (1933). (3) Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1116-1132 (1936); Cent. 1937, I 573; C.A. 31, 1003 (1937). (4) Davydova, Papkina, Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 1992-1994 (1937); Cent. 1939, I 2397; C.A. 32, 482 (1938). (5) Froebe, Hochstetter, Monatsh. 23, 1082-1083 (1902). (6) Kondakov, J. Russ. Phys.-Chem. Soc. 17, 302 (1885). (7) Ostromuislenskii, J. Russ. Phys.-Chem. Soc. 47, 1989-1991 (1915); Cent. 1916, II 308; C.A. 10, 1342 (1916). (8) Badische Anlin- und Soda-Fabrik, Ger. 258,555, May 31, 1912; Cent. 1913, I 1640. (9) Badische Anlin- und Soda-Fabrik, Ger. 251,100, June 7, 1911; Cent. 1912, II 1318. (10) Ayres, Ind. Eng. Chem. 21, 902 (1929).

Badische Anilin- und Soda-Fabrik, Ger. 257,600, Oct. 28, 1911; Cent. 1913, I 1246. (12)
 Gutner, Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1062-1067 (1938); Cent. 1939, II 4221; C.A. 33, 3755 (1939). (13) Harries, Ger. 243,075, Aug. 3, 1910; Cent. 1912, I 535. (14) Badische Anilin-

und Soda-Fabrik, Ger. 255,519, March 15, 1911; Cent. 1913, I 476.

3:7980 *n*-BUTYL CHLOROFORMATE
$$C_5H_9O_2Cl$$
 Beil. III — III_1 — III_2 — $IIII_2$ — $IIIII_2$ — $IIII_2$ — $IIII_2$ — $IIII_2$ — $IIII_2$

B.P. 137.8° at 734.5 mm. (1)
$$D_4^{25} = 1.074$$
 (1) $n_D^{18} = 1.4132$ (2) 137.6° at 730 mm. (2) (3) $n_D^{8.4} = 1.417$ (1) 37-38° at 13 mm. (2)

Colorless mobile lachrymatory liq. with sharp but pleasant odor. — Insol. aq. and only slowly hydrolyzed by it even on htg. (1).

[For prepn. (35% yield (3)) from *n*-butyl alc. (1:6180) + phosgene (3:5000) see (1) (3); from di-*n*-butyl carbonate (1:3626) + PCl₅ see (2).]

 \bar{C} on htg. with quinoline dec. at 81° (4) into n-butyl chloride (3:7160) + CO₂.

- D n-Butyl carbamate: from \(\tilde{\Chi}\) by shaking with conc. aq. NH4OH (1); pr. from alc., m.p. 54° (1).
- n-Butyl-N-phenylcarbamate (n-butyl carbanilate): from \bar{C} in ether by treatment with ether soln. of aniline (1 mole) + pyridine (1 mole) (1); pr., m.p. 65.5° (1), 61° (5). [For corresp. products from many other substituted anilines see (1).]
- ① n-Butyl phenylcarbazate: from \tilde{C} (3.9 g.) + phenylhydrazine (3.1 g.) + pyridine (3.1 g.) in aq. (15 ml.); after solidification of the sepg. yel. oil it is washed with aq. and recryst. from C_6H_6 : white scaly cryst., m.p. 70° (6).

T980 (1) Chattaway, Saerens, J. Chem. Soc. 117, 708-711 (1920).
 Kohlrausch, Sabathy, Monatsh. 72, 307 (1939).
 Hamilton, Sly, J. Am. Chem. Soc. 47, 436-437 (1925).
 Carré, Bull. soc. chim. (5) 3, 1069 (1936).
 Weizmann, Garrard, J. Chem. Soc. 117, 328 (1920).
 Dos, J. Am. Chem. Soc. 48, 1954 (1926).

[For prepn. of \tilde{C} from 2-methylhexanol-5 (isoamyl-methyl-carbinol) [Beil. I-416, I₁-(206), I₁-(445)] by saturation with dry HCl and stdg. for 6 weeks (90% yield (1)) or htg. in s.t. at 140° (2) see indic. refs.]

 \ddot{C} on conversion with Mg in dry ether to RMgCl and treatment with O_2 gives (60% yield (1)) 2-methylhexanol-5, b.p. 151-152° at 736 mm., $n_D^{20}=1.4180~(N-(\alpha-naphthyl)-carbamate)$, m.p. 84-85° (1).

3:7985 (1) Whitmore, Johnston, J. Am. Chem. Soc. 60, 2267 (1938). (2) Rohn, Ann. 190, 312-313 (1877).

B.P. 138-139° at 748 mm. (1)
$$D_4^{24} = 0.8788$$
 (1) $n_D^{24} = 1.4302$ (1) $D_4^{20} = 0.8895$ (2) $D_D^{20} = 1.4349$ (2)

[For prepn. of $\bar{\rm C}$ from n-amyl methyl ketone (heptanone-2) (1:5460) with PCl₅ in C₆H₆ (40% yield together with 23% yield 2,2-dichloroheptane (3:9424)) see (2); for prepn from heptyne-1 (1:8085) + AcCl + SnCl₄ see (2) (both cis-4-chlorononen-3-one-2, b.p. 99° at 10 mm., $D_4^{25} = 0.9830$, $D_5^{25} = 1.4607$, and trans-4-chlorononen-3-one-2, b.p. 89° at 10 mm., $D_4^{25} = 0.9752$, $D_5^{25} = 1.4665$ are also formed (1).]

C with powdered KOH in mineral oil at 250° does not (2) yield heptyne-1 (dif. from 1-chloroheptene-1 (3:8219)).

3:7988 (1) Kroeger, Sowa, Nieuwland, J. Org. Chem. 1, 163-169 (1936). (2) Bachmann, Hill, J. Am. Chem. Soc. 56, 2730-2732 (1934).

3:7990
$$\alpha$$
-ETHYL- n -BUTYRYL CHLORIDE $C_6H_{11}OCl$ Beil. II - 334 (Diethylacetyl chloride) CH_3 . CH_2 . CH_3 - CH_4 CH_5 $CH_$

B.P. 138.0-138.8° at 750 mm. (1)
$$D_4^{20} = 0.9825$$
 (1) $n_D^{20} = 1.4234$ (3); 134-137° (2) 1.4239 (3) 71° at 88 mm. (3) $D_4^0 = 0.9992$ (1) 40° at 20 mm. (3)

[For prepn. of C from 2-ethylbutanoic acid (1:1115) with PCl₅ (2), or with SOCl₂ (1) (85-90% yield (3)) see indic. refs.]

- [C on htg. with sodium diethylacetate yields (2) corresp. anhydride, b.p. 230° (2).]
- [\tilde{C} with Cl₂ yields (4) α -chloro-diethylacetyl chloride, b.p. 93° at 70 mm. (amide, m.p. 58° (4)); \tilde{C} with Br₂ yields (5) α -bromo-diethylacetyl bromide, b.p. 98-100° at 25 mm. (5); for reactn. of \tilde{C} with AlCl₃ + C₆H₆ see (6).]
- [\bar{C} (1 mole) upon addition to ter-butyl MgCl (3.7 moles) in dry ether yields (3) (by virtue of reducing actn. of the tertiary RMgX cpd.) 2-ethylbutanol-1 (1:6223), 2,2-dimethyl-4-ethylhexanol-3 (b.p. 131-132° at 150 mm., $D^{20}_{-}=0.8339$, $n^{20}_{D}=1.4340-1.4362$, $N-(\alpha-naphthyl)$ carbamate, m.p. 63-64°), and hexamethylethane (1:7090), m.p. 103° (3).]
- $\bar{\mathbf{C}}$ on hydrolysis yields 2-ethylbutanoic acid (1:1115) q.v. (for the amide, anilide, p-toluidide, and other derivatives corresponding to $\bar{\mathbf{C}}$ see 1:1115).
- 3:7990 (1) Hommelen, Bull. soc. chim. Belg. 42, 243-250 (1933). (2) Freund, Hermann, Ber. 23, 189-190 (1890). (3) Whitmore and 11 others, J. Am Chem Soc. 63, 646, 651-652 (1941). (4) Altwegg, Pivot, U.S 1,493,182, May 6, 1924; Brst. 209,706, March 5, 1924; Cent. 1924, II 1485; C.A. 18, 2058 (1924). (5) Fourneau, Nicolitch, Bull. soc. chim. (4) 43, 1238-1239 (1928). (6) Apolit, Ann. chim. (10) 2, 80 (1924).

CHAPTER XVIII

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 2. D_4^{20} less than 1.1500

(3:8000-3:8499)

3:8000 3-CHLOROBUTANOL-2
$$CH_3$$
- CH - CH_3 - CH_9OCl Beil. I - 373 (β -Butylene chlorohydrin; Cl OH I_1 - I_2 -(403) chlorohydrin)

B.P.
$$138-140^{\circ}$$
 (1) $D_0^{18} = 1.0692$ (3) (4) $n_D^{20} = 1.4422$ (9) $138-139^{\circ}$ at 753 mm. (2) $136.0-137.5^{\circ}$ at 760 mm. (3) (4) $134-138^{\circ}$ (9) $76-79^{\circ}$ at 100 mm. (5)

[See also d,l-erythro-3-chlorobutanol-2 (3:8004) and d,l-threo-3-chlorobutanol-2 (3:8002).]

 $\bar{\mathbf{C}}$ in this present discussion designates the ordinary mixture of stereoisomeric configurations of 3-chlorobutanol-2.

Colorless somewhat viscous liq. of agreeable odor. $-\bar{C}$ is sol. at 20° in 15 vols. aq. (2); its sepn. from dilute aq. solns. is best effected by steam distillation at reduced pressure (6) cf. (9).

[For prepn. of \bar{C} from ordinary butene-2 (mixt. of cis and trans stereoisomers) by addn. of HOCl (yields: 55% {11}, 50% {3}, 20% {5}) {4} {1} {2}, with Cl₂ + steam at 100° (60–65% \bar{C} together with 10–30% 2,3-dichlorobutane (3:7615) {6}), with Cl₂ + aq. at 40–50° (50–60% yield (6)) {9}, or with N-chlorourea in dil. aq. acid 15–17° in pres. of CuCl₂ (best yield 79.9% \bar{C} + 20.1% 2,3-dichlorobutane (3:7615) obtd. in 5% AcOH (7), but proportion of the two products varies widely with nature of acid used) see indic. refs.]

[For tabular and graphic data on equilibrium consts. of binary system \bar{C} + aq., and ternary system \bar{C} + 2.3-dichlorobutane (3:7615) + aq. see (8).]

Č in s.t. at 180°, or Č with aq. in s.t. at 100° for 10 hrs. or at 120° for 3 hrs., gives (80–100% yield (3)) (10) butanone-2 (ethyl methyl ketone) (1:5405) + HCl (cf. also (14)).

[\bar{C} with solid KOH (5), or with 40-50% aq. NaOH or KOH (15-20% excess) at 75-90° (11) (10), or with aq. KOH, K_2CO_3 , or PbO at ord. temp. (3) (4) (2) causes elimination of HCl and gives (yields: 87-90% (11), 75-81% (10), 66% (5)) 2,3-epoxybutane (α,β -dimethylethylene oxide) (1:6116) (mixt. of cis and trans stereoisomers).

[The simple alkyl ethers of \tilde{C} have been prepared by indirect means; e.g., from butene-2 by action of corresp. alkyl hypochlorites dislvd. in the corresp. alc. or by action of N,N'-dichlorourea in the corresp. alc.: e.g., methyl ether (3-chloro-2-methoxybutane), b.p. 116°, $D_4^{15}=1.0230,\ n_{D_4}^{14}=1.4225$ (12); ethyl ether (3-chloro-2-ethoxybutane), b.p. 122-124°, $D_4^{15}=0.9812,\ n_{D_4}^{15}=1.4260$ (12); for n-propyl, isopropyl, and isoamyl ethers see (12).]

- ---- 3-Chlorobutyl-2 benzoate: b.p. 263-265.5 u.c. (7).
- ---- 3-Chlorobutyl-2 p-nitrobenzoate: unreported.
- ---- 3-Chlorobutyl-2 3,5-dinitrobenzoate: unreported.

3:8000 (1) Fourneau, Puyal, Bull. soc. chim. (4) 31, 427-428 (1922). (2) Henry, Compt. rend. 145, 499 (1907). (3) Krassuski, J. Russ. Phys.-Chem. Soc. 34, 287-315 (1902); Cent. 1902, II 20. (4) Krassuski, Compt. rend. 145, 763 (1907). (5) Norton, Hass, J. Am. Chem. Soc. 58, 2147 (1936). (6) Batalin, Ugryumov, J. Gen. Chem. (U.S.S.R.) 4, 871-874 (1934); Cent. 1936, I 986; C.A. 29, 2147 (1935). (7) Likhosherstov, Alekseev, J. Gen. Chem. (U.S.S.R.) 3, 927-932 (1933); Cent. 1934, II 1437; C.A. 28, 3053-3054 (1934). (8) Bushmakin, Gol'dman, Kuchinskaya, Sintet. Kauchuk 4, No. 1, 33-35 (1935); Cent. 1936, I 1131; C.A. 29, 4248 (1935). (9) Batalin, Ugryumov, Tikhomirov, Sintet. Kauchuk 3, No. 6, 6-12 (1934); Cent. 1935, II 1935; not in C.A. (10) Batalin, Ugryumov, Sintet. Kauchuk 5, No. 6, 8-16 (1936); Cent. 1936, II 3357; C.A. 30, 6701 (1936).

(11) Wilson, Lucas, J. Am. Chem. Soc. 58, 2398-2399 (1936). (12) Likhosherstov, Alekseev, J. Gen. Chem. (U.S.S.R.) 4, 1279-1282 (1934), Cent. 1936, I 4287, C.A. 29, 3306 (1935). (13) Likhosherstov, Petrov, J. Gen. Chem. (U.S.S.R.) 9, 2000-2008 (1939); C.A. 34, 4380-4381 (1940). (14) Gutner, Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1729-1735 (1936), Cent. 1937, I 3786; C.A. 31, 4265 (1937).

B.P. 130.8° at 748 mm. (1)
$$D_4^{25} = 1.0586$$
 (1) $n_D^{25} = 1.4386$ (1) 52.0 ° at 30 mm. (1) $D_4^{20} = 1.0626$ (2) $D_D^{20} = 1.4403$ (2) $D_4^{20} = 1.0626$ (2) $D_D^{20} = 1.4403$ (2)

[See also ord. 3-chlorobutanol-2 (3:8000) and d,l-erythro-3-chlorobutanol-2 (3:8004).]

[For prepn. of Č from cis-2,3-epoxybutane (1:6116) (2 moles) with conc. HCl (3 moles) at 5° or below (77% yield) see (1); from cis-butene-2 with ter-butyl hypochlorite (3:7165) in AcOH/H₂SO₄ (61% yield (1)) or with Ca(OCl)₂ in AcOH (2) see indic. refs.; from the diacetate of meso-butanediol-2,3 (1:6452) in conc. HCl contg 1 drop conc. H₂SO₄ with large excess dry HCl gas at —10° for 90 hrs. (43% yield) see (1). — Note that Č cannot be obtd. from butene-2 with aq. N-chloroacetamide (1).]

 $[\bar{C}\ (1\ mole)\ with\ SOCl_2\ (1.5\ moles)\ refluxed\ 3\ hrs., then kept at 100° for\ 3\ hrs. more, gives <math>(17.4\%\ yield\ \{1\})\ d_1l^2$,3-dichlorobutane (3:7615); note, however, that $\bar{C}\ (1\ mole)$ with SOCl₂ $(2\ moles)\ htd.\ 2\ hrs.\ at\ 95° in\ pres.\ of\ pyridine\ gives <math>(24\%\ yield\ \{1\})\ meso-2,3$ -dichlorobutane (3:7580). — Note that $\bar{C}\ with\ conc.\ HCl\ or\ with\ conc.\ HCl\ +\ ZnCl_2\ fails$ to give any dichlorobutane; note also that $\bar{C}\ fails\ to\ react\ with\ 60\%\ HBr\ even\ in\ s.t.\ at\ 100° for\ 3\ hrs. <math>\{1\}$.

[Č with very conc. aq. KOH at 90-95° loses HCl and gives (75% yield (1)) cis-2,3-epoxybutane (1:6116).]

3:8002 (1) Lucas, Gould, J. Am. Chem. Soc. 63, 2541-2551 (1941). (2) Wilson, Lucas, J. Am. Chem. Soc. 58, 2396-2402 (1936).

B.P. 135.4° at 748 mm. (1)
$$D_4^{25} = 1.0610$$
 (1) $n_D^{25} = 1.4397$ (1) $55.9-56.1$ ° at 30 mm. (1)

[See also ord. 3-chlorobutanol-2 (3:8000) and d,l-threo-3-chlorobutanol-2 (3:8002).]

[For prepn of \bar{C} from trans-2,3-epoxybutane (1:6116) (2 moles) with conc. HCl (3 moles) at 5° or below (82 5% yield) see {1}.]

[$\bar{\mathbb{C}}$ (1 mole) with SOCl₂ (1.5 moles) refluxed 3 hrs., then kept at 100° for 3 more hrs gives (16% yield {1}) meso-2,3-dichlorobutane (3:7580); $\bar{\mathbb{C}}$ (1 mole) in pyridine (2.2 moles) treated with SOCl₂ (2 moles) at 100° for 3 hrs. gives (63% yield {1}) d,l-2,3-dichlorobutane (3:7615), and $\bar{\mathbb{C}}$ (3 moles) with PCl₃ (1 mole) at 100° for 3 hrs also gives (20% yield {1}) d,l-2,3-dichlorobutane (3:7615); note, however, that $\bar{\mathbb{C}}$ (1 mole) with PCl₅ (3.9 moles) in CHCl₃ refluxed 2 hrs. gives (42.7% yield {1}) a mixt. of d,l- and meso- forms of 2,3-dichlorobutane. — Note that $\bar{\mathbb{C}}$ with conc. HCl or with conc HCl + ZnCl₂ fatls to give any dichlorobutane; note also that $\bar{\mathbb{C}}$ fatls to react with 60% HBr even in s.t at 100° for 3 hrs. {1}.] $[\bar{\mathbb{C}}$ with aq. KOH loses HCl and gives (1) trans-2,3-epoxybutane (1:6116).]

3:8004 (1) Lucas, Gould, J. Am. Chem. Soc. 63, 2541-2551 (1941).

50-53° at 28 mm. (2)

50-51° at 20 mm. (3)

Principal component of comml. "amylene dichloride" (5).

[For prepn. of \bar{C} from pentene-2 (unsym.-ethyl-methyl-ethylene) (1:8215) + Cl_2 at -17° (3) or below -5° (4) see indic. refs.; for formn. of \bar{C} (together with other products) from pentane (1:8505) + Cl_2 see (2) (5).]

 \bar{C} on boilg. with 10% alc. KOH gives (2) 2-chloropentene-2 (3:7285), but \bar{C} with aq. K_2CO_3 gives no pentanediol-2,3 (see below).

C on boilg, with Zn dust in alc. or on htg. with Na in xylene at 120° gives (6) pentene-2 (1:8215).

 $[\tilde{C} + aq. \text{ vapor passed at } 300^{\circ} \text{ over MgCl}_2 \text{ gives } (48-50\% \text{ yield (7)}) \text{ pentadiene-1,3} (1:8035).]$

Č on protracted (250 hrs.) boilg. with 35 pts. aq. gives (3) traces of the corresp. glycol, pentanediol-2,3 [Beil. I-482], and either or both pentanone-2 (1:5415) and/or pentanone-3 (1:5420).

3:8010 (1) Kondakov, Ber. 24, 931 (1891). (2) Lemke, Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 1995-1998 (1937); Cent. 1939, I 2397; C.A. 32, 482 (1938). (3) Froebe, Hochstetter, Monatsh. 23, 1085-1086 (1902). (4) Tishchenko, Schtschigelskaya, J. Gen. Chem. (U.S.S.R.) 7, 1246-1248 (1937); Cent. 1938, II 2576. (5) Ayres, Ind. Eng. Chem. 21, 902 (1929). (6) Bourgeul, Bull. soc. chim. (4) 35, 1634-1635 (1924); Ann. chim. (10) 3, 370 (1925). (7) Lemke, Tishchenko, Russ. 50,691, March 31, 1937; Cent. 1938, II 174.

3:8012 1-CHLOROBUTANONE-2 (Chloromethyl ethyl ketone)
$$CH_3$$
— CH_2 — C — CH_2 — CH_3 — CH_4

[See also 3-chlorobutanone-2 (3:7598).]

Liquid with penetrating odor. — Insol. aq.

[For prepn. of \tilde{C} from ethyl methyl ketone (butanone-2) (1:5405) with Cl_2 in pres. of $CaCO_3$ + aq. (yields of \tilde{C} about 25% always accompanied by 75% of the isomeric 3-chlorobutanone-2 (3:7598)) see (1) (3) (6) (10) (12); with Cl_2 in vapor phase (13) (14), with Cl_2 or SO_2Cl_2 in sunlight (8) (11), or with N-chlorourea (5) see indic. refs. — For formn. of \tilde{C} from 1-chlorobutanol-2 (3:8025) by oxidn. with chromic acid (4), from butene-1 with HOCl (4), from 2-chloromethyl-2-ethyl-4-methyl-1,3-dioxolone-5 by hydrol. with AcOH/HCl (9), or from 2-(chloromethyl)butene-1 (3:9214) by ozonolysis (18) see indic. refs.]

[C on reduction using yeast gives (15) 1-chlorobutanol-2 (3:8025).]

C on oxidn. with HNO₃ (8) (11) yields chloroacetic acid (3:1370).

[C on hydrolysis, e.g., by refluxing overnight with K formate in MeOH, yields (1) butanone-2-ol-1 (propionyl-carbinol) [Beil. I-826, I₂-(870)], b.p. 153-154°, 50.5-51.0° at 14 mm. (1); note, however, that C with K acetate in EtOH gives (6) (8) (11) (65-70% yield (6)) propionyl-carbinyl acetate, b.p. 176° (8) (11), 178-180° (6).]

[C with conc. aq. KCN even in the cold yields (8) (11) the corresp. nitrile, propionylacetonitrile [Beil. III-671], b.p. 164-165° (8) (11), colorless liq., insol. aq. — C with conc. aq. (NH₄)₂SO₃ at 70° yields (7) butanone-2-sulfonic acid-1. — C with NaN₃ in aq. contg. AcOH yields (10) 1-azidobutanone-2, oil, b.p. 56° at 2 mm. (10).]

[C with thiourea refluxed for 2 hrs. gives (72% yield (16)) 2-amino-4-ethylthiazole hydrochloride, cryst. from alc./acetone, m.p. 185.5-187.5° u.c.; this salt with conc. aq. NH₄OH gives the free base, m.p. 35°, b.p. 118-120° at 7 mm. (16) (corresp. acetyl deriv., m.p. 117.5° u.c. (16)). — C with thiobenzamide + NaOAc htd. in alc. gives (67% yield (17)) 4-ethyl-2-phenylthiazole, yel. cryst. from xylene, m.p. 117-118° (17).]

Č with phenylhydrazine yields (4) a prod., yel. cryst. from AcOH, m.p. 210-215° dec., whose structure is in doubt.

- ① Chloromethyl ethyl ketone semicarbazone: m.p. 121° (5), 120-121° (18).
- © Condens. prod. of C with N-methyl-β-carbohydrazidopyridinium p-toluenesulfonate: cryst. from 1:1 EtOH/ether, m.p. 136-137° cor. (19). [From C + indicated reagent refluxed 15 min. in abs. alc. (19).]
- ① 1-(Phthalimido)butanone-2: ndls. from hot aq., m.p. 107° (12). [From Č with K phthalimide in dry xylene 2 hrs. at b.p. (27% yield (12)).]

3:8012 (1) Levene, Haller, J. Biol. Chem. 74, 348 (1927). (2) Blaise, Bull. soc. chim. (4) 15, 733 (1914). (3) Justoni, Chimica e industria (Italy) 24, 89-94 (1942); Cent. 1943, I 383. (4) de

Montmollin, Matile, Helv. Chim. Acta 7, 107-109 (1924). (5) Béhal, Detoeuf, Compt. rend. 153, 1230 (1911). (6) Kling, Bull. soc. chim. (3) 33, 325-326 (1905); Ann. chim. (8) 5, 538-539 (1905). (7) Backer, Strating, Zuithoff, Rec. trav. chim. 55, 762-764 (1936). (8) van Reymenant, Bull. acad. roy Belg. 1906, 724-742; Cent. 1901, I 95-96. (9) Blaise, Bull. soc. chim. (4) 15, 673 (1914). (10) Forster, Fierz, J. Chem. Soc. 93, 675, 677 (1908).

(11) Henry, Bull. acad. roy. Belg. 1900, 57-63; Cent. 1900, I 1123. (12) Kolshorn, Ber. 37, 2474 (1904). (13) Justoni, Chimica e industria (Italy) 24, 195-201 (1942); Cent. 1943, I 1659. [14] I.G., French 813,131, May 26, 1937, Cent. 1937, II 2071. (15) Santomauro, Biochem. Z.
151, 50 (1924); Cent. 1924, II 2272. (16) Bergeim, Coy, Lott, J. Am. Chem. Soc. 62, 1873 (1940).
[17] Friedman, Sparks, Adams, J. Am. Chem. Soc. 59, 2263 (1937). (18) Gutner, Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1062-1067 (1938); Cent. 1939, II 4221. (19) Allen, Gates, J. Org. Chem. 6, 596-601 (1941).

3:8015 1,1-DICHLOROPENTANE

C₅H₁₀Cl₂ Beil. S.N. 10

CH₃.CH₂.CH₂.CH₂.CHCl₂

B.P. 139.4-140.2° (1)

[For prepn. of \vec{C} from isovaleraldehyde (1:0140) with PCl₅ see (1); for formn. of \vec{C} (together with other prods.) from pentane (1:8505) by vapor-phase photochemical chlorination see (2).]

3:8015 (1) Kohlrausch, Köppl, Monatsh. 65, 197 (1935). (2) Hass, Huffman, J. Am. Chem. Soc. 63, 1233-1235 (1941).

3:8020 d.l-α-METHYL-n-VALERYL CHLORIDE C₆H₁₁OCl Beil. S.N. 162 (Methyl-n-propyl-acetyl chloride) CH₃.CH₂.CH₂.CH₁. C=O

 $D_4^{20} = 0.9781 (1)$ $D_4^{0} = 0.9979 (1)$ B.P. 140.0-140.8° at 745 mm. (1)

[For prepn. of C from 2-methylpentanoic acid (1:1117) with SOCl₂ see (1).] [The dextrorotatory isomer of C has also been reported (2).

Č on hydrolysis yields 2-methylpentanoic acid (1:1117) q.v. (for the amide, anilide, p-toluidide, and other derivatives corresponding to \bar{C} see 1:1117).

3:8020 (1) Hommelen, Bull. soc. chim. Belg. 42, 243-250 (1933). (2) Levene, Mikesa, J. Biol. Chem. 84, 576 (1929).

3:8023 4-CHLOROHEPTENE-3 CI C7H18Cl Beil. I - 220 **I**1---CH₃.CH₂.CH₂.C=CH.CH₂.CH₃ I2-(197)

 $D_{-}^{14} = 0.883 (2) \quad n_{\rm D}^{14} = 1.437 (2)$ B.P. 141° 138.5-139.5° cor. (2)

Two geom, stereoisomers of C are possible, but only C has yet been recognized.

[For prepn. of C from heptanone-4 (di-n-propyl ketone) (butyrone) (1:5447) with

C on treatment with NaNH2 in pseudocumene at 140° yields (3) heptyne-3 (1:8095) together with a solid prod. which with aq. yields (3) heptyne-1 (1:8085).

3:8023 (1) Tawildarow, Ber. 9, 1442 (1876). (2) Bourgeul, Compt. rend. 178, 1559 (1924); Bull. soc. chim. (4) 35, 1636-1637 (1924); Ann. chim. (10) 3, 372 (1925). (3) Bourgeul, Compt. rend, 178, 1985 (1924); Ann. chim. (10) 8, 342 (1925).

3:8025 d,l-1-CHLOROBUTANOL-2 H
$$C_4H_9OCl$$
 Beil. I — I_1 — I_2 —(α -Butylene chlorohydrin) $CH_3.CH_2.C.CH_2Cl$ I_2 —(402)

B.P. 141° (1)
$$D_4^{25} = 1.068$$
 (2) $n_D^{25} = 1.4410$ (2) $68-70^{\circ}$ at 27 mm. (2) $53-65^{\circ}$ at 17 mm. (5) $D_4^{18} = 1.040$ (3) $n_D^{18} = 1.4353$ (3) 52° at 15 mm. (3)

[See also 2-chlorobutanol-1 (3:9160).]

Colorless liq. when freshly distd. but turns red on stdg. and darkens with time (3). — On distn. at ord. press. partially dec. with loss of HCl (3) [and probable forms. of 1,2-epoxybutane (see below)].

[For prepn. of \bar{C} from butene-1 + HOCl (40-50% yield) see (1) cf. (5); from chloroacetaldehyde (3:7212) + C_2H_5MgBr in ether see (3) (5); for prepn. (44% yield) by hydrolysis of corresp. trichloroacetate (obtd. by chlorination of sec.-butyl trichloroacetate) see (2).]

C on oxidn. with CrO3 yields (1) 1-chlorobutanone-2 (3:8012).

Č with hot conc. KOH gives (50% yield (1)) 1,2-epoxybutane (1:6118), b.p. 61-62° (4). [For study of this reaction see (4).]

- ---- Chloromethyl-ethyl-carbinyl acetate: unreported.
- --- Chloromethyl-ethyl-carbinyl benzoate: unreported.
- —— Chloromethyl-ethyl-carbinyl p-nitrobenzoate: unreported.
- --- Chloromethyl-ethyl-carbinyl 3,5-dinitrobenzoate: unreported.
- --- 1-(N-Phthalimido)butanol-2: unreported.
- © Chloromethyl-ethyl-carbinyl N-phenylcarbamate: m.p. 78.5-79° (3).

3:8025 (1) de Montmollin, Matile, Helv. Chim. Acta 7, 106-107 (1924). (2) Waddle, Adkins, J. Am. Chem. Soc. 61, 3363 (1939). (3) Helferich, Speidel, Ber. 54, 2636-2637 (1921). (4) Moureu, Dodé, Bull. soc. chim. (5) 4, 288-289 (1937). (5) Olson, Whitacre, J. Am. Chem. Soc. 65, 1020 (1943).

3: 8028 METHYL
$$\beta$$
-CHLOROISOCROTONATE $C_{\delta}H_{7}O_{2}Cl$ Beil. II - 417 CH₃—C—Cl II₁-(190) CH₅OCC—C—H

B.P. 142.4° cor. (1)
$$D_4^{20} = 1.138$$
 (1) (3) $141-142^{\circ}$ (2) $D_4^{18.9} = 1.1361$ (3) $n_D^{18.9} = 1.45733$ (3) $42-43^{\circ}$ at 13 mm. (3) $D_-^{15} = 1.143$ (1)

[See also methyl β -chlorocrotonate (3:9244).]

[For prepn. of \bar{C} from β -chloroisocrotonic acid (3:1300) in MeOH soln. satd. with HCl gas (1) (3) or htd. with 10% conc. H₂SO₄ (yields: 70% (2), 60-62% (4)) see indic. refs.; from β -chloroisocrotonoyl chloride (see under β -chloroisocrotonic acid (3:1300)) with MeOH (yields: 90-95% (4), 80% (2)) see indic. refs.]

[\bar{C} with NaSH in MeOH gives (40-45% yield (2)) methyl β -mercaptocrotonate; note that the prod. is apparently a mixture of the two geometrically stereoisomeric thioenols together with the keto form, viz., methyl thioacetoacetate, CH₃.CS.CH₂.COOCH₃; for details see (2).]

[C with Na salt of ethyl mercaptan below 5° gives (80% yield (4)) a mixt. (b.p. 116-132°

at 14 mm.) of methyl β -ethylmercaptocrotonate and methyl β -ethylmercaptoisocrotonate. — \tilde{C} with Na salt of benzyl mercaptan gives (85% yield (4)) methyl β -benzylmercaptocrotonate, cryst. from ether or MeOH, m.p. 69-70° (4), 73° (2); note the change to the other series of stereoisomers and also that this same prod. is obtd. (78% yield (2)) from the Na thioenolate of methyl β -mercaptocrotonate with benzyl chloride.

Č with hydrazine hydrate splits out HCl and MeOH with consequent ring closure yielding (5) (6) 5-methylpyrazolone-3 [Beil. XXIV-19, XXIV₁-(189)], m.p. 215° (5) (6).

3:8028 (1) Geuther, Frolich, Zeit. für Chemie 1869, 274. (2) Scheibler, Topouzada, Schulze, J. prakt. Chem. (2) 124, 16-20 (1930). (3) von Auwers, Ber. 45, 2807 (1912). (4) Scheibler, Voss, Ber. 53, 381-387 (1920). (5) Frei, Atti V congr. nazl. chim. pura applicata, Rome 1935, Pt. I, 361-365 (1936); Cent. 1937, I 4630; C.A. 31, 3914 (1937). (6) Freri, Gazz. chim. ital. 66, 25 (1936); Cent. 1936, II 621; C.A. 30, 6387 (1936).

3: 8C30 d,l-3-CHLORO-2-METHYLBUTANOL-2
$$C_5H_{11}$$
OCl I_1 — I_2 -(424) (Trimethylethylene chlorohydrin; C_1 C_3 — C_4 — C_5 — C_5 — C_6 —

Liq. sol. in 15-16 pts. aq. at room temp. (1).

[For prepn. of \tilde{C} from 2-methylbutene-2 (trimethylethylene) (1:8220) with HOCl (50% yield (1) (2)) or with N-chlorourea in acid solution (70% yield (5)) see indic. refs.; for prepn. of \tilde{C} from 3-chloropentanone-2 (a-chloroethyl methyl ketone) (3:7893) (3) (4) or from ethyl a-chloropropionate (3:8125) (6) with MeMgBr (3) or MeMgI (4) see indic. refs.; note that a mixture of \tilde{C} with 2-chloro-2-methylbutanol-3 (3:9290) results from 2,3-epoxy-2-methylbutane (trimethylethylene oxide) [Beil. XVII-13], b.p. 75°, by ring cleavage with HCl (4).]

 $\bar{\rm C}$ on distillation over P₂O₅ (1) or on htg. at 130° with anhydrous oxalic acid (1:0535) (5) or with H₂SO₄ (92% yield (7)) gives 3-chloro-2-methylbutene-2 (trimethylvinyl chloride) (3:7335), b.p. 97-98°, + 1-chloro-2-methylbutene-2 (β , γ -dimethylallyl chloride) (3:7485), b.p. 110°.

 \bar{C} on boilg. with aq. + BaCO₃ yields (5) 2-methylbutanediol-2,3 (trimethylethylene glycol) [Beil. I-482, I₁-(251), I₂-(549)]; \bar{C} on htg. with KOH (3) (6), alc. KOH (40% yield (5)), or better powdered KOH in ether (70% yield (5)) gives 2,3-epoxy-2-methylbutane (see above).

C on htg. in a s.t. with aq. at 140° (8) or by itself at 155° (8), or on htg. with aniline (70% yield (5)), gives 2-methylbutanone-3 (isopropyl methyl ketone) (1:5410).

Č with MeMgI as directed (9) yields 2,3-dimethylbutanol-2 (dimethyl-isopropyl-carbinol) (1:6187).

3:8630 (1) Krassuski, J. Russ. Phys.-Chem. Soc. 33, 1-26 (1901); Cent. 1901, I 995. (2) Mokiewsky, J. Russ. Phys.-Chem. Soc. 30, 885-900 (1898); Cent. 1899, I 589. (3) Fourneau, Tiffeneau, Compt. rend. 145, 439 (1907). (4) Nilsson, Smith, Z. physik. Chem. A-166, 144-145 (1933). (5) Detoeuf, Bull. soc. chim. (4) 31, 170-171 (1922). (6) Henry, Bull. soc. chim. Belg. 20, 152-156 (1906); Cent. 1906, II 1178; Rec. trav. chim. 26, 420 (1907). (7) Groll, Burgin (to Shell Development Co.), U.S. 2,042,223, May 26, 1936; Cent. 1937, I 1274; C.A. 30, 4875 (1936). (8) Krassuski, J. Russ. Phys.-Chem. Soc. 34, 287-315 (1902); Cent. 1902, II 19. (9) Earl, J. Proc. Roy. Soc. N.S. Wales, 61, 71 (1928); Cent. 1929, I 803; C.A. 23, 815 (1929).

3:8032 1-CHLOROHEPTYNE-1

C7H11Cl

Beil. S.N. 12

CH₃.CH₂.CH₂.CH₂.CH₂.C=C-Cl

B.P. 141-142° at 760 mm. (1)
$$D_4^{24} = 0.9250$$
 (3) $n_D^{24} = 1.4411$ (3) 65° at 49 mm. (2) 65° at 45 mm. (3) $D_-^{18} = 0.918$ (1) (5) $n_D^{18} = 1.441$ (1) (5) 58.0-58.4° at 35 mm. (4)

[For prepn. of \tilde{C} from heptyne-1 (n-amylacetylene) (1:8085) via conversion with NaNH₂ in ether (1) or in liq. NH₃ (4) to C_6H_{11} . C=C—Na and subsequent reactn. with benzene-sulfonyl chloride (yield: 52% (5), 60% (1)) or p-toluenesulfonyl chloride (yield: 60-65% (1) (5)) see indic. refs.; via conversion with KNH₂ in liq. NH₃ (3) to C_6H_{11} —C=C.K and subsequent treatment with Cl₂ in dry ether at -70° see (3).]

Refractive indices of \bar{C} on Pulfrich instrument: $n_{\bar{C}}^{12.9} = 1.4402$; $n_{\bar{D}}^{12.9} = 1.4429$; $n_{\bar{F}}^{12.9} = 1.4492$; $n_{\bar{C}}^{12.9} = 1.4540$ (1).

 \bar{C} with HgSO₄/H₂SO₄ gives (24–28% yield (1)) 1-chloroheptanone-2, b.p. 72–75° at 20 mm., $D_{-}^{20} = 0.802$, $n_{D}^{20} = 1.450$ (1) (see, however, different values below).

C refluxed 6 hrs. with alc. NaOEt gives (74% yield (1)) n-heptanoic acid (1:1140).

[\bar{C} with HgO.BF₃ cat. in MeOH gives (30% yield (2)) 1-chloro-2,2-dimethoxyheptane, b.p. 80-82° at 8 mm., $D_4^{25}=0.9842$, $n_D^{25}=1.4325$ (2); this on hydrolysis with 15% HCl yields (2) 1-chloroheptanone-2, b.p. 80-82° at 13 mm., $D_4^{26}=0.9896$, $n_D^{26}=1.4387$ (2) (cf. values given above for prepn. by different method).]

[$\bar{\mathbf{C}}$ with KCN in aq. MeOH gives (43% yield (2)) 1-cyano-2-methoxyheptene-1, b.p. 124-131° at 15 mm., $D_4^{25}=0.9205, n_D^{25}=1.4462$ (2) (prob. a mixt. of geom. stereoisomers).] $\bar{\mathbf{C}}$ fails to react with KI; after htg. 4 hrs. with 10 pts. N KI $\bar{\mathbf{C}}$ was recovered unchanged (1).

3:8632 (1) Truchet, Ann. chim. (10) 16, 325, 331-334, 337, 343-351 (1931). (2) Pflaum, Wenzke, J. Am. Chem. Soc. 56, 1106 (1934). (3) McCusker, Vogt. J. Am. Chem. Soc. 59, 1307-1309 (1937). (4) Cleveland, Murray, Taufen, J. Chem. Phys. 10, 173 (1942). (5) Bourgeul, Truchet, Compt. rend. 190, 754 (1930).

3: 8035
$$d_{*}l^{-}\beta$$
-METHYL- n -VALERYL CHLORIDE $C_{6}H_{11}OCl$ Beil. S.N. 162 (sec.-Butyl-acetyl chloride) $CH_{3}.CH_{2}.CH_{2}.CH_{2}.CH_{2}$ CH_{3} Cl B.P. 142.5–143.0° at 749 mm. (1) $D_{4}^{20} = 0.9781$ (1)

142-144° (2) 140° at 738 mm. (3) $D_4^0 = 0.9963$ (1)

[For prepn. of C from 3-methylpentanoic acid (1:1125) with SOCl₂ see (1) (2) (3),]

[$\bar{\mathbf{C}}$ with AlCl₃ + C₆H₆ in CS₂ gives (3) (sec.-butyl-acetyl)benzene (β -methyl-n-valerophenone, b.p. 160–161° at 50 mm. (semicarbazone, m.p. 179–180°); $\bar{\mathbf{C}}$ with diethyl-zinc yields (2) 3-methylheptanone-5, b.p. 156.5–157.5°, $D_4^{15}=0.825, n_D^{15}=1.4159$ (semicarbazone, m.p. 101–102°).]

 $\tilde{\mathbf{C}}$ on hydrolysis yields 3-methylpentanoic acid (1:1125) q.v. (for the amide, anilide, p-toluidide, and other derivatives corresponding to $\tilde{\mathbf{C}}$ see 1:1125).

3:8035 (1) Hommelen, Bull. soc. chim. Belg. 42, 243-250 (1933). (2) Colonge, Bull. soc. chim. (4) 49, 448 (1931). (3) Stenzl, Fichter, Helv. Chim. Acta 20, 849 (1937).

3:8040 CHLOROCYCLOHEXANE
$$CH_2-CH_2$$
 $C_0H_{11}Cl$ Beil. V - 21 (Cyclohexyl chloride) H_2C CH_2-CH_2 CH_2-CH_2 $V_{1-}(8)$ $V_{2-}(11)$

B.P. M.P.
$$143^{\circ}$$
 at 768 mm. (1) -43.9° (4) $D_{4}^{20.3} = 1.0000$ (8) $n_{D}^{20.3} = 1.46264$ (8) (13) $n_{D}^{20.3} = 1.462644$ (9) (13) $n_{D}^{20.3} = 1.462644$ (13) $n_{D}^{20.3} = 1.4626444$ (13) $n_{D}^{20.3} = 1.462644$

Colorless liq. with somewhat penetrating but not disagreeable odor. — Volatile with steam. — Stable when pure and dry; in presence of moisture and traces of HCl, however, turns yellow, then brown (1).

[For prepn. of \bar{C} from cyclohexanol (1:6415) + conc. HCl under various conditions (yield: 93% (12), 90% (7), 85% (3), 60-70% (9)) see (1) (10) (7) (3) (9); from cyclohexane by chlorination with Cl₂ (11) (1) (6) (18) (33) or with SO₂Cl₂ (5) (13) see indic. refs.; from cyclohexene (1:8070) with ter-BuCl (3:7045) in liq. HF at 0-5° (65% yield) see (34).]

Č on treatment with alc. KOH (14) (6) (8), or on passing over dehydrohalogenating catalysts such as CaO, BaCl₂, etc., at elevated temps. (15) (16) (17) (19), or even somewhat on distillation (7), loses HCl to give cyclohexene (1:8070), b.p. 83°.

[For study of behavior of \bar{C} with AlCl₃ in CS₂ or cyclohexane see (20); for reactn. of \bar{C} with C₆H₆ + AlCl₃ to give 60-78% yield of phenylcyclohexane (1:7595), b.p. 238.7°, see (9) (21); for reactn. of \bar{C} with NaOC₆H₁₁ to yield dicyclohexyl ether, b.p. 124-126° at 10 mm., see (22); for study of reactivity of \bar{C} with KI (23) (24), NaOMe, pyridine, or piperidine (24) see (23) (24); for reactn. of \bar{C} with oxalyl chloride (3:5060) giving (60% yield (31)) hexahydrobenzoyl chloride (3:8580), b.p. 180-181° u.c., see (31).]

Č with Mg in dry ether gives under optimum conditions 96.5% yield (25) RMgCl; this on oxidn. with O₂ at 25° gives (81% yield (26)) cyclohexanol (1:6145) q.v., accompanied by small amts. of dicyclohexyl ether and dicyclohexyl (1:8490). [Note that Č on reactn. with Ag 3,5-dinitrobenzoate does not (27) yield expected cyclohexyl 3,5-dinitrobenzoate, m.p. 112-113°.]

- © Cyclohexanecarboxylic acid (hexahydrobenzoic acid) (1:0575): m.p. 30-31°, b.p. 233°, Neut. Eq. 128. [From RMgCl on treatment with CO₂ and subsequent acidification (85% yield (25) (28)).]
- © Cyclohexanecarboxylic acid anilide (hexahydrobenzanilide): m.p. 146° cor. (29), 143-144° u.c. (30). [From RMgCl (30) (or RMgBr (29)) by reactn. with phenyl isocyanate.]
- O Cyclohexanecarboxylic acid p-toluidide (hexahydrobenzo-p-toluidide): unrecorded.
- Φ Cyclohexanecarboxylic acid α-naphthalide (hexahydrobenzo-α-naphthalide): m.p. 188° u.c. (32). [From R.MgBr + α-naphthyl isocyanate (32).]

3:8040 (1) Markownikow, Ann. 302, 9-11 (1898). (2) Kohlrausch, Stockmair, Z. physik. Chem. B-31, 400 (1936). (3) van Woerden, Rec. trav. chim. 45, 135 (1926). (4) Nagornov, Rotinyants, Ann. inst. anal. phys. chim. (U.S.S.R.) 3, 162-173 (1926); Cent. 1927, I 2648; C.A. 21, 3780 (1927). (5) Kharasch, Berkmann, J. Org. Chem. 6, 815 (1941). (6) Sabatier, Mailhe, Ann. chim. (8) 10, 531 (1907); Bull. soc. chim. (3) 29, 976 (1903). (7) van de Vloed, Bull. soc. chim. Belg. 48, 255, 261 (1939). (8) Krause, Pohland, Ber. 57, 1066 (1924). (9) Mayes, Turner, J. Chem. Soc. 1929, 502. (10) I. Zugravescu, S. Zugravescu, Bul. Soc. Chim. România 19-A, 85-92 (1937); Cent. 1939, II 1279.

(11) Fortey, J. Chem. Soc. 73, 940 (1898). (12) Norris, Mulliken, J. Am. Chem. Soc. 42, 2097 (1920). (13) Kharasch, Brown, J. Am. Chem. Soc. 61, 2142-2150 (1939). (14) Ref. 1, pp. 27-28. (15) B.A.S.F. Ger. 252,499; Cent. 1912, II 1708. (16) B.A.S.F. Ger. 254,473; Cent. 1913, I 346. (17) Faragher, Garner, J. Am. Chem. Soc. 43, 1716-1724 (1921). (18) Levine, Cass (to du Pont), U.S. 2,154,049, April 11, 1939; C.A. 33, 5414 (1939). (19) Levine, Cass (to du Pont), U.S. 2,183,574, Dec. 19, 1939; C.A. 34, 2396 (1940). (20) Nenitzescu, Ionescu, Ann. 491, 202-206 (1931).

(21) Neunhoeffer, J. prakt. Chem. (2) 133, 105-107 (1932). (22) Fichter, Siegrist, Helv. Chim. Acta 15, 703 (1932). (23) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925). (24) Tronow, Ladigina, Ber. 63, 3060-3067 (1930). (25) Gilman, Zoellner, J. Am. Chem. Soc. 53, 1945-1948 (1931). (26) Wuyts, Bull. soc. chim. Belg. 36, 230-232 (1927). (27) Tseng, Chu, Natl. Central Univ. (Nanking) Sci. Repts., Ser. A, 1, No. 2, 5-7 (1931); C.A. 26, 2166 (1932); Cent. 1938, I 669. (28) Gilman, Kirby, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 361-364, Note 10 (1941). (29) Schwartz, Johnson, J. Am. Chem. Soc. 53, 1056 (1931). (30) Underwood, Gale, J. Am. Chem. Soc. 56, 2119 (1934).

(31) Kharasch, Brown, J. Am. Chem. Soc. 64, 332 (1941). (32) Gilman, Furry, J. Am. Chem. Soc. 50, 1216 (1928). (33) Zellner (to Tide Water Associated Oil Co.), U.S. 2,370,342, Feb. 27, 1945; C.A. 39, 3534 (1945). (34) Simons, Meunier, J. Am. Chem. Soc. 65, 1269-1271 (1943).

3: 8045
$$d$$
, l -3,4-DICHLOROPENTENE-2 Cl Cl C₅H₈Cl₂ Beil. I - 210 CH₃—CH₂—CH—CH₃ I₁—I₂—

B.P. 142-144° at 736 mm. (1)

Two geom. stereoisomers of \bar{C} are possible, but as yet only this one is recognized. [For prepn. of \bar{C} from 3-chloropenten-2-ol-4 with PCl₃ see (1).]

Č on boilg, with aq. is partially reconverted (1) to 3-chloropenten-2-ol-4 [Beil. I-443], b.p. 158-159° at 724.4 mm.

C adds Br₂ yielding (1) 2,3-dibromo-3,4-dichloropentane, b.p. 140-145° at 31 mm. (1).

3:8045 (1) Garzarolli-Thurnlackh, Ann. 223, 160-161 (1884).

B.P.
$$140-145^{\circ}$$
 (1)
 $140-144^{\circ}$ (5)
 $86-90^{\circ}$ at 104 mm. (5)
 49° at 21 mm. (2)
 $46-48^{\circ}$ at 12 mm. (3)
 $D_{4}^{18} = 0.879$ (2)

Note that some evidence exists (1) that in certain reactions C reacts (by virtue of allyl transposition) as its synionic isomer 2-chloroheptene-3 (but this has not itself been characterized).

[For prepn. from hepten-2-ol-4 (propenyl-n-propyl-carbinol) [Beil. I-447, I2-(488)]

(1) (4) (p-nitrobenzoate, m.p. 40-41° (2); N-(p-xenyl) carbamate, m.p. 103.5° (2)) with PCl₅ (73% yield (4)) (1) (5) or with PCl₃ + pyridine at 0° (2) see indic. refs.] [The levorotatory isomer of $\bar{\mathbf{C}}$ (from dextrorotatory hepten-2-ol-4, with PCl₃ + pyridine at 0° (2)) has b.p. 44° at 14 mm., $n_D^{21} = 1.4430$ (2).]

[\bar{C} with phenol + K_2CO_3 in acctone gives (65% yield (4)) (3) phenyl α -(n-propyl)crotyl ether, b.p. 153-154° at 23 mm. (4), 103-104° at 4 mm. (3), $D_{20}^{20} = 0.9282$ (3), $n_D^{21} = 1.5000$ (3). — For studies of the rearr. of this ether on htg. see (1).] [For similar reaction of \bar{C} with o-cresol see (3).]

3:8656 (1) Hurd, Williams, J. Am. Chem. Soc. 58, 2636-2637 (1936). (2) Arcus, Kenyon, J. Chem. Soc. 1938, 1918. (3) Hurd, Puterbaugh, J. Org. Chem. 2, 382-384 (1938). (4) Hurd, Cohen, J. Am. Chem. Soc. 53, 1920-1922 (1931). (5) Reif, Ber. 41, 2743 (1908).

[For prepn. of \bar{C} from 3-ethylpentanol-3 (triethylcarbinol) (1:6218) with dry HCl at 10–15° (88% yield (4)), with HCl (1), or with cone. HCl + ZnCl₂ at room temp. (3) see indic. refs.; for formn. of \bar{C} (2% yield (5)) as by-product of reactn. of triethylcarbinol with AlCl₃+ C₆H₆ (main prod. is 40% yield of 3-ethyl-3-phenylpentane, b.p. 225–226° at 745 mm., 107–108° at 20 mm., $n_{c}^{25} = 1.4953$, $n_{c}^{20} = 1.4975$) see (5); for prepn. of \bar{C} from 3-ethylpentene-2 (1:8330) with HCl gas in AcOH (3) or with conc. or fumg. HCl (2) see (2) (3).]

C with Mg in dry ether as directed (4) gives 58% yield corresp. RMgCl.

 $\bar{\mathbf{C}}$ converted (as above) to RMgCl, treated with formaldehyde gas, gives (10% yield (4)) 2,2-diethylbutanol-1, b.p. 75-78° at 12 mm, $n_{\mathrm{D}}^{20} = 1.443$ (4).

3:8655 (1) Schreiner, J. prakt. Chem. (2) 82, 296 (1910). (2) Nasarov, Ber 70, 623 (1937). (3) Lucas, J. Am. Chem. Soc. 51, 252-253 (1929). (4) Whitmore, Badertscher, J. Am. Chem. Soc. 55, 1560-1562, 1566 (1933). (5) Huston, Fox, Binder, J. Org. Chem. 3, 253 (1939).

3:8075 d,I-3,4-DICHLORO-2-METHYLBUTANE
$$C_5H_{10}Cl_2$$
 Beil. I - 137 (Isopropylethylene dichloride) Cl Cl CH_3 I_{1-} (47) I_{2-} I_{2-}

[For prepn. of $\ddot{\mathbf{C}}$ from 3-methylbutene-1 (isopropylethylene) (1:8200) + $\mathbf{Cl_2}$ see (1); for formn. (together with 1,4-dichloro-2-methylbutane (3:8360) and 2,4-dichloro-2-methylbutane (3:8105)) from 4-chloro-2-methylbutane (isoamyl chloride) (3:7365) with $\mathbf{Cl_2}$ in light see (2) (4).]

 \tilde{C} is scarcely attacked by K_2CO_3 (1). — \tilde{C} on boilg. with aq. for 100 hrs. can be recovered unchanged to extent of 85%, the remainder yielding traces of 2-methylbutanediol-1,2 [Beil. I-482], 2-methylbutanene-3 (isopropyl methyl ketone) (1:5410), and 2-methylbutyne-1 (isopropylacetylene) (1:8010) (3).

[Č passed over soda-lime at 470° gives (2) 2-methylbutadiene-1,3 (isoprene) (1:8020).

3:8075 (1) Kondakow, J. Russ. Phys.-Chem. Soc. 20, 144 (1888). (2) Perkin, J. Soc. Chem. Ind. 31, 616-624 (1912). (3) Froebe, Hochstetter, Monatsh. 23, 1079-1081 (1902). (4) Badische Anilin- u. Soda-Fabrik, Ger. 261,677, March 14, 1911; Cent. 1913, II 325.

B.P. 143.4-144.4° at 751 mm. (1)
$$D_4^{20} = 0.8690$$
 (2) $n_D^{20} = 1.4237$ (1) 48.3° at 21 mm. (2) $D_4^{15} = 0.8732$ (2) 1.4228 (2)

[For prepn. of \bar{C} from heptanol-3 [Beil. I_1 -(205), I_2 -(444) (2)] with conc. HCl + ZnCl₂ (yield 60-64% (2)), 30% (1)) see (1) (2).] [A dextrorotatory form of \bar{C} has been prepd. (3) by cat. hydrogenation of levorotatory 3-chloroheptene-1: b.p. 87-90° at 113 mm., $n_D^{25} = 1.4221$ (3).]

Č converted to corresp. acetate by 7 hrs. reflux with KOAc + AcOH, then hydrolyzed by 6 hrs. boilg. with 20% alc. KOH, and the resultant heptanol-3 oxidized with CrO₃/H₂SO₄ gives (2) heptanone-3 [Beil. I-699, I₃-(359), I₂-(754)] (semicarbazone, m.p. 88-89° (2)).

3:8080 (1) Dillon, Lucas, J. Am. Chem. Soc. 50, 1711-1714 (1928). (2) Sherrill, J. Am. Chem. Soc. 52, 1985-1988 (1930). (3) Levene, Rothen, J. Biol. Chem. 119, 191-192 (1937).

3: 8085 4-CHLOROHEPTADIENE-1,6 Cl
$$C_7H_{11}Cl$$
 Beil. I -257 (Diallylcarbinyl chloride) CH_2 — $CH.CH_2$ — $CH_2.CH$ — CH_2 — CH_3 — CH_4 — CH_4 — CH_5 — CH_6

B.P. 144° dec. (1)

[For prepn. of \bar{C} from heptadien-1,6-ol-4 (diallylearbinol) [Beil. I-455, I₂-(506)] with PCl₅ see (1).]

C with alc. KOH readily removes 1 HCl yielding a heptatriene, b.p. 115° (1).

3:8085 (1) Saytzeff, Ann. 189, 141-145 (1877).

3: 8090
$$\gamma$$
-METHYL-n-VALERYL CHLORIDE $C_6H_{11}OCl$ Beil. II - 329 (Isocaproyl chloride, CH₃.CH.CH₂.CH₂.C=O II₁— II₂-(289) B.P. 143.8–144.6° at 745 mm. (1) $D_4^{20} = 0.9725$ (1) 141.9–144.7° (2) 141–142° (3) $D_4^0 = 0.9922$ (1) [129–130° (8)]

[For prepn. of \bar{C} from 4-methylpentanoic acid-1 (isocaproic acid) (1:1127) with PCl₅ (63% yield (4)), with PCl₃ + ZnCl₂ (68% yield (4)), or with SOCl₂ (1) (2) (5) (8) (82% yield (4)) see indic. refs.]

[\bar{C} with Br₂ followed by abs. alc. gives (94% yield (6)) ethyl α -bromo-isobutylacetate, b.p. 100-102° at 17 mm. (6); for study of catalytic reduction of \bar{C} see (7).]

 $\bar{\mathbf{C}}$ on hydrolysis yields isobutylacetic acid (isocaproic acid) (1:1127) q.v. (for the amide, anilide, p-toluidide, and other derivatives corresponding to $\bar{\mathbf{C}}$ see 1:1127).

3:8696 (1) Hommelen, Bull. soc. chim. Belg. 42, 243-250 (1933). (2) Kohlrausch, Pongratz, Z. physik. Chem. B-22, 383 (1933). (3) Freundler, Bull. soc. chim. (3) 13, 833 (1895). (4) Clark, Bell. Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (5) Curtius, Hambsch, J. prakt. Chem. (2) 125, 194 (1930). (6) Guha, Muthanna, Ber. 71, 2670 (1938). (7) Grignard, Mingasson, Compt. rend. 185, 1173-1176 (1927). (8) Rupe, Giesler, Helv. Chim. Acta 11, 664 (1928).

B.P. 144-145° at 758 mm. (1)
$$D_4^{20} = 0.8710$$
 (3) $n_D^{20} = 1.4237$ (1) 143.1-144.4° at 751 mm. (2) 0.8619 (1) 1.4231 (3) 48.9° at 21 mm. (3) $D_4^{15} = 0.8751$ (3) 1.4199 (2)

[For prepn. of \bar{C} from heptanol-4 (1:6228) with conc. $HCl + ZnCl_2$ (1) (2) (3) (yield: 60-64% (3), 35% (1)) see indic. refs.]

C converted to corresp. acetate by 7-hr. reflux with KOAc + AcOH, then hydrolyzed by 6-hr. boilg. with 20% alc. KOH, and the resultant heptanol-4 (1:6228) oxidized with CrO₃/H₂SO₄ gives (3) heptanone-4 (1:5447) q.v. (semicarbazone, m.p. 129° by this route, 132° from authentic heptanone-4 (3)).

Č with powdered or alc. KOH or NaOH slowly regenerates heptanol-4 (1:6228) without any trace of olefin (1).

3:8095 (1) Mathus, Gibon, Bull. soc. chim. Belg. 34, 306 (1925). (2) Dillon, Lucas, J. Am. Chem. Soc. 50, 1711-1714 (1928). (3) Sherrill, J. Am. Chem. Soc. 52, 1985-1989 (1930).

B.P. 140-150° dec. (1)
$$D_4^{25} = 0.8568$$
 (2) $n_D^{25} = 1.4363$ (4) $49.5-51^\circ$ at 15 mm. (2) $n_D^{20} = 1.4263$ (4)

1.4257 (3)

1.4250 (2)

Č decomposes very easily on distn. (cf. (3)).

[For prepn. of \bar{C} from 2-methylheptanol-2 (n-amyl-dimethyl-carbinol) [Beil. I-420, I₁-(209), I₂-(452) (2) (3)] with HCl gas (yield 81% (2), 73% (3)) or with AcCl (1) see indic. refs.]

 $\bar{\mathbf{C}}$ on distn. over powdered KOH gives 2-methylheptene-2 (α,α -dimethyl- β -n-butyl-ethylene) [Beil. I-222, I₁-(93)], b.p. 122-123° at 755 mm., $D_{-}^{20} = 0.816$ (1).

C with Mg in dry ether as directed (2) gives 59.9% yield RMgCl.

Č on conversion to RMgCl and subsequent treatment with CO₂ gives (in addition to much olefin) (22% yield (2)) dimethyl-n-amyl-acetic acid, b.p. 118°, $n_D^{20} = 1.4335-1.4305$ (2) (amide, m.p. 102.5-103.5° (2)).

3:8160 (1) Muset, Bull. acad. roy. Belg. 1906, 775-789; Cent. 1907, I 1313; C.A. 1, 1696 (1907). (2) Whitmore, Badertscher, J. Am. Chem. Soc. 55, 1559-1567 (1933). (3) Whitmore, Williams, J. Am. Chem. Soc. 55, 409 (1933). (4) Smart, Quayle, J. Am. Chem. Soc. 67, 21-23 (1945).

3: 8103 METHYL
$$d_il$$
- α -CHLORO- n -BUTYRATE $C_bH_9O_2Cl$ Beil. II - 277 CH₃.CH₂.CH_.COOCH₃ II₁— II₂—

$$D_{-}^{14} = 1.0979 (1) \quad n_{\rm D}^{14} = 1.42526 (1)$$

[For prepn. of \bar{C} from α -chloro-n-butyronitrile with MeOH + HCl see (1).] For the amide corresp. to \bar{C} see α -chloro-n-butyric acid (3:9130).

3:8103 (1) Henry, Bull. acad. roy. Belg. (3) 35, 507-520 (1898); Cent. 1898, I 273.

3:8105 2,4-DICHLORO-2-METHYLBUTANE
$$C_5H_{10}Cl_2$$
 Beil. I - 135 (Isoprene bis-hydrochloride) Cl Cl I_{1-} (47) CH_2 — CH_2 — CH_3 CH_3

B.P.
$$145-146^{\circ}$$
 (1) $D_4^{20} = 1.0654$ (1) $n_D^{20} = 1.44549$ (5) $144-148^{\circ}$ (5) 142° (2) $52-53^{\circ}$ at 12 mm. (1) 39° at 10 mm. (5)

[Earlier work on this compd. seems now to have been carried out on impure material and should be disregarded.]

[For prepn. of C from 4-chloro-2-methylbutene-2 (isoprene monohydrochloride) (3:7465) with conc. HCl satd. with HCl gas see (1) (5); for prepn. of C from 2-methylbutadiene-1,3 (isoprene) (1:8020) with conc. HCl see (2) (5); for formn. of C from 2-methylbutane (isopentane) (1:8500) (together with 2,3-dichloro-2-methylbutane (3:7975) and 1,4-dichloro-2-methylbutane (3:8360)) see (3); for formn. of C (together with 1,4-dichloro-2-methylbutane (3:8360) and 3,4-dichloro-2-methylbutane (3:8075)) from 4-chloro-2-methylbutane (isoamyl chloride) (3:7365) + Cl₂ in light see (4).]

 \bar{C} on hydrolysis with boilg. 20% K₂CO₃ (3) or 20% aq. NaOH (5) gives 2-methylbutane-diol-2,4 [Beil. I-483, I₁-(251)], b.p. 108° at 16-17 mm., $D_{20}^{20}=0.9852, n_D^{20}=1.4434$ [N,N-bis (phenylcarbamate), m.p. 113.8-114.6°] (3) cf. (5).

C on oxidn. with KMnO₄ yields (3) β-hydroxyisovaleric acid [Beil. III-327, III₁-(122)].

3:8105 (1) Aschan, Ber. 51, 1307 (1918). (2) Ostromuislenskii, J. Russ. Phys.-Chem. Soc. 47, 1983-1988 (1915); Cent. 1916, II 307, C.A. 10, 1341 (1916). (3) Davydova, Papkina, Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 1992-1994 (1937); Cent. 1939, I 2397; C.A. 32, 482 (1938). (4) Perkin, J. Soc. Chem. Ind. 31, 616-624 (1912). (5) Soday (to United Gas Improvement Co.), U.S. 2,376,396, May 22, 1945; C.A. 39, 3548-3549 (1945).

 $n_{\rm D}^{20} = 1.4660 (3)$

3:8110 d,l-1-CHLOROBUTEN-3-OL-2 C_4H_7OCl Beil. S.N. 25 (Chloromethyl-vinyl-carbinol) $CH_2 = CH - CH - CH_2$ OH Cl

OH Cl **B.P.**144–147° (1) $D_4^{20} = 1.111$ (3)

76° at 60 mm. (2) 1.4643 (2) 64.0-64.8° at 30 mm. (3) $D_4^{15} = 1.1214$ (1) $n_D^{15} = 1.468$ (1)

[See also 2-chlorobuten-3-ol-1 (3:9113).]

[For prepn. of \tilde{C} from butadiene-1,3 with HOCl generated from $Ca(OCl)_2 + CO_2$ (3) or from N-chlorourea + acid in cold (1) (yields of \tilde{C} : 75% (1), 52% (3)) see indic. refs.]

 $\ddot{\mathbf{C}}$ with Br₂ in CHCl₃ adds 1 mole halogen giving (1) 1-chloro-3,4-dibromobutanol-2, b.p. 129–130° at 10 mm.; $D_4^{20}=2.042, D_4^{15}=2.0504; n_D^{20}=1.561, n_D^{15}=1.564$ (1); note that this prod. on oxidn. with Na₂Cr₂O₇ + H₂SO₄ at 35° gives (1) 1-chloro-3,4-dibromobutanone-2, b.p. 132–133° at 25 mm.; $D_4^{20}=2.0521, D_4^{15}=2.0589; n_D^{20}=1.554, n_D^{15}=1.559$ (1).

 \tilde{C} with 50% aq. NaOH at 115-185° for 1 hr. (3) or with 60% KOH (1) loses HCl ring closing to (yields: 87% (2), 84% (3)) 3,4-epoxybutene-1, b.p. 65.0-65.8° at 739 mm., $D_4^{20} = 0.875$, $n_D^{20} = 1.4170$ (3) cf. (1). [For various reactions of this product see (1) (2) (3) (4).]

[For study of rate of hydrolysis of C with aq. NaOH see (2).]

- —— 1-Methoxybuten-3-ol-2 ($\bar{\mathbf{C}}$ methyl ether): b.p. 143-144° (1) (4), 69-71° at 49 mm (3); $D_{\mathbf{A}}^{20} = 0.9470$ (1) (4); $n_{\mathbf{D}}^{20} = 1.4343$ (1) (4), 1.4297 (3): corresp. 3,5-dimitrobenzoate, m.p. 70-71° (3). [From $\bar{\mathbf{C}}$ (3) or from 3,4-epoxybutene-1 (above) (1) (4) with MeOH/NaOMe in 51-52% yields (3) (1).]
- —— 1-Ethoxybuten-3-ol-2 (\tilde{C} ethyl ether): b.p. 153-157°; $D_4^{15} = 0.9214$; $n_D^{15} = 1.4330$ (1) (4). [Presumably from \tilde{C} (although not actually reported) or from 3,4-epoxybutene-1 (above) (1) (4) with EtOH/NaOEt.]
- 1-Chlorobuten-3-yl-2 acetate: b.p. 163-166°; $D_4^{15} = 1.1308$; $n_D^{15} = 1.4610$ (1).
- ① 1-Chlorobuten-3-yl-2 3,5-dinitrobenzoate: m.p. 61.5-63.5° u.c. (3). [Note that this prod. depresses m.p. of corresp. deriv. (m.p. 65.5° u.c.) from 2-chlorobuten-3-ol-1 (3:9113).]

3:8110 (1) Petrov. J. Gen. Chem. (U.S.S.R.) 8, 131-140 (1938); Cent. 1939, I 2596; C.A. 32, 5369 (1938). (2) Kadesch, J. Am. Chem. Soc. 68, 46-48 (1946). (3) Kadesch, J. Am. Chem. Soc. 68, 41-45 (1946). (4) Petrov, Acta Univ. Voronegiensis 8, No. 2, 71-79 (1935); Cent. 1936, II 2333-2334; C.A. 32, 4524 (1938).

Colorless mobile liq. with characteristic odor.

[For prepn. from 2,4,4-trimethylpentene-1 (1:8340) or 2,4,4-trimethylpentene-2 (1:8345) ("diisobutylene") with conc. HCl (satd. at -20°) in s.t. at 100° (1) (2), with HCl gas in cold (5) or at -10° to -25° in pres. of ZnCl₂ (4) (almost quant. yield (5)) see indic. refs.] \bar{C} on distillation loses HCl and regenerates "diisobutylene" (4) (2).

C with alc. KOH yields diisobutylene (see above).

[For reactn. of \bar{C} with phenol + alc. NaOC₆H₆ yielding phenyl diisobutyl ether, b.p. 250-260° see (3); note, however, that this prod. in s.t. at 250° for 2 hrs. rearr. to p-(diisobutyl)phenol, m.p. 84° (3).]

[For reaction of \bar{C} with $(CH_3)_2Zn$ yielding 2,2,4,4-tetramethylpentane (1:8645), b.p. 122.3° , $n_D^{25} = 1.4051$, see (4).]

[For reactn. of \tilde{C} with silver cyanate, followed by alk. hydrolysis to yield 4-amino-2,2,4-trimethylpentane (acetyl deriv., m.p. 99°; reactn. prod. with phenyl isocyanate, m.p. 137°) see (5).]

[\bar{C} with 2-methyl butane (isopentane) (1:8500) + AlCl₃ shaken for 2 min. gives (6) 2-chloro-2-methylbutane (ter-amyl chloride) (3:7220).]

3:8113 (1) Butlerow, Ann. 189, 51-52 (1877). (2) Kondakov, J. Russ. Phys.-Chem. Soc. 28, 790 (1896); J. prakt. Chem. (2) 54, 449-450 (1896). (3) Natelson, J. Am. Chem. Soc. 56, 1585 (1934). (4) Howard, J. Research Natl. Bur. Standards 24, 678-679, 681 (1940). (5) Whitmore, Wilson, Capinjola, Tongberg, Fleming, McGrew, Cosby, J. Am. Chem. Soc. 63, 2041 (1941).
 (6) Bartlett, Condon, Schneider, J. Am. Chem. Soc. 66, 1537 (1944).

3:8115 2-CHLORO-3-ETHYL-3-METHYLPENTENE-1 C₈H₁₅Cl Beil. S.N. 11

$$CH_3.CH_2$$
— C — $C=CH_2$
 CH_2 — CH_3
 $n_D^{25} = 1.4450 (1)$

CH₃ Cl

B.P. 147° at 743 mm. (1)
$$n_D^{25} = 1.4450 (1)$$
 53° at 20 mm. (1) $D_4^{20} = 0.9147 (1)$

[For prepn. of \bar{C} from 3-ethyl-3-methylpentanone-2 [Beil. I₂-(760)] (1) with PCl₅ (65% yield) see (1).]

 $\bar{\text{C}}$ with NaNH₂ in mineral oil at 160–165° gives 45% yield 3-ethyl-3-methyl-pentyne-1, b.p. 98–100° at 745 mm., $D_4^{20}=0.7360,\,n_D^{20}=1\,4102$ (Ag salt, darkens 167°, melts 191.5°) (1).

3:8115 (1) Davis, Marvel, J. Am. Chem. Soc. 53, 3844-3845 (1931).

3: 8117
$$\alpha$$
-CHLOROCROTONALDEHYDE C_4H_5 OCl Beil. I - 731 (2-Chlorobuten-2-al-1) CH_3 .CH=C-CHO I_1 - I_2 -(789) B.P. 147-150° at 760 mm. (1) $D_4^{23} = 1.1404$ (4) $n_D^{23} = 1.478$ (4) 147-149° (2) $D_4^{15} = 1.1422$ (4) 146-148° (4) $D_4^{15} = 1.1590$ (4) $D_4^{15} = 1.1590$ (4)

Colorless lachrymatory liq. gradually becoming colored in light. — Spar. sol. aq.; eas. sol. alc., ether, CHCl₃. — Volatile with steam. — Note that although two geometrical isomers are possible only this one (configuration uncertain) is known.

[For prepn. of \bar{C} from α,β -dichloro-n-butyraldehyde (3:9102) by elimination of HCl through steam distillation of its soln. in aq. NaOAc (70-80% yield (5)) (4) (1) (2) see indic. refs.; for form. of \bar{C} (together with other prods.) from acetaldehyde (1:0100) with Cl₂ (3), from α,α,β -trichloro-n-butyraldehyde ("butylchloral") (3:5910) with Zn + aq. or Zn + HCl (6), from chloroacetaldehyde (hemihydrate) (3:7212) with acetaldehyde + trace fumg. HCl (7), from α -chloro- β -hydroxy-n-butyraldehyde (α -chloroacetaldol) (itself obtd. from crotonaldehyde (1:0150) by addn. of HOCl (8)) by steam distillation (8) see indic. refs.]

 \bar{C} with Cl_2 (3) (7) (2) in CCl_4 soln. (4) adds 1 mole halogen yielding α,α,β -trichloro-n-butyraldehyde ("butyrchloral") (3:5910). — \bar{C} with Br_2 (1 mole) below 0° rapidly adds 1 mole halogen yielding (5) α -chloro- α,β -dibromo-n-butyraldehyde (not distillable without decompn. even in vac.); this prod., however, slowly combines with aq. yielding corresp. monohydrate, cryst., m.p. 45-50° (5), or on oxidn. with excess fumg. HNO₃ at 100° for several hrs. gives α -chloro- α,β -dibromo-n-butyric acid, colorless pr. from conc. HNO₃, m.p. 91-92° (5).

[\tilde{C} on reduction with Al(OEt)₃ under H₂ (9) or with Zr isopropylate in isopropyl alc. (10) yields β -chlorocrotonyl alc. (2-chlorobuten-2-ol-1) (3:8240), b.p. 159°.]

[\bar{C} with ethylene glycol (1:6465) + a little 20% H₃PO₄ gives (22% yield (1)) the corresp. cyclic acetal (" α -chlorocrotylidene-ethylene glycol"), b.p. 76-80° at 14 mm. (1); for formn. of analogous cyclic acetals from \bar{C} with other glycols see (11).]

[Č with liq. HCN as directed gives (88% yield (4)) the corresp. cyanohydrin, 3-chloro-2-hydroxypenten-3-nitrile, b.p. 137-138° at 26 mm., $D_{\rm A}^{21} = 1.964$, $n_{\rm D}^{21} = 1.4762$ (4).]

 \bar{C} with naphthoquinone-1,4 (1:9040) in C_6H_6 treated with trace of piperidine undergoes condensation of Diels-Alder type yielding {12} 2-chloroanthraquinone (3:4922).

[For conversion of \bar{C} with EtOH to corresponding α -chlorocrotonaldehyde diethylacetal (14), b.p. 181–184°, see (14).]

[C with sodium salt of anthrahydroquinone bis-sulfuric acid ester in $Ac_2O/AcOH +$ piperidine at 100° for ½ hr. yields (13) the corresp. benzanthrone, presumably Bz-2-chloro-Bz-1-methylbenzanthrone (12-chloro-13-methylbenzanthrone) (for ring numbering see Beil. VII₁-(288)).]

3:8117 (1) Hibbert, Houghton, Taylor, J. Am. Chem. Soc. 51, 613 (1929). (2) Chem. Fabrik vorm. Weiler-ter-Meer, Ger. 351,137, April 3, 1922; Cent. 1922, IV 155. (3) Pinner, Ber. 8, 1321-1322 (1875); Ann. 179, 29-32 (1875). (4) Moureu, Murat, Tampier, Bull. soc. chim. (4) 29, 32-34 (1921). (5) Chattaway, Irving, Outhwaite, J. Chem. Soc. 1933, 993-995. (6) Sarnow, Ann. 164, 108 (1872). (7) Lieben, Zeisel, Monatsh. 4, 532-536 (1883). (8) Leopold, van Zütphen (to I.G.), Ger. 559,329, Feb. 20, 1933; Cent. 1933, I 2608. (9) Bayer and Co., U.S. 1,572,742, Feb. 9, 1926; Cent. 1926, I 3627: Brit. 235,584, June 27, 1926; Cent. 1926, II 1097; I.G., Ger. 437,160, Nov. 18, 1926; Cent. 1927, I 802. (10) I.G., Brit. 370,490, May 5, 1932; Cent. 1932, II 3304.

(11) Billig (to I.G.), U.S. 2,131,998, Oct. 4, 1938; Cent. 1939, I 3454; C.A. 33, 271 (1939); Ger. 667,793, Nov. 19, 1938; Ger. 669,805, Jan. 1, 1939; Cent. 1939, I 2294. (12) Nicodemus, Vollmann, Schloffer (to I.G.), Ger. 715,201, Dec. 16, 1941; Cent. 1942, I 1811. (13) Hrubesch, Schlichting (to I.G.), Ger. 720,467, May 7, 1942; Cent. 1942, II 2087. (14) The Distillers Co. Ltd., Staudinger, Tuerck, Lichtenstein, Brit. 554,570, July 9, 1943; C.A. 39, 312 (1945).

3:8120 2,4-DICHLOROPENTANE Cl Cl
$$C_5H_{10}Cl_2$$
 Beil. I — $C_7H_{10}Cl_{10}$ CH₃ $C_7H_{10}Cl_{10}$ CH₄ $C_7H_{10}Cl_{10}$ CH₅ $C_7H_{10}Cl_{10}$ $C_7H_{10}C$

B.P. 147–150° (1)
$$D_{-}^{18} = 1.063$$
 (1) $n_{0}^{18} = 1.447$ (1) $62-62.5$ ° at 12 mm. (2) $D_{4}^{12} = 1.0529$ (2) $n_{C}^{12} = 1.4495$ (2)

[For prepn. of C from penten-1-ol-4 (allyl-methyl-carbinol) [Beil. I-443] with PCls. followed by aq., see (1) (some 4-chloropentene-1 (3:7350) is also formed (1)); for formn, of \bar{C} (together with other prods.) from pentane (1:8505) + Cl_2 see (3).

[For study of hydrolysis of \bar{C} with N/10 alc. KOH see (2).]

3:8120 (1) Pariselle, Compt. rend. 154, 712 (1912). (2) Tishchenko, J. Gen. Chem. (U.S.S.R.) 9, 1380-1388 (1939); C.A. 34, 1611 (1940). (3) Lemke, Tishchenko, J. Gen. Chem. 7, 1995-1998 (1937); Cent. 1939, I 2397; C.A. 32, 482 (1938).

3: 8125 ETHYL
$$d$$
, l - α -CHLOROPROPIONATE $C_5H_9O_2Cl$ H_1 -(111) Cl CC_2H_5 H_1 -(111) H_2 -(226) H_1 -(226) H_1 -(226) H_2 -(226) H_1 -(226) H_2 -(226) H_2 -(226) H_1 -(226) H_2 -(226) H_2 -(226) H_2 -(226) H_1 -(226) H_2

[For prepn. of \bar{C} from α -chloropropionic acid (3:6125) + EtOH + HCl see (8); from α -chloropropionyl chloride (3:5320) + EtOH see (2) (3) (4) (9) (10) (11); from ethyl d, l-lactate (1:3303) + SOCl₂ + pyridine (95% yield) see (5); from ethyl α -aminopropionate hydrochloride + $NaNO_2$ + HCl see (12).]

[C with alc. NaOEt yields (13) ethyl ethoxypropionate [Beil. III-280, III₁-(109), III₂-(206)], b.p. 155°, but C with dry NaOEt yields (14) (15) both cis and trans forms of diethyl cyclobutane-1,3-dicarboxylate [Beil. IX-726].]

[For reactn. of C with excess C₆H₅MgBr in ether yielding 1,1,2-triphenylpropene-1 [Beil. V-723, V₁-(356)], m.p. 89-90°, see (16); for study of cat. hydrogenation of C see (8); for NaOEt condensation of \bar{C} with citral (1:0230) or with citronellal (1:0220) see (17) (18); for NaOEt condensation with cyclohexanone see (10).

 \bar{C} on hydrolysis yields EtOH (1:6130) + $d_{\nu}l_{\nu}\alpha$ -chloropropionic acid (3:6125). [For study of kinetics of hydrolysis see (20) (21) (22).]

For the amide, anilide, p-toluidide, and other derivatives corresp. to \tilde{C} see d.l- α -chloropropionic acid (3:6125).

D Ethyl α -(tetrachlorophthalimido)propionate: rods from dioxane, poured into 2 vols. MeOH and aq. added, m.p. 159-160° (23). [From C + K tetrachlorophthalimide as directed (23).1

3:8125 (1) Perkin, J. Chem. Soc. 65, 428 (1894). (2) Brühl, Ann. 203, 24-25 (1880). (3) Beckurts, Otto, Ber. 9, 1592 (1876). (4) Simpson, J. Am. Chem. Soc. 40, 674 (1918). (5) Darzens, Compt. rend. 152, 1601 (1911). (6) Burkard, Kahovec, Monatsh. 71, 340 (1938). (7) Schjanberg, Z.

7ena. 105, 1001 (1911). (o) Burkerd, Ranovec, Mondain. 11, 340 (1950). (7) Schlanders, Z. physik. Chem. A-172, 230 (1935). (8) Paal, Müller-Lobeck, Ber. 64, 2144-2147 (1931). (9) Wurts, Ann. 107, 195 (1858). (10) Ulrich, Ann 109, 268 (1859). (11) Brühl, Ber. 9, 35 (1876). (12) Barker, Skinner, J. Am. Chem. Soc. 46, 412-413 (1924). (13) Wurtz, Ann. chim. (3) 59, 169-170 (1860). (14) Haworth, Perkin, J. Chem. Soc. 73, 336-339 (1898). (15) Markownikow, Krestownikow, Ann. 208, 334-349 (1881). (16) Levy, Compt. rend. 172, 385 (1921); Bull. soc. chim. (4) 29, 894 (1921). (17) Barbier, Helv. Chim. Acta 17, 1026-1030 (1934). (18) Givaudan et Cie, Ger. 596,255, May 11, 1934; Cent. 1934, II 1214. (19) Yarnall, Wallis, J. Org. Chem. 4, 277-278 (1939). (20) Anantakrishman, Krishnamurti, Proc. Indian Acad. Sci. 14-A, 270-278 (1941); C.A. 36, 1837 (1942).

(21) Drushel, Am. J. Sci. (4) 34, 69-74 (1912); Cent. 1912, II 704; C.A. 6, 2593 (1912). (22) Bolin, Z. anorg. allgem. Chem. 177, 246-248 (1929).

3:8132 4,4-DICHLORO-2,2-DIMETHYLBUTANE
$$C_6H_{12}Cl_2$$
 Beil. S.N. 10 (1,1-Dichloro-3,3-dimethylbutane) CH_3 Cl CH_3 CH_4 CH_5 CH_5

B.P. M.P.
$$-56.5^{\circ}/-56.0^{\circ}$$
 (1) $D_4^{20} = 1.0262$ (1) $n_4^{20} = 1.4389$ (1)

[For prepn. of \bar{C} from vinyl chloride (3:7010) with 2-methylbutane (isobutane) + AlCl₃ at -10° (40% yield) or with ter-butyl chloride (3:7045) see (1).]

C with aq. in s.t. at 300° hydrolyzes to ter-butylacetaldehyde, b.p. 102-103° (corresp. methone, m.p. 162-163°; corresp. 2,4-dinitrophenylhydrazone, m.p. 146-147°) (1).

3:8132 (1) Schmerling, J. Am. Chem. Soc. 67, 1438-1441 (1945).

B.P. 148.4-148.8° (1)
$$D_{25}^{25} = 1.0773$$
 (2) $n_{\rm D}^{25} = 1.4453$ (2) 146.0-146.2° (2) 1.0667 (2) 1.4448 (2) 145.8-146.2° at 739 mm. (2) 58-59° at 28 mm. (3) $D_{4}^{20} = 1.0872$ (1) $n_{\rm D}^{20} = 1.4485$ (1)

Colorless oil, insol. aq., volatile with steam.

[For prepn. of \bar{C} (70% yield (2)) from 1-chloropentanol-2 (3:8225) with SOCl₂ + diethylaniline or from pentene-1 (1:8205) in CCl₄ at 0°+Cl₂ (50% yield (2)) (1) see (1) (2).]

[For form. of \tilde{C} (together with other prods.) from pentane (1:8505) (3) or from 1-chloropentane (3:7460) (4) with Cl_2 see indic. refs.]

Č with alc. KOH gives (3) 1-chloropentene-1 (3:7420), but Č with K₂CO₃ does not (3) yield the corresp. glycol.

3:8140 (1) Tishchenko, Shchigel'skaya, J. Gen. Chem. (U.S.S.R.) 7, 1246-1248 (1937); Cent. 1938, II 2576, C.A. 31, 6189 (1937). (2) Koelsch, McElvain, J. Am. Chem. Soc. 51, 3393-3394 (1929). (3) Lemke, Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 1995-1998 (1937); Cent. 1939, I 2398; C.A. 32, 482 (1938). (4) Hass, Huffman, J. Am. Chem. Soc. 63, 1233-1235 (1941).

[For prepn. of \bar{C} from α -chloro-isovaleric acid (3:0050) with PCl₃ see (1).] \bar{C} on hydrolysis with aq. yields α -chloro-isovaleric acid (3:0050).

3:8144 (1) Servais, Rec. trav. chim. 20, 53 (1901).

3:8145 $\alpha_{j}\alpha_{j}\beta$ -TRIMETHYL-n-BUTYRYL CHLORIDE C₇H₁₃OCl Beil. S.N. 162 (Dimethyl-isopropyl-acetyl chloride) CH₃

B.P. 148-150° (1)

[For prepn. of \bar{C} from dimethyl-isopropyl-acetic acid [Beil. II-346, II₁-(147)] see (1).] \bar{C} on hydrolysis yields dimethyl-isopropyl-acetic acid (see above), camphoraceous cryst. from pet. ether, m.p. 50° (2) (3), 41-42° (1).

- Dimethyl-isopropyl-acet-amide: m.p. 133-134° (2), 129° (1).
- 3:8145 (1) Locquin, Leers, Compt. rend. 179, 55 (1924). (2) Haller, Bauer, Compt. rend. 149, 6 (1909). (3) Richard, Ann. chim. (8) 21, 353 (1910).

3:8147 ETHYL
$$\alpha$$
-CHLORO-ISOBUTYRATE Cl C₆H₁₁O₂Cl Beil. II -295 CH₃—C—COOC₂H₅ II₁—II₂—

B.P.
$$148.5^{-}149^{\circ}$$
 cor. (1) $D_{-}^{0} = 1.062$ (1) $n_{\rm D}^{16} = 1.4109$ (5) $148-149^{\circ}$ (2) $147-148.5^{\circ}$ at 760 mm. (5)

[For prepn. of \bar{C} from α -chloro-isobutyric acid (3:0235) with EtOH + HCl see (3); from α -chloro-isobutyryl chloride (3:5385) with EtOH see (2).]

 $[\bar{C}$ on htg. with 1-5% FeCl₃ at 100° or above loses HCl yielding (4) ethyl methacrylate, b.p. 118-119° (4).]

3:8147 (1) Balbiano, Ber. 11, 1693 (1878).
 42) Henry, Rec. trav. chim. 26, 84-85 (1907); Compt. rend. 142, 1023 (1906), Bull. acad. roy Belg. 1906, 206-226; Cent. 1906, 11 227.
 43) Balbiano, Gazz. chim. tal. 8, 372 (1878).
 44) Barrett (to du Pont), U.S. 2,013,648, Sept. 10, 1935; Cent. 1936, 1 3217; C.A. 29, 6902 (1935)
 45) Kahovee, Kohlrausch, Monatsh. 74, 116 (1943).

3: 8150
$$\beta$$
-CHLOROISOPROPYL ACETATE CH₂Cl C₅H₉O₂Cl Beil. II - 130 (2-Acetoxy-1-chloropropane) HC-O.COCH₃ II₁- II₂-

B.P.
$$149-150^{\circ}$$
 (1) (2) $D_{-}^{20}=1.0788$ (3) $n_{D}^{20}=1.4223$ (3) $147-149^{\circ}$ at 745 mm. (3)

[For prepn. (72% yield (3)) from propylene + ter-butyl hypochlorite (3:7165) + AcOH see (3); for prepn. from 1-chloropropanol-2 (3:7747) + AcCl see (2); for formn. from 1,2-diacetoxypropane + HCl gas see (4).]

1 ml. aq. dis. 8 ml. \bar{C} . — With N/10 HCl at 35° or 45° \bar{C} hydrolyzes much more slowly than isopropyl acetate (1:3041), but no chloride ion is liberated at 35° (1).

- ① 1-Phthalimido-2-acetoxypropane [Beil. XXI₁-(369)]: from \tilde{C} on htg. 2 hrs. with K phthalimide; m.p. 99-100° (5).
- 3:8150 (1) Henry, Cent. 1902, II 1093. (2) Bancroft, J. Am. Chem. Soc. 41, 427 (1919). (3) Irwin, Hennion, J. Am. Chem. Soc. 63, 859 (1941). (4) Dewael, Bull. soc. chim. Belg. 39, 400 (1930). (5) Gabriel, Ohle, Ber. 50, 808 (1917).

3: 8152 TETRAHYDRO-α-FURFURYL CHLORIDE C₅H₉OCl Beil, S.N. 2362 (2-(Chloromethyl)tetrahydrofuran) CH₉—CH₉

B.P.
$$150-151^{\circ}$$
 at 762 mm. (1) $D_4^{20} = 1.1102$ (2) $n_D^{20} = 1.4560$ (2) $149.0-149.5^{\circ}$ at 721 mm. (2) $47-48^{\circ}$ at 15 mm. (3) $n_D^{12} = 1.45922$ (1) $41-42^{\circ}$ at 11 mm. (3) $38.5-39^{\circ}$ at 10 mm. (2)

Water-white liq. with mild and pleasant odor. — Č has no lachrymatory properties and is relatively stable (2); its chlorine atom is extremely unreactive (2).

[For prepn. of \bar{C} from tetrahydro- α -furfuryl alcohol (1:6445) with SOCl₂ + pyridine (yields: 75% (2), 73-75% (3)) see indic. refs.; note that attempts to replace SOCl₂ by PCl₃ (excess) in dry ether (2) were *not* successful; for formn. of \bar{C} from 5-chloropentanediol-1,4 (1) by dehydrative ring closure with 15% H_2SO_4 at 100° for 2 hrs. (19% yield) see (1).]

C with metallic Na in dry ether under reflux, subsequently decomposed by water, gives (yields: 82% (4), 76-83% (3)) penten-4-ol-1 (penten-1-ol-5) [Beil. I-443, I₂-(483)], b.p. 141.0-141.5° at 758 mm. (5), 139° at 760 mm. (6), 138.8-139.3° at 760 mm. (7); $D_4^{25} = 0.8588$ (7), $D_4^{20} = 0.8457$ (5); $n_D^{20} = 1.43085$ (5), $n_D^{15.5} = 1.4312$ (8), $n_D^{15} = 1.4305$ (9) (corresp. allophanate, m.p. 148° (6), 147-148° (9); corresp. N-phenylcarbamate, oil, b.p. 183.5° at 16 mm. (8)).

 \ddot{C} with thiourea refluxed in alc. 4 days gives (10) S-(tetrahydro- α -furfuryl)isothiourea, isolated as corresp. picrate, m.p. 153.0–153.5° (10).

3:8152 (1) Paul, Ann. chim. (10) 18, 385-386 (1932). (2) Kirner, J. Am. Chem. Soc. 52, 3251-3255 (1930). (3) Brooks, Snyder, Org. Syntheses 25, 84-86 (1945). (4) Gaubert, Linstead, Rydon, J. Chem. Soc. 1937, 1972. (5) Juvala, Ber. 63, 1993 (1930). (6) Paul, Compt. rend. 195, 1290-1291 (1932). (7) Ginnings, Herring, Coltrane, J. Am. Chem. Soc. 61, 807 (1939). (8) Robinson, Smith, J. Chem. Soc. 1936, 196. (9) Paul, Compt. rend. 192, 1574 (1931). (10) Sprague, Johnson, J. Am. Chem. Soc. 59, 2440-2441 (1937).

B.P. 150-151° at 745 mm. (1)
$$D_4^{20} = 0.8825$$
 (1) $n_D^{20} = 1.4299$ (1) $52-53°$ at 20 mm. (1)

[For prepn. of \bar{C} from allyl chloride (3:7035) with 2-methylpropane (isobutane) + AlCl₃ at -10° (35-40% yield accompanied by 13-15% yield 4,5-dichloro-2,2-dimethylpentane (3:8516) see (1).]

Č on hydrolysis with aq. MgO in s.t. at 225° for 4 hrs. gives $(54\% \text{ yield } \{1\})$ 3,4-dimethylpentanol-1, b.p. $168-169^{\circ}$, $n_D^{20} = 1.4288$ (corresp. 3,5-dimitrobenzoate, m.p. $51-52^{\circ}$; corresp. $N-(\alpha-\text{naphthylcarbamate})$, m.p. $41-42^{\circ}$) (1).

 \tilde{C} with Mg in dry ether gives corresp. RMgCl cpd.; this prod. on hydrolysis with aq. $(NH_4)_2SO_4$ gives (54% yield (1)) 2,3-dimethylpentane (1:8554) or on oxidn. with air gives (62% yield (1)) 3,4-dimethylpentanol-1 (see preceding paragraph); see also below.

Φ γ,8-Dimethylcaproanilide: nacreous flakes from dil. alc., m.p. 80-81° (1). [From C by conversion to RMgCl and reaction with phenyl isocyanate (1) according to method of (2) cf. (3).]

3:8153 (1) Schmerling, J. Am. Chem. Soc. 67, 1438-1441 (1945). (2) Schwartz, Johnson, J. Am. Chem. Soc. 53, 1063-1068 (1931). (3) Underwood, Gale, J. Am. Chem. Soc. 56, 2117-2120 (1934).

3:8155
$$d$$
, l -1-CHLORO-3-METHYLHEXANE $C_7H_{15}Cl$ Beil. I — CH_3 Cl I_1 — CH_3 . CH_2 . CH_2 — C — CH_2 . CH_2 I_2 -(119)

B.P. 150-152° at 758 mm. (1)
$$D_4^{20} = 0.8766$$
 (1) $n_D^{20} = 1.4274$ (1)

[For prepn. of \bar{C} from 3-methylhexanol-1 [Beil. I₂-(445)] with alc. HCl in s.t. at 100° see (1).] [The dextrorotatory form of \bar{C} has also been prepd. (2) from levorotatory 3-methylhexanol-1 with SOCl₂; b.p. 66° at 25 mm.; $D_4^{29} = 0.854$; $n_D^{30} = 1.4282$ (2).]

3:8155 (1) Dewael, Weckering, Bull. soc. chim. Belg. 33, 498 (1924). (2) Levene, Marker, J. Biol. Chem. 91, 90 (1931).

3:8160 ISOPROPYL CHLOROACETATE
$$C_5H_9O_2Cl$$
 Beil. II - 198 $II_1 II_2 II_2 II_2 II_2 II_2 II_2 II_3-$

B.P.
$$150.4-151.6^{\circ}$$
 (1) $D_4^{25} = 1.0812$ (3) $n_D^{25} = 1.4175$ (3) 149.5° at 760 mm. (2) $D_4^{20} = 1.0888$ (5) $n_D^{20} = 1.4192$ (5) 149.5° at 747 mm. (3) $D_4^{15} = 1.0944$ (4) $149-150^{\circ}$ at 760 mm. (4)

Oil with agreeable odor; insol. aq., sol. alc., ether.

[For prepn. (38.8% yield (3)) from isopropyl alc. (1:6135) + chloroacetic ac. (3:1370) see (3) (4); for prepn. (34.2% yield (3)) from propylene + chloroacetic ac. (3:1370) see (3).]

[For study of insecticidal action of vapor of C see (2).]

3:8160 (1) Cheng, Z. physik. Chem. B-24, 309 (1934). (2) Roark, Cotton, Ind. Eng. Chem. 20, 512-514 (1928). (3) Dorris, Sowa, Nieuwland, J. Am. Chem. Soc. 56, 2689-2690 (1934). (4) Steinlen, Bull. acad. roy. Belg. (3) 34, 101-108 (1897); Cent. 1897, II 659. (5) Schjanberg, Z. physik. Chem. A-172, 228 (1935).

3:8165 ISOPROPYL d,l-α-CHLOROPROPIONATE C₆H₁₁O₂Cl Beil. S.N. 162

B.P.
$$151.5-152.5^{\circ}$$
 at 760 mm. (1) $D_4^{20} = 1.0315$ (2) $n_D^{20} = 1.4149$ (2) $46.1-46.9^{\circ}$ at 12 mm. (1)

3:8165 (1) Burkard, Kahovec, *Monatsh.* 71, 340 (1938). (2) Schjanberg, *Z. physik. Chem.* A-172, 230 (1935).

[For prepn. of \bar{C} from n-caproic acid (1:1130) with PCl₅ (62% yield (6)), with PCl₃ (84% yield (1)) (4) or with PCl₃ + ZnCl₂ (89% yield (6)), with SOCl₂ (yield: 95% (9), 77% (6)) (5) (11), with benzoyl chloride (80% yield (7)), or with oxalyl dichloride (3:5060) (12) see indic. refs.; for formn. of \bar{C} from ozonide of heptync-1 (1:8085) with SOCl₂ see (13).]

[$\tilde{\mathbf{C}}$ htd. with sodium *n*-caproate gives (72% yield (1)) *n*-caproic anhydride (1:1150), b.p. 142.9° at 14.5 mm., f.p. -40.6° , $D_{4}^{20} = 0.91983$, $n_{D}^{20} = 1.42971$ (1).]

[\bar{C} with 2 moles Br₂ yields (5) α -bromo-n-caproyl chloride, b.p. 106-107° at 31 mm. (5), 102-105° at 30 mm. (14).]

[For reactn. of \bar{C} with various acylureas see (15); with vanillylamine see (10) (16); with cyclohexene (1:8070) + AlCl₃ yielding n-amyl o-chlorocyclohexyl ketone see (17).]

[\bar{C} with AlCl₃ + phenol yields (18) 56% o-(n-hexanoyl)phenol, b.p. 145-147° at 15 mm. (19), 142-143° at 10 mm. (18), m.p. 22° (19), 17.2-17.4° (18), D_{-}^{24} = 1.0260 (18), n_{D}^{25} = 1.5254 (18) (phenylhydrazone, m.p. 102-103° (19), semicarbazone, m.p. 179° (18)) and 34% p-(n-hexanoyl)phenol, m.p. 63-64° (19), 61° (18), b.p. 207-208° at 10 mm. (18) (benzoate, m.p. 105.5° (18)). — For reactn. of \bar{C} with resorcinol (1:1530) leading to 4-(n-hexanoyl)-1,3-resorcinol (n-amyl 2,4-dihydroxyphenyl ketone) (1:1443) see (20) (21).]

 $\tilde{\mathbf{C}}$ on hydrolysis yields *n*-caproic acid (*n*-hexanoic acid) (1:1130). — For the amide, anilide, *p*-toluidide, and other derivs. corresp. to $\tilde{\mathbf{C}}$ see *n*-caproic acid (1:1130).

3:8168 (1) Simon, Bull. soc. chim. Belg. 38, 51, 56, 59 (1929). (2) Kohlrausch, Pongratz, Z. physik. Chem. B-22, 382 (1933). (3) Norstedt, Wahlforss, Ber. 25, Referate, 637 (1862). (4) Reitter, Z. physik. Chem. 36, 138 (1901). (5) Bardan, Bull. soc. chim. (5) 1, 142 (1934). (6) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (7) Brown, J. Am. Chem. Soc. 60, 1325-1328 (1938). (8) Ponzio, de Gaspari, J. prakt. Chem. (2) 58, 397 Note (1898). (9) Fierz-David, Küster, Helv. Chim. Acta 22, 89 (1939). (10) Ford-Moore, Phillips, Rec. trav. chim. 53, 855 (1934).

(11) Meyer, Monatsh. 22, 418 (1901). (12) Averill, Roche, King, J. Am. Chem. Soc. 51, 868 (1929). (13) Paillard, Wieland, Helv. Chim. Acta 21, 1359-1360 (1938). (14) Marvel, Noyes, J. Am. Chem. Soc. 42, 2273 (1920). (15) Stoughton, J. Org. Chem. 2, 514-521 (1938). (16) Nelson, J. Am. Chem. Soc. 41, 2123-2124 (1919). (17) Nenitzescu, Cioranescu, Ber. 69, 1823 (1936). (18) Sandulesco, Girard, Bull. soc. chim. (4) 47, 1305-1310 (1930). (19) Coulthard, Marshall, Pyman, J. Chem. Soc. 1930, 280-291. (20) Pope, Brit. 287,967, April 26, 1928; Cent. 1929, I 439; C.A. 23, 395 (1929).

(21) Cox, Rec. trav. chim. 50, 848-850 (1931).

3:8170 1,3-DICHLORO-2-METHYLBUTENE-2
$$CH_3$$
 $C_5H_8Cl_2$ Beil. S.N. 11

B.P. 151-153° (1)
$$D_4^{19} = 1.1276$$
 (1) $n_C^{19} = 1.4737$ (1)

Two geom. stereoisomers of C are possible, but only this one has been reported.

[For formn. of C from 1,2,3-trichloro-2-methylbutane (3:6100) by loss of 1 HCl through distn. over KOH see (2); from 3,3-dichloro-2-methylbutene-1 (3:7690) by htg. (allylic transposition) see (1).]

 \bar{C} on oxidn. with KMnO₄ in acetone gives (2) acetic acid (1:1010) and methylglyoxal [Beil. I-762, I₁-(395), I₂-(819)].

3:8170 (1) Tishchenko, J. Gen. Chem. '(U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4223; C.A. 33, 4190 (1939). (2) Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1116-1132 (1936); Cent. 1937, I 573; C.A. 31, 1003 (1937).

B.P.
$$152-153^{\circ}$$
 (1) $D_{-}^{0} = 1.068$ (1) $145-149^{\circ}$ (2)

[For prepn. of \bar{C} from chloroacetone (3:5425) with EtMgBr see (1) (2) (3) (4) (5); note that in this reactn. \bar{C} is accompanied by 3-methylhexanol-4 [Beil. I-416], whose b.p. (150°) is so close to that of \bar{C} that separation by distillation is impossible.]

 \bar{C} on distillation (5) or on treatment with Ac₂O + conc. H₂SO₄ (5) yields 1-chloro-2-methylbutene-1 (3:7303) and 1-chloro-2-methylbutene-2 (3:7485); \bar{C} on distn. over anhydrous oxalic acid (1:0535) yields (6) both these halo-olefins and also 2-(chloromethyl)-butene-1 (3:9214). [\bar{C} on distn. over anhydrous oxalic acid (1:0535) and passing the resultant vapors over soda-lime or burnt lime at 600° yields (7) 2-methylbutadiene-1,3 (isoprene) (1:8020).]

C with PCl₅ yields (5) 1-chloro-2-methylbutene-1 (3:7303).

Č with conc. aq. NaOH at 40-50° gives (63% yield (9) (1) (4) (10) 1,2-epoxy-2-methylbutane (unsym.-ethyl-methyl-ethylene oxide) [Beil. XVII-13, XVII₁-(8)], b.p. 82°.

3:8175 (1) Fourneau, Tiffeneau, Compt. rend. 145, 437-438 (1907). (2) Tiffeneau, Compt. rend. 134, 774 (1902). (3) Bruylants, Bull. acad. roy. Belg. (5) 17, 1008-1026 (1931). (4) Kyriakides, Am. Chem. Soc. 36, 657-663 (1914). (5) Seyer, Chalmers, Trans. Roy. Soc. Can. (3) 29, III 337 (1926); Cent. 1927, II 1811; C.A. 21, 2663 (1927). (6) Chalmers, Trans. Roy. Soc. Can. (3) 22, III 75-76 (1928); Cent. 1929, I 632; C.A. 23, 2694 (1929). (7) Harries, Ann. 383, 178 (1911). (8) Harries, Ger. 243,075 + 243,076, Jan. 31, 1912; Cent. 1912, I 535. (9) Fourneau, Benoit, Firmenick, Bull. soc. chim. (4) 47, 870 (1930). (10) Riedel, Ger. 199,148, June 3, 1908; Cent. 1996, II 121.

3:8180-3:8205

3:8180
$$\beta$$
-CHLORO- n -PROPYL ACETATE H $C_6H_9O_2Cl$ Beil. II - 129 (1-Acetoxy-2-chloropropane) CH₃-C-CH₂.O.CO.CH₃ Π_1 -(58) Π_2 -

B.P. 152-153° at 750 mm. (1)
$$D_4^{20} = 1.095$$
 (2) $n_D^{20} = 1.42213$ (2) $D_{20}^{20} = 1.098$ (3)

Colorless oil with agreeable odor. - Insol aq.

[Note that \bar{C} has never been obtd. in authentically pure state. The prepn. of Henry (1) was later shown (4) to be actually a mixt. of \bar{C} with 2-acetoxy-1-chloropropane (3:8150); that of Dewael (2) was admittedly such a mixture.]

Henry's material was obtd. from 1-chloropropanol-2 by treatment with KOAc and conversion of the presumably resultant 1-acetoxypropanol-2 with SOCl₂ to \tilde{C} ; Dewael's material was obtd. from 1,2-diacetoxypropane by treatment with HCl gas.

3:8180 (1) Henry, Cent. 1902, II 929, 1093. (2) Dewael, Bull. soc. chim. Belg. 39, 400 (1930). (3) Henry, Cent. 1903, II 486. (4) Gabriel, Ohle, Ber. 50, 806 (1917).

B.P. 153° (1)
$$D_4^{20} = 0.8924$$
 (2) $n_D^{25} = 1.4590$ (1) 69–70° at 9 mm. (2) 0.8816 (1) $n_D^{20} = 1.4452$ (2)

Note that two geom. stereoisomers of \tilde{C} are possible; also the possibility that by allylic transposition \tilde{C} may react in the form of its as yet unrecognized synionic isomer, 2-chloroctene-3.

[For prepn. of \ddot{C} from octen-2-ol-4 [Beil. I₂-489] (1) (2) with PCl₅ in ether at 0° (43% yield (2)), with HCl (3), or with Cl₂ (1) see indic. refs.]

[$\bar{\mathbf{C}}$ with phenol + $K_2\mathrm{CO}_3$ in acctone yields phenyl α -(n-butyl)crotyl ether, b.p. 107-108° at 4 mm., $D_{18}^{18} = 0.9208$, $n_D^{18} = 1.4955$ (2); $\bar{\mathbf{C}}$ similarly with o-cresol yields α -(n-butyl)crotyl o-tolyl ether, b.p. 118-119° at 4 mm., $D_{18}^{18} = 0.9143$, $n_D^{18} = 1.4950$ (2).]

3:8185 (1) Karasev, Khabarova, J. Gen. Chem. (U.S.S.R.) 16, 1641-1646 (1940); C.A. 35, 3225 (1941) (English translation in Foreign Petroleum Tech. 9, 42-51 (1941)). (2) Hurd, Puterbaugh, J. Org. Chem. 2, 381-386 (1937). (3) Knorr, (to I.G.) Ger. 553,279, June 24, 1932; Cent. 1932, II 2370.

3:8205 d,l-4-CHLORO-6-METHYLHEPTENE-1
$$C_8H_{16}Cl$$
 Beil. I -222 (4-Chloro-2-methylheptene-6; allyl-isobutyl-carbinyl chloride) CH_2 — CH_2 — CH_2 — CH_2 — CH_3 — CH_4

B.P. 150-155° dec. (1)

[For prepn. of \tilde{C} from 2-methylhepten-6-ol-4 (allyl-isobutyl-carbinol) [Beil. I-448] with PCl₅ see (1).]

 $\ddot{\mathbf{C}}$ on htg. with powdered KOH at 140° loses HCl yielding (1) 2-methylheptadiene-4,6 [Beil, I-258], b.p. 116-118°, $D_{-2}^{22} = 0.741$ (1).

3:8265 (1) Fournier, Bull. soc. chim. (3) 15, 400-401 (1896).

3:8210-3:8217

3: 8210 3-CHLORO-3-ETHYL-2-METHYLPENTANE C₈H₁₇Cl Beil. I -164
(3-Chloro-3-methoethylpentane; Cl H
diethyl-isopropyl-carbinyl chloride)
CH₃.CH₂ C
CH₄ CH₅

B.P. 150-155° dec. (1).

[For prepn. from 3-ethyl-2-methylpentanol-3 (diethyl-isopropyl-carbinol) [Beil. I-423, I_{2} -(454)] with PCl₅ see (1).]

3:8210 (1) Grigorowitsch, Pavlov, J. Russ. Phys.-Chem. Soc. 23, 169 (1891).

3:8215 ISOAMYL CHLOROFORMATE $C_6H_{11}O_2Cl$ Beil. III - 12 (Isoamyl chlorocarbonate) iso- $C_6H_{11}O$.CO.Cl III₁-(6) III₂-(11)

B.P. 154.3° cor. (1) $D_i^{15} = 1.0321$ (2) $n_{\text{He}}^{16} = 1.41916$ (2)

[For prepn. from isoamyl alc. (1:6200) + phosgene (3:5000) see (1).]

- ➡ Isoamyl N-phenylcarbamate (isoamyl carbanilate): m.p. 57-58° (6), 57-59° (7),
 55° (8), 55-56° (9). [This deriv. is not recorded directly from C but should be preparable by actn. of aniline, cf. (5).]
- 3:8215 (1) Roese, Ann. 205, 230 (1880). (2) von Auwers, Ber. 60, 2140 (1927). (3) Marckwald, Ber. 37, 1040 (1904). (4) Béhal, Bull. soc. chim. (4) 25, 480 (1919). (5) Chattaway, Saerens, J. Chem. Soc. 117, 708-711 (1920). (6) Locquin, Bull. soc. chim. (3) 31, 600 (1904). (7) Levene, Allen, J. Biol. Chem. 27, 440 (1916). (8) Marckwald, Ber. 37, 1049 (1904). (9) Nekrassow, Melnikow, J. prakt. Chem. (2) 126, 92 (1930).

3: 8217 1-CHLOROPENTANONE-2
$$C_6H_9OCl$$
 Beil. I — (Chloromethyl *n*-propyl ketone) $CH_3.CH_2.CH_2.CH_2.CH_2$ I_1 -(350) I_2 -(738)

B.P. 154.5-156° sl. dec. (1)

58-59° at 17 mm. (1)

55-57° at 15 mm. (2

Liquid with penetrating odor. — Very spar. sol. aq.; volatile with steam.

[For prepn. of \bar{C} from 1-chloropentanol-2 (3:8225) by oxidn. with $K_2Cr_2O_7/H_2SO_4$ see (2); from 2-chloromethyl-4-methyl-2-propyl-1,3-dioxolone-5 [Beil. XIX₁-(657)] by hydrolytic cleavage with alk., or from 2-chloromethyl-4,4-dimethyl-2-propyl-1,3-dioxolone-5 [Beil. XIX₁-(657)] by hydrolytic cleavage with aq. HCl/AcOH on warming (75-80% yield), see (1).]

[$\ddot{\mathbf{C}}$ with dry K formate in MeOH refluxed overnight yields (2) pentanone-2-ol-1 [Beil. I₂-(872)], b.p. 62-64° at 18 mm. (2), 54-56° at 11 mm., $D_4^{20} = 0.9860$, $n_2^{20} = 1.4234$ (3).]

Č readily forms a cpd. with satd. aq. NaHSO₃ soln. (2).

Č does not react (4) with benzenediazonium hydroxide (diazotized aniline in NaOAe soln.), cf. chloroacetone (3:5425).

① 1-Chloropentanone-2 semicarbazone: m.p. 157° (instantaneous fusion on Hg bath) with decomp. (1).

3:8317 (1) Blaise, Bull. soc. chim. (4) 15, 672-673 (1914); Compt. rend. 155, 48 (1912). (2) Levene, Haller, J. Biol. Chem. 77, 560-561 (1928). (3) Schmidt, Ascherl, Ber. 58, 358 (1925). (4) Fayrel, Bull. soc. chim. (5) 1, 990 (1934).

3:8219 1-CHLOROHEPTENE-1 CH_3 . $(CH_2)_4$.CH=CHCl $C_7H_{18}Cl$ Beil. I - 219 I₁---

I₂-(196)

B.P. 155° cor. (1) 149-150° at 733 mm. (2) 148° (3) 78-82° at 75 mm. (4)

Note that although two geom. steroisomers of $\tilde{\mathbf{C}}$ are possible only one has yet been recognized.

[For prepn. of \tilde{C} from 1,1-dichloroheptane (3:8650) by elimination of 1 HCl with alc. KOH (1) (3) (note, however, that yields are low (4) and the process has sometimes (5) failed), or better large excess solid KOH at 200° (62% yield (4)), see indic. refs.; from n-heptaldehyde (1:0183) with PCl₅ see (6).

 \bar{C} with KOH in mineral oil at 250° (4), or with NaNH₂ in toluene or xylene at 100-150° (6), or in mineral oil (Nujol) at 150-155° (7) gives (yields: 54% (7), 37% (4)) heptyne-1 (1:8085), b.p. 98°.

[$\bar{\rm C}$ with perbenzoic acid (benzoyl hydrogen peroxide) in CHCl₃ for 25 days gives (2) corresp. oxide, viz., 1-chloro-1,2-epoxyheptane, b.p. 93-95° at 50 mm., $D_4^{16}=0.9874$, $n_D^-=1.4370$ (2).]

[Č with NaSC₂H₅ in n-BuOH under reflux or better in EtOH at 138° under pressure gives (8) ethyl hepten-1-yl sulfide, b.p. 196-202°.]

3:8219 (1) Limpricht, Ann. 103, 82-83 (1857). (2) Prileschajew, Ber. 59, 196-197 (1926). (3) Welt, Ber. 30, 1496 (1897). (4) Bachmann, Hill, J. Am. Chem. Soc. 56, 2731 (1934). (5) Guest J. Am. Chem. Soc. 47, 801 (1925). (6) Bourgeul, Compt. rend. 177, 823 (1923); 178, 1560 (1924). (7) Johnson, McEwen, J. Am. Chem. Soc. 48, 473 (1926). (8) Loevenich, Losen, Dierichs, Ber. 60, 954 (1927).

3: 8220 ter-BUTYL CHLOROACETATE $C_6H_{11}O_2Cl$ Beil. S.N. 160 $(CH_3)_3C.O.CO.CH_2Cl$

B.P. 155° sl. dec. (1) $n_D^{20} = 1.4260$ (2) 60.2° at 15 mm. (1) 1.4230 (1) $48-49^{\circ}$ at 11 mm. (2)

Colorless liq. heavier than aq. (1).

[For prepn. (yield: 63% (2), 60% (1)) from ter-butyl alc. (1:6140) + chloroacetyl chloride (3:5235) + dimethylaniline see (1) (2).]

Hydrolysis yields (1) ter-butyl alc. (1:6140) + chloroacetic acid (3:1370) (1); Sap. Eq. = 150.5 (1).

3:8220 (1) Westheimer, Shookhoff, J. Am. Chem. Soc. 62, 271 (1940). (2) Baker, Org. Syntheses 24, 21 (1944).

3:8223-3:8225

B.P. 155° sl. dec. (1)

[For prepn. of \tilde{C} from 3-ethylhexanol-3 (diethyl-n-propyl-carbinol) [Beil. I-421, I₁-(210), I₂-(454)] with PCl₅ see (1).]

[O with diethylamine loses HCl (2) yielding an olefin (2).]

[For data on density and parachor of C at 0°, 15°, 25°, 50°, and 65° see (3).]

3:8223 (1) Butlerow, Bull. soc. chim. (2) 5, 23 (1866). (2) Montagne, Ann. chim. (10) 13, 111 (1930). (3) Quayle, Owen, Beavers, J. Am. Chem. Soc. 61, 3107-3111 (1939).

3:8224 METHYL
$$d,l$$
- β -CHLORO- n -BUTYRATE $C_5H_9O_2Cl$ Beil. II - 277 CH₃.CH.CH₂.COOCH₃ II₁— II₂—

B.P. 155-156° at 750 mm. (1)

$$D_4^{20} = 1.0996 (2) \quad n_D^{20} = 1.4258 (2)$$

[For prepn. of \tilde{C} from methyl crotonate (1:3121) by addn. of HCl, from β -chloro-n-butyronitrile + MeOH + HCl, or from methyl n-butyrate (1:3080) with Cl₂ see (1).] \tilde{C} on hydrolysis yields MeOH (1:6120), crotonic acid (1:0425), and HCl.

3:8224 (1) Henry, Bull. acad. roy. Belg. (3) 35, 507-520 (1898); Cent. 1898, II 273. (2) Schjanberg, Z. physik. Chem. A-172, 232 (1935).

3: 8225
$$d$$
, l -1-CHLOROPENTANOL-2 $C_5H_{11}OCl$ Beil. I — (Chloromethyl- n -propyl- CH_3 . CH_2 . CH_2 — CH —— CH_2 I_1 —— carbinol; n -propylethylene chlorohydrin) OH Cl I_2 -(419)

B.P.
$$157-160^{\circ}$$
 at 735 mm. (1) $D_{25}^{25} = 1.0143$ (1) $n_{\rm D}^{25} = 1.4404$ (1) $68-75^{\circ}$ at 30 mm. (2) $66-67^{\circ}$ at 18 mm. (3) $D_{20}^{20} = 1.037$ (2) $n_{\rm D}^{20} = 1.4520$ (2) $59-62^{\circ}$ at 14 mm. (4) 1.031 (3) 1.4422 (3)

[For prepn. of C from pentenc-1 (1:8205) with HOCl (43% yield) see (2); from 1-chloro-2,3-epoxypropane (epichlorohydrin) (3:5358) with MgEt₂ (70% yield (3)) or with EtMgBr (16-19% yield (1)) see indic. refs.; from chloroacetaldehyde (3:7212) with n-PrMgBr see (4).]

 $\bar{\mathbb{C}}$ with AcCl yields (1) 1-chloro-2-acetoxypentane, b.p. 186–188° at 740 mm., $D_{25}^{25}=1.0825$, $n_{25}^{25}=1.4328$ (1); $\bar{\mathbb{C}}$ with NaSMe gives (45% yield (2)) 1-methylthiolpentanol-2, b.p. 90° at 18 mm., $D_{20}^{20}=0.943$, $n_{20}^{20}=1.4792$ (2); $\bar{\mathbb{C}}$ with SOCl₂ + diethylaniline gives (70% yield (1)) 1,2-dichloropentane (3:8140); $\bar{\mathbb{C}}$ with 2 moles EtMgBr yields (3) heptanol-4 (1:6228).

 \bar{C} on oxidn. with $K_2Cr_2O_7 + H_2SO_4$ yields (4) 1-chloropentanone-2 (3:8217), b.p. 55-57° at 15 mm. (4); \bar{C} on oxidn. with aq. KMnO₄ yields (1) n-butyric acid (1:1035) q.v.

© Chloromethyl-n-propyl-carbinyl 3,5-dinitrobenzoate: pl. from alc., m.p. 84-85° (3), 83-84° (1); from \bar{C} on htg. with 3,5-dinitrobenzoyl chloride until no more HCl is evolved (1).

3:8225 (1) Koelsch, McElvain, J. Am. Chem. Soc. 51, 3392, 3393 (1929). (2) Glavis, Ryden, Marvel, J. Am. Chem. Soc. 59, 709 (1937). (3) Magrane, Cottle, J. Am. Chem. Soc. 64, 484-487 (1942). (4) Levene, Haller, J. Biol. Chem. 77, 560 (1928).

3: 8228 CHLOROACETALDEHYDE DIETHYLACETAL
$$C_6H_{13}O_2Cl$$
 Beil. I - 611 (Chloroacetal) CH_2 — $CH(OC_2H_5)_2$ I_1 -(328) I_2 -(676) B.P. 157.4° {1} $D_{20}^{20} = 1.017$ (3) $D_{20}^{20} = 1.017$

[For prepn. from vinyl acetate (b.p. 69-71°) by treatment in abs. EtOH soln. with Cl₂ in dark and in a solid CO₂/acetone cooling bath (83% yield) see (3); from acetaldehyde diethylacetal ("acetal") (1:0156) with Cl₂ at 50° in presence of abs. alc. NaOEt (90% yield) see (4); from paraldehyde (1:0170) by chlorination and subsequent treatment with EtOH see (5) (6); from EtOH (1:6130) by treatment with Cl₂ see (7) (8).]

[For prepn. of \bar{C} from chloroacetaldehyde (3:7212) on warming with EtOH see (9); from chloroacetaldehyde ethyl alcoholate (chloroacetaldehyde ethyl-hemi-acetal) [Beil. I-611] in EtOH with dry HCl gas see (10); from α,β -dichloroethyl ethyl ether (3:5640) with 2 vols. abs. EtOH (2) or with NaOEt (11) (12) (13) see indic. refs.]

Č is comml. chem. in U.S. (1943) (14); Č is widely used in org. synthesis as source of combined chloroacetaldehyde (3:7212) and otherwise.

The acetal portion of \tilde{C} is stable to alkali but readily hydrolyzed by aq. acids; the chlorine atom, however, behaves like a reactive alkyl halide; all these characteristics are illustrated in the reactns, cited below.

 $\tilde{\mathbf{C}}$ on warming with dil. $\mathbf{H}_2\mathbf{SO}_4$ yields (15) chloroacetaldehyde (3:7212) accompanied by some bis-(β -chloro- α -ethoxyethyl) ether, b.p. abt. 165°; $\tilde{\mathbf{C}}$ on satn. at 100° with dry HCl gas yields (9) $\alpha_i\beta$ -dichloroethyl ethyl ether (3:5640). — $\tilde{\mathbf{C}}$ on htg. with AcOH at 120° or with anhydrous oxalic acid at 100–150° yields (12) chloroacetaldehyde (3:7212) + ethyl acetate (1:3015) or diethyl oxalate (1:1055) respectively.

[\bar{C} htd. with NaOEt in s.t. at 140–150° for 30 hrs. (11) (13) (17) or with abs. alc. NaOEt at 160° under press. (16) gives (66% yield (16)) ethoxyacetaldehyde diethylacetal, b.p. 168° (11) (this prod. on boilg. with dil. H₂SO₄ (17) (13) (16) hydrolyzes to EtOH (1:6130) + ethoxyacetaldehyde (1:0159), b.p. 105–106°). — \bar{C} htd. with 10% excess of satd. abs. alc. KOH in s.t. for 75 hrs. gives (95% yield (18)) glycolaldehyde diethylacetal (hydroxyacetaldehyde diethylacetal) (1:0191), b.p. 167°.] [For reactn. of \bar{C} with many other alcs. (19) (20) and phenols (21) in pres. of alk. see indic. refs.]

[$\bar{\mathbf{C}}$ htd. with Na or Mg at 120–130° (22) or with Na in ether at 0–20° (23) yields ethyl vinyl ether (1:7810), b.p. 35.7°, + EtOH and prob, also ethoxyacetaldehyde diethylacetal (see above). — $\bar{\mathbf{C}}$ on boilg. with Zn dust yields (2) ethyl chloride (3:7015) + EtOH (1:6130). — $\bar{\mathbf{C}}$ with excess phenyl MgBr at 120° as directed (24) gives 31% yield α,β -diphenylethyl ethyl ether (α -ethoxydibenzyl) [Beil. VI₁-(329)].]

[\ddot{C} htd. with 4-5 vols. conc. aq. NH₄OH in s.t. at 130° for 12-14 hrs. (25) or \ddot{C} +20 vols. satd. alc. NH₃ in s.t. at 130° (26) (27) (28) or refluxed in pres. of NaI (29) yields amino-acetaldehyde diethylacetal [Beil. IV-308, IV₁-(449), IV₂-(758)], b.p. 163°. — \ddot{C} htd. with alc. hydrazine hydrate under press. for 6 hrs. at 115-120° yields (30) hydrazinoacetaldehyde diethylacetal [Beil. IV-553].]

[Č with aniline + NaNH₂ in ether gives (77% yield (31)) N-(phenyl)aminoacetalde-

hyde diethylacetal [Beil. XII-213], b.p. 92-94° at 0.3 mm.; for corresp. behavior with benzylamine (32) or primary aliph. amines (33) see indic. refs.] — C with 3 moles phenylhydrazine htd. several hrs. at 130° yields (34) glyoxal-bis-(phenylhydrazone), yel. tbls. from alc. or ether, m.p. 177° u.c., 179° cor. (34).

C on acid hydrolysis (3) yields ethyl alcohol (1:6130) and chloroacetaldehyde (3:7212) q.v.

3:8228 (1) Lecat, Rec. trav. chim. 45, 622 (1926). (2) Paterno, Mazzara, Gazz. chim. ital. 3, 254-256 (1873); Ber. 6, 1202 (1873). (3) Filachione, J. Am. Chem. Soc. 61, 1705-1706 (1939). (4) Anselm, Galitzenstein, Ger. 639,507, Dec. 7, 1936; Cent. 1937, I 2023; C.A. 31, 3940 (1927). (5) Freundler, Bull. soc. chim. (4) 1, 70-71 (1907). (6) Soc. des Usines Chimiques Rhone-Poulenc, French 711,095, Sept. 2, 1931; Cent. 1932, I 130. (7) Lieben, Ann. 104, 114-115 (1857). (8) Fritsch, Ann. 279, 300 (1879). (9) Natterer, Monatsh. 5, 497-499 (1884). (10) Fritsch, Schumacher, Ann. 279, 308 (1894).

(11) Lieben, Ann. 146, 193-201 (1868). (12) Natterer, Monatsh. 3, 444-449 (1882). (13) Kluger, Monatsh. 26, 880-882 (1905). (14) Chem. Eng. News 21, 1986 (1943). (15) Frank, Ann. 206, 341-344 (1880). (16) Leuchs, Geiger, Ber. 39, 2645 (1906). (17) Eissler, Pollak, Monatch. 27, 1130-1132 (1906). (18) Beyerstedt, McElvain, J. Am. Chem. Soc. 58, 530 (1936). (19) Sabetay, Bull. soc. chim. (4) 45, 1161-1169 (1929). (20) Hallonquist, Hibbert, Can. J. Research

8, 129-136 (1933); Cent. 1933, II 1017; C.A. 27, 2133 (1983).

(21) Parfumerie Houbigant, Sabetay, French 673,379, Feb. 14, 1930; Cent. 1936, II 2694. (22) Wislicenus, Ann. 192, 106-109 (1878). (23) Leuchs, Lemcke, Ber. 47, 2577 (1914). (24) Späth, Monatsh. 35, 466-467 (1914). (25) Wolff, Ber. 21, 1482 (1888); 26, 1832 (1893). (26) Wolff, Marburg, Ann. 363, 179-182 (1908). (27) Marckwald, Ber. 25, 2355 (1892). (28) Buck, Wrenn, J. Am. Chem. Soc. 51, 3613 (1929). (29) Wohl, Ber. 39, 1953 (1906). (30) Fischer, Hunsalz, Ber. 27, 178-179 (1894).

(31) Wohl, Lange, Ber. 40, 4728 (1907). (32) Rügheimer, Schön, Ber. 41, 17-18 (1908). (33) Paal, van Gember, Arch. Pharm. 246, 306-314 (1908). (34) Fischer, Ber. 26, 97 (1893).

B.P. 157-159.5° at 750 mm. (1)
$$D_4^{25} = 0.8788$$
 (1) $n_D^{25} = 1.4394$ (1)

Although two geom. stereoisomers of C are possible only this one has as yet been reported. [For prepn. of C from octyne-4 (di-n-propylacetylene) (1:8110) with AcCl + SnCl₄ (both stereoisomers of 4-chloro-3-n-propylhepten-3-one-2 are also formed: cis, b.p. 117-118° at 28 mm., $D_4^{25} = 0.9680$, $n_D^{25} = 1.4587$; trans, b.p. 112-113° at 28 mm., $D_4^{25} = 0.9592$, $n_{\rm D}^{25} = 1.4601 \, (1) \, \text{see} \, (1).$

3:8230 (1) Kroeger, Sowa, Nieuwland, J. Org. Chem. 1, 163-169 (1936).

3:8235
$$d_{r}$$
- α -ETHYL- n -VALERYL CHLORIDE C_{r} H₁₃OCl $(d_{r}$ - d_{r} -Ethylpentanoyl chloride-1; CH₃.CH₂.CH₂.CH . C=O ethyl- n -propyl-acetyl chloride) C_{r} - C_{r}

B.P. 158-160° 50° at 11 mm. (2)

[For prepn. of C from 2-ethylpentanoic acid-1 (ethyl-n-propyl-acetic acid) (1:1133) with PCl₃ (1) or SOCl₂ (2) see indic. refs.]

C on hydrolysis yields ethyl-n-propyl-acetic acid (1:1133) q.v. (for the amide, anilide, p-toluidide, and other derivatives corresponding to C see 1:1133).

3:8235 (1) Rasetti, Bull. soc. chim. (3) 33, 687 (1905). (2) Reichstein, Trivelli, Helv. Chim. Acta **16,** 974 (1933); **15,** 258-259 (1932).

3:8240-3:8243

3:8240 2-CHLOROBUTEN-2-OL-1 H Cl C₄H₇OCl Beil. I - 442
$$I_1$$
— I_2 —(481) CH₈—C=C—CH₂OH I_1 — I_2 —(481) B.P. 159° at 760 mm. (1) $D_4^{23} = 1.0950$ (4) $n_C^{23} = 1.45093$ (4)

B.P. 159° at 760 mm. (1)
$$D_4^{23} = 1.0950$$
 (4) $n_C^{23} = 1.45093$ (4) $158-161$ ° (2) 158.3 ° cor. at 742.5 mm. (3) $D_4^{20} = 1.118$. (1) $n_D^{20} = 1.46823$ (1) $52-53$ ° at 19 mm. (4)

Note: cis and trans stereoisomers of $\ddot{\mathbf{C}}$ are theoretically possible but have not definitely been reported.

[For prepn. of \tilde{C} from 2-chlorobuten-2-al-1 (α -chlorocrotonaldehyde) (3:8117) by reduction in abs. alc. with $H_2 + Al(OEt)_3$ (2) or with $Mg(OEt)_2$.EtOMgCl (1) see (2) (1); for formn. of \tilde{C} (together with 3-chlorobuten-3-ol-2) (3:9115) from either the low-boilg. (3:5360) or high-boilg. (3:5615) stereoisomer of 1,2-dichlorobutene-2 by hydrolysis with 2 pts. aq. + 1 mole CaCO₃ for 4 hrs. at 70° see (4); for prepn. of \tilde{C} from 2,2,3-trichlorobutanol-1 (3:1336) with Zn dust + HCl see (3).]

D 2-Chlorobuten-2-yl-1 $N-(\alpha$ -naphthyl)carbamate: m.p. 95-96° (4).

3:8240 (1) Meerwein et al., *J. prakt. Chem.* (2) **147**, 225 (1936). (2) I. G. Farbenindustrie, Ger. 437,160, Nov. 18, 1926; *Cent.* **1927**, I 802. (3) Garzarolli-Thurnlackh, *Ann.* **213**, 375-379 (1882). (4) Tishchenko, *J. Gen. Chem.* (U.S.S.R.) **7**, 658-662 (1937); *Cent.* **1937**, II 371-372; *C.A.* **31**, 5754 (1937).

B.P. 159-160° (1)

[For preparation of \bar{C} from acetyl chloride (3:7065) + propylene in pres. of ZnCl₂ see (1); for reactn. of acetyl chloride with propylene in pres. of activated carbon at 100-300° and at press. of 20-200 atm. cf. (2).]

3:8243 (1) Kondakow, J. Russ. Phys.-Chem. Soc., **26**, 15 (1883). (2) Frohlich, Wiezevich (to Standard Oil Development Co.), U.S. 2,006,198, June 25, 1935; Cent. **1936**, I 2827.

B.P. F.P.
$$159.45-159.55^{\circ}$$
 at 760 mm . $(1) -34.0^{\circ}$ $(12) D_4^{25} = 1.07762$ $(4) 159.5^{\circ}$ cor. at 759.5 mm . $(2) -34.5^{\circ}$ $(11) D_4^{20} = 1.08246$ $(4) 159.38^{\circ}$ at 760.1 mm . $(3) -34.7^{\circ}$ $(13) D_4^{20} = 1.08246$ $(4) 159.15^{\circ}$ at 760 mm . $(4) -35.1^{\circ}$ $(8) 1.08173$ $(14) 159.0-159.2^{\circ}$ cor. $(5) -36.5^{\circ}$ $(4) 1.0785$ $(1) 158.93-158.97^{\circ}$ at 760 mm . $(6) 158.7-158.9^{\circ}$ at 760.4 mm . $(8) 158.3-159.3^{\circ}$ at 760.4 mm . $(8) 158.3-159.3^{\circ}$ at 760.4 mm . $(8) 158.3-159.3^{\circ}$ at 760.4 mm . $(3) 142.3^{\circ}$ at 558.9 mm . $(3) 142.3^{\circ}$ at 391.1 mm . $(3) 134.2^{\circ}$ at 391.1 mm . $(3) 112.1^{\circ}$ at 191.0 mm . $(3) 112.1^{\circ}$ at 191.0 mm . $(3) 132.3^{\circ}$ at 106.0 mm . $(3) 132.3^{\circ}$ at 106.0 mm . $(3) 132.2^{\circ}$ at 106.0 mm .

[For f.p./compn. data on system: $\bar{C}+p$ -chlorotoluene (3:8287) (eutectic, f.p. -50° conts. 73% \bar{C}) see (8) (112); for D_{20}^{20} /compn. data on this system see (8); for n_{D}^{10} /compn. data on this system see (15). — For f.p./compn. data on systems \bar{C} + chlorobenzene (3:7903) (13), $\bar{C}+m$ -dichlorobenzene (3:5960) (16), \bar{C} + bromobenzene (16) see indic. refs.]

[For prepn. of \bar{C} from o-toluidine [Beil. XII-772, XII₁-(372)] via diazotization and use of Cu₂Cl₂ reactn. (yields: 85% (23), 79–90% (21), 74 79% (7), 70% (18)) (19) (20) (22), or Cu powder (66% yield (24)) (25), or mere boilg, with HCl (26), or use of CuH (27), or CaCl₂ (28) see indic. refs.; for prepn. from o-toluenediazonium chloride (solid) [Beil. XVI-495, XVI₁-(358)] with C₆H₆ + AlCl₃ (29), from o-toluenediazonium chloroplatinate on htg. (30), or from o-toluenediazopiperidide by htg. with HCl (31) see indic. refs.; for prepn. of \bar{C} from o-cresol (1:1400) via conv. with PCl₅ at 140° to tris-(o-toloxy)phosphoric acid dichloride and htg. of latter at 180° see (32); for prepn. of \bar{C} from p-toluenesulfonyl chloride via chlorination to 2-chlorotoluenesulfonyl chloride-4 followed by hydrolysis with 10% H₂SO₄ (33) to 2-chlorotoluenesulfonic acid-4 (see below) and subsequent replacement of $-SO_3H$ by H with superheated steam in 80% H₂SO₄ (overall yield 88–90% (33)) cf. (34) (35); for prepn. of \bar{C} from 2-chlorotoluenesulfonic acid-5 (see below) or its sodium salt by steam distn. of its soln. in 75% H₂SO₄ see (8).]

[For prepn. of \bar{C} from toluene with Cl_2 in pres. of Fe (8) (36) (38), or I_2 (37) (39), Fe + I_2 (15), Al/Hg (45), MoCl₅ (36), SbCl₅ (39), or PbCl₂ (8), from toluene via electrolysis of its suspension in boilg. HCl (40) or in HCl/AcOH at 35° (41), from toluene by boilg. with PbCl₂.2NH₄Cl (42), from toluene with SO₂Cl₂ + cat. (43) especially AlCl₃ (43) (44), from toluene with n-butyl chlorosulfonate (46), from toluene with NCl₃ (47) see indic. refs.: no m-chlorotoluene is formed by any of these methods, but the proportion of \bar{C} to its ac-

companying p-isomer (3:8287) varies widely, e.g., from 100% \tilde{C} with PbCl₂ + NH₄OH (42), through 62% o/28% p with PbCl₂ (8), to 2.5 o/1 p via the electrolytic methods (40) (for details the orig. refs. must be consulted).] — [For sepn. of \tilde{C} from polychlorotoluenes via const.-boilg. mixt. with aq. see (79).]

[For prepn. of C from hydrazone of o-chlorobenzaldehyde (3:6410) by Wolff-Kishner reduction (35-82% yield) see [113].]

[For thermal anal. of system: C + SbCl₃ see (48).]

[\overline{C} with H₂ in pres. of Pd/CaCO₃ in alc./alk. soln. loses all its chlorine as HCl (49); \overline{C} with HI + P at 302° for 5 hrs. gives 80% yield (50) toluene (1:7405).]

 \bar{C} on oxidn. with CrO₃ is completely destroyed (30); \bar{C} on oxidn. with boilg. aq. KMnO₄ (74–78% yield (51)) (52) (36) (53) or \bar{C} on cat. oxidn. with air over granular tin vanadate at 287° (13.8% yield (54)) cf. (55) or \bar{C} + KCN + NiCl₂ in dil. alc. 20 hrs. at 260–270° (7.5% yield (63)) gives σ -chlorobenzoic acid (3:4150); \bar{C} with CrO₂Cl₂ followed by aq. (51.5% yield (56)) (57) or \bar{C} on oxidn. with Ce cpds. (58) or with air over Ta₂O₅ (59) cf. (60) or \bar{C} with MnO₂ + H₂SO₄ (61) or PbO₂ + dil. H₂SO₄ (24% yield (62)) gives σ -chlorobenzaldehyde (3:6410).

[\tilde{C} with Cl₂ in pres. of Al/Hg gives (64) a mixt. contg. 2,3- (3:6345), 2,4- (3:6290), 2,6- (3:6270), together with some 2,5-dichlorotoluene (3:6245). — \tilde{C} with Cl₂ + 3% PCl₅ in light gives (65) (19) o-chlorobenzyl chloride (3:6400); \tilde{C} with Cl₂ + PCl₅ at 150-180° (66) (67) (68) cf. (70) gives o-chlorobenzal (di)chloride (3:6625); \tilde{C} with Cl₂ + PCl₃ (73) or with Cl₂ at 160-190° (69) gives (64% yield (69)) (70) (71) o-chlorobenzotrichloride (3:6880).]

[\bar{C} with Br₂ in pres. of Al/Hg in CCl₄ gives (74) mainly 5-bromo-2-chlorotoluene [Beil. V-307, V₁-(155)], together with a smaller amt. of 4-bromo-2-chlorotoluene [Beil. V-307, V₁-(155)]; the former is also obtd. (75) from \bar{C} + Br₂ + HNO₃ + H₂SO₄ in AcOH. — \bar{C} with Br₂ (76) (77) yields o-chlorobenzyl bromide [Beil. V₁-(155)] (for studies of rate of side-chain bromination of \bar{C} see (78)).]

 $[\tilde{C} + I_2 + HNO_3 + H_2SO_4]$ in AcOH gives (75) 2-chloro-5-iodotoluene [Beil. V-315].] $[\tilde{C}$ with AlCl₃ + HCl gas as directed (7) undergoes partial rearr. to both *m*-chlorotoluene (3:8275) and *p*-chlorotoluene (3:8287); for anal. of mixts. of the three isomers see (7).]

[\bar{C} with AcCl (80) or better Ac₂O (81) + AlCl₃ gives (70% yield (81)) 4-chloro-3-methylacetophenone [Beil. VII-307], b.p. 254.2-254.4° at 753.4 mm., $n_D^{25} = 1.5521$ (81). — \bar{C} with β -chloropropionyl chloride (3:5690) + AlCl₃ in CS₂ gives (68% yield (82)) (83) 2-chloro-5-(β -chloropropionyl)toluene, colorless pr. from C₆H₆, m.p. 46° (82), which on ring closure with conc. H₂SO₄ gives (82) (83) 6-chloro-7 (or 5)-methylindanone-1, cryst. from alc., m.p. 74-75° (82) (83). — \bar{C} with trichloroacetonitrile + AlCl₃ (4 moles) at 80-90° satd. with HCl gas for 2 days gives (40% yield (84)) 4-chloro-3-methyl- ω , ω -trichloroacetophenone, b.p. 155-160° at 11 mm. (84). — \bar{C} with fumaryl (di)chloride + AlCl₃ in CS₂ at 50-60° for 2 hrs. gives (51% yield (85)) trans-bis-1,2-(4-chloro-3-methylbenzoyl) ethylene, pale yel. cryst. from alc., m.p. 167° (85).]

[$\ddot{\mathbf{C}}$ with benzoyl chloride + AlCl₃ gives (83% yield (86)) 3-chloro-4-methylbenzophenone [Beil. VII₁-(236)], lfts. from alc., m.p. 82-83° (86); $\ddot{\mathbf{C}}$ with o-chlorobenzoyl chloride (3:6640) + AlCl₃ in CS₂ for 12 hrs. gives (87) 2',3-dichloro-4-methylbenzophenone, cryst. from alc., m.p. 43.5° (87). — $\ddot{\mathbf{C}}$ with naphthalene-bis-1,4(or 5)-(dicarboxylic acid dichloride) + AlCl₃ gives (88) bis-1,4(or 5)(chlorotoluoyl)naphthalene (used for ring closure to corresp. dibenzpyrenequinones).]

[C with phthalic anhydride + AlCl₃ at 90° gives (89) (90) (91) a mixt. (93% yield (90)) of two o-(chlorotoluoyl)benzoic acids A + B: A, m.p. 183-184° (90), 182-183° (91) (89), the main prod., is regarded variously as either (90) o-(3-chloro-4-methylbenzoyl)benzoic acid or (91) o-(4-chloro-3-methylbenzoyl)benzoic acid but in any case with conc. H₂SO₄

ring-closes to give (92% yield (90)) (91) 2-chloro-3-methylanthraquinone, colorless tbls. from toluene, m.p. 219° (91) cor. (90); B, m.p. 176–177° (91), the minor prod., regarded (91) as o-(2-chloro-3-methylbenzoyl)benzoic acid, with conc. H_2SO_4 ring-closes to give 1-chloro-2-methylanthraquinone, yel.-br. ndls. from toluene, m.p. 171° (91), 170–171° (90).] — [For reactn. of \tilde{C} with 3,4-dichlorophthalic anhydride (3:3695) (92) or with pyromellitic anhydride (93) see indic. refs.]

[\tilde{C} with aq. NaOH in pres. of Cu at 350-360° under press. yields (94) a mixt. contg. 41% o-cresol (1:1400) + 59% m-cresol (1:1730) (for extensive study of hydrolysis of \tilde{C} as means of prepn. of m-cresol (1:1730) see (112)); \tilde{C} with NH₃ + cat. under press. as directed (95) (96) (97) yields o-toluidine (for behavior of \tilde{C} with liquid NH₃ see (98)). — \tilde{C} with aniline + Cu at 175° yields (99) phenyl-o-tolylamine. — \tilde{C} with diphenylamine + K at 240-245° in H₂ gives (by rearr.) (100) N,N-diphenyl-m-toluidine, m.p. 69-70°.] — [Note that \tilde{C} does not react with aq. sodium sulfanilate + Na₂CO₃ (dif. from benzyl chloride (3:8535)) and use in sepn. of \tilde{C} from the latter (8).]

[$\bar{\mathbf{C}}$ on mononitration, e.g., with 4 pts. HNO₃ (D=1.52) at 0° (101) gives a mixt. contg. all four possible isomers, viz., 43% 2-chloro-5-nitrotoluene [Beil. V-329, V₁-(163)], m.p. 42.9° (101), 44° (102), 21% 2-chloro-6-nitrotoluene [Beil. V-327, V₁-(162)], m.p. 35.3° (101), 37° (103) (104), 19% 2-chloro-3-nitrotoluene [Beil. V-328, V₁-(163)], m.p. 22.1° (101), 21.5° (105), and 17% 2-chloro-4-nitrotoluene [Beil. V-329, V₁-(163)], m.p. 62.3° (101), 65° (105A).]

 \bar{C} on dinitration, e.g., with mixt. of 3 wt. pts. HNO₃ (D=1.48) + 9 wt. pts. conc. H₂SO₄ at 100° (106), or with 2 vol. pts. HNO₃ (D=1.42) + 5 vols. pts. conc. H₂SO₄ at 100° as directed (107), gives mainly (55–60% (107)) 2-chloro-3,5-dinitrotoluene [Beil. V-345, V₁-(169)], cryst. from alc., m.p. 64° (107), 63–64° (106), accompanied by smaller amts. of three isomers, viz., 2-chloro-4,5-dinitrotoluene, m.p. 88.5° (18–20% (107)), 2-chloro-5,6-dinitrotoluene, m.p. 106.5° (18–20% (107)), and 2-chloro-4,6-dinitrotoluene, m.p. 49° (1-2% (107)) [the two other possible dinitro-2-chlorotoluenes have been prepd. by indirect means, viz., 2-chloro-3,4-dinitrotoluene, m.p. 89° (108), and 2-chloro-3,6-dinitrotoluene, m.p. 62–63° (109)].

[\bar{C} on monosulfonation with fumg. H₂SO₄ (37) or 100% H₂SO₄ (23) (8) or CISO₃H (110) (see below) yields 2-chlorotoluenesulfonic acid-5 [Beil. XI-95]; \bar{C} sulfonates more readily (8) than p-chlorotoluene (3:8287) and may thus be used to separate \bar{C} from the latter (8) (111).]

D 2-Chlorotoluenesulfonamide-5 (4-chloro-3-methylbenzenesulfonamide-1): cryst. from dil. alc., m.p. 126° u.c. (110). [From C with ClSO₃H as directed (110) followed by conv. of the intermediate 2-chlorotoluenesulfonyl chloride-5, cryst. from pet. ether, m.p. 63° u.c. (110), with (NH₄)₂CO₃.]

3:8245 (1) Matthews, J. Am. Chem. Soc. 48, 570 (1926). (2) Wibaut, Rec. trav. chim. 32, 247 (1913). (3) Feitler, Z. physik. Chem. 4, 71-72 (1889). (4) Timmermans, Hennaut-Roland, J. chim. phys. 27, 410-411 (1930). (5) Perkin, J. Chem. Soc. 69, 1203 (1896). (6) Stuckey, Saylor, J. Am. Chem. Soc. 62, 2923 (1940). (7) Norris, Turner, J. Am. Chem. Soc. 61, 2128-2131 (1939). (8) Wahl, Normand, Vermeylen, Bull. soc. chim. (4) 31, 570-583 (1922). (9) Kohlrausch, Pongratz, Monatsh. 63, 441 (1934). (10) Timmermans, Bull. soc. chim. Belg. 36, 505 (1927).

(11) Rule, McLean, J. Chem. Soc. 1931, 689. (12) Haase, Ber. 26, 1053 (1893). (13) Linard, Bull. soc. chim. Belg. 34, 369, 393 (1925). (14) Seubert, Ber. 22, 2520 (1889). (15) Chindraux, Hels. Chim. Acta 12, 925-227 (1929). (16) Timmermans, Bull. soc. chim. Belg. 43, 633-634 (1934). (17) Marvel, McElvain, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 170-172 (1941); (1st ed.), 163-165 (1932); 3, 33-35 (1923). (18) Erdmann, Ann. 272, 145-147 (1892). (19) Behrend, Nissen, Ann. 269, 393-394 (1892). (20) Heller, Tischner, Ber. 44, 250-255 (1911).

(21) Heller, Z. angew. Chem. 23, 389-392 (1910). (22) Sandmeyer, Ber. 17, 2651 (1884).

- (23) Wynne, J. Chem. Soc. 61, 1072-1075 (1892). (24) Gattermann, Ber. 23, 1221 (1890).
 (25) Ullmann, Ber. 29, 1878, Note (1896). (26) Gasiorowski, Wayss, Ber. 18, 1939 (1885).
 (27) Neogi, Mitra, J. Chem. Soc. 1928, 1332. (28) Kuhn, Eichenberger, French 663,236, Aug. 19, 1929; Cent. 1929, II 3069. (29) Mohlau, Berger, Ber. 26, 1998 (1893). (30) Beilstein, Kuhlberg, Ann. 156, 79 (1870).
- (31) Wallach, Ann. 235, 247 (1886). (32) Autenrieth, Geyer, Ber. 41, 157 (1908). (33) McMaster, Carol, Ind. Eng. Chem. 23, 218-219 (1931). (34) Soc. Chem. Ind. Basel, Ger. 133,000, July 9, 1902; Cent. 1902, II 313-314. (35) B.A.S.F., Ger. 294,638, Oct. 16, 1916; Cent. 1916, II 860. (36) Seelig, Ann. 237, 130-131, 151-155 (1887). (37) Hübner, Majert, Ber. 6, 790-795, 1672 (1873). (38) Book, Eggert, Z. Elektrochem. 29, 521-527 (1923); Cent. 1924, I 1741. (39) Wertyporoch, Ann. 493, 163 (1932). (40) Cohen, Dawson, Crosland, J. Chem. Soc. 87, 1034-1037 (1905).
- (41) Fichter, Glantzstein, Ber. 41, 2484-2487 (1916). (42) Seyewetz, Biot, Compt. rend. 135, 1121 (1902); Bull. soc. chim. (3) 29, 221-222 (1903). (43) O. Silberiad, C. Silberiad, Parke, J. Chem. Soc. 127, 1724-1731 (1925). (44) O. Silberiad, J. Chem. Soc. 127, 2678 (1925). (45) Cohen, Dakin, J. Chem. Soc. 79, 1119-1120 (1901). (46) Barkenbus, Hopkins, Allen, J. Am. Chem. Soc. 61, 2452-2453 (1939). (47) Stoll, Bull. soc. chim. Belg. 38, 77-91 (1929). (48) Menschutkin, J. Russ. Phys.-Chem. Soc. 44, 1940 (1912), Cent 1913, I 805. (49) Busch, Stöve, Ber. 49, 1069 (1916). (50) Klages, Liccke, J. prakt. Chem. (2) 61, 322 (1900).
- (51) Clarke, Taylor, Org. Syntheses, Coll. Vol. 2 (1st ed.), 135-136 (1943); 16, 20-21 (1930). (52) Graebe, Ann. 276, 55-56 (1893). (53) Emmerling, Ber. 8, 880 (1875). (54) Maxted, Dunsby, J. Chem. Soc. 1928, 1411. (55) Maxted, Coke, Brit. 237,688, Aug. 21, 1925; Cent. 1928, I 1712. (56) Law, Perkin, J. Chem. Soc. 93, 1636 (1908). (57) Stuart, Elliot, J. Chem. Soc. 53, 803 (1888). (58) M.I.B., Ger. 174,238, Sept. 10, 1906, Cent. 1906, II 1297. (59) Craver (to Barrett Co.), Brit. 189,091, 189,097, Jan. 17, 1923; Cent. 1923, II 746. (60) Charlot, Ann. chim. (11) 2, 469-470 (1934); Bull. soc. chim. (4) 53, 577 (1933).
- (61) Gilliard, Monet, Cartier, Ger. 101,221, Sept. 23, 1897, Cent. 1899, I 960. (62) Olivier, Weber, Rec. trav. chim. 53, 881 (1934). (63) Slebodzinski, J. prakt. Chem. (2) 143, 118 (1935). (64) Cohen, Dakin, J. Chem. Soc. 79, 1117 (1901). (65) Meisenheimer, Zimmermann, von Kummer, Ann. 446, 225 (1926). (66) Shoesmith, Slater, J. Chem. Soc. 1926, 218. (67) Asinger, Lock, Monatsh. 62, 333, Note 14 (1933). (68) Erdmann, Ann. 272, 151 (1892). (69) Booth, Elsey, Burchfield, J. Am. Chem. Soc. 57, 2067 (1935). (70) Kyndes (to National Aniline and Chem. Co.), U.S. 1,733,268, Oct. 29, 1929; Cent. 1930, I 3831.
- (71) Britton (to Dow Chem. Co), U.S. 1,878,463, Sept. 20, 1932; Cent. 1933, I 311. (72)
 Scottish Dyes, Ltd., Bangham, Thomas, Brit. 308,231, April 18, 1929; Cent. 1929, II 1348.
 (73) Fox, Ber. 26, 653 (1893). (74) Cohen, Smithells, J. Chem. Soc. 105, 1910 (1941). (75)
 Varma, Sahay, J. Indian. Chem. Soc. 11, 293-294 (1934). (76) Leonaud, J. Chem. Soc. 109, 570-571 (1916). (77) Thomson, Stevens, J. Chem. Soc. 1932, 61. (78) Sampey, Fawcett, Moorehead, J. Am. Chem. Soc. 62, 1839-1840 (1940). (79) Buchheim (to Chem. Fabrik von Heyden, Ger. 616,596, Aug. 1, 1935; Cent. 1935, I 3703. (80) Claus, J. prakt. Chem. (2) 43, 356-357 (1891).
- (81) Allen, Bridgess, J. Am. Chem. Soc. 49, 1846 (1927).
 (82) Mayer, Müller, Ber. 60, 2281–2283 (1927).
 (83) Mayer (to I.G.), Ger. 515,110, Jan. 15, 1931, Cent. 1931, II 908.
 (84) Houben, Fischer, Ber. 64, 2648–2650 (1931).
 (85) Conant, Lutz, J. Am. Chem. Soc. 47, 891 (1925).
 (86) Heller, Ber. 46, 1500 (1931).
 (87) de Diesbach, Bulliard, Helv. Chim. Acta 7, 625 (1924).
 (88) I.G., French 657,245, May 18, 1929; Cent. 1930, I 130.
 (89) Heller, Schulke, Ber. 41, 3636–3637 (1908).
 (90) Ullmann, Dasgupta, Ber. 47, 556–558 (1914).
- (91) Keimatsu, Hirano, J. Pharm. Soc. Japan 49, 17-20 (1929); Cent. 1929, I 2532. (92) Kumatsu, Hirano, J. Pharm. Soc. Japan 49, 158-163 (1929); Cent. 1930, I 1303. (93) de Diesbach, Schmidt, Helv. Chrm. Acta 7, 648-650 (1924). (94) Britton (to Dow Chem. Co.), U.S. 1,996,744, April 9, 1935; Cent. 1935, II 1962. (95) Williams (to Dow Chem. Co.), U.S. 1,775,360, Sept. 9, 1930; Cent. 1931, II 1195. (96) Federal Phosphorus Co., Brit. 370,774, May 5, 1932; Cent. 1932, II 1237. (97) Booth (to Swann Rosearch, Inc.), U.S. 1,954,469, April 10, 1934; Cent. 1934, II 1846. (98) Kraus, White, J. Am. Chem. Soc. 45, 773-774 (1923). (99) Soc. Chem. Ind. Basel, Brit. 250,819, May 13, 1926; Cent. 1927, I 804. (100) Haeussermann, Ber. 34, 39-40 (1901); Haeussermann, Bauer, Ber. 31, 2988-2989 (1898).
- (101) Wibaut, Rec. trav. chim. 32, 256-286 (1913). (102) Goldschmidt, Hönig, Ber. 20, 200 (1887). (103) Green, Lawson, J. Chem. Soc. 59, 1017 (1891). (104) Ullmann, Panchaud, Ann. 359, 110-111 (1906). (105) Holleman, Rec. trav. chim. 27, 456 (1908). (105A) Ullmann, Wagner, Ann. 355, 360 (1907). (106) Borsche, Fiedler, Ber. 45, 271-272 (1912). (107) Morgan, Drew, J. Chem. Soc. 117, 784-793 (1920). (108) Morgan, Glover, J. Chem. Soc. 119, 1700-1706 (1921).

(109) Morgan, Glover, J. Chem. Soc. 125, 1597-1601 (1924). (110) Huntress, Carten, J. Am. Chem. Soc. 62, 512-513 (1940).

(111) Wahl, Brit. 159,837, March 31, 1921; French 524,537, Sept. 6, 1921; Swiss 96,185, Sept. 16, 1922; Ger. 376,634, June 5, 1923; Cent. 1921, IV 124. (112) Shreve, Marsel, Ind. Eng. Chem. 38, 254-261 (1946). (113) Lock, Stach, Ber. 76, 1253-1255 (1943).

B.P.		F.P.	
159.5° (1)	at 759 mm. (10)	-69.5° (6)	$D_4^{20} = 0.8766 (10)$
159.2°	at 750 mm. (2)		0.8725 (6)
158.8-160.0°	(3)		$n_{\rm D}^{20} = 1.42844 (4)$
158.5-159.5°	(4)		1.42571 (10)
117.0-117.5° con	r. at 163 mm. (5)		$D_4^{15} = 0.8783 (6)$
61.4°	at 27 mm. (6)		

[For prepn. of \bar{C} from heptanol-1 (1:6240) by shaking 2 days with conc. HCl + ZnCl₂ in cold (60% yield (4)) see (4) (8); with PCl₃ + ZnCl₂ (70% yield), PCl₅ + ZnCl₂ (78% yield), or SOCl₂ + pyridine (81% yield) see (4); with SOCl₂ but without pyridine (80% yield) see (10); with conc. HCl in s.t. at 120–130° see (2); with HCl over Al₂O₃ at 420–440° see (7): for formation from *n*-heptylamine + NOCl see (8): for formation during chlorination of *n*-heptane see (9).]

[For study of reaction of \bar{C} with KI in acctone see (5); for difficulty in forming R.MgCl see (1); note, however, that \bar{C} with Mg in dry ether + trace I₂ gives (97.5% yield (11)) RMgCl.]

D N-(n-Heptyl)tetrachlorophthalimide: lfts. from EtOH, m.p. 145-146° (12). [From C (?) or from n-heptyl bromide with K tetrachlorophthalimide (12).]

3:8250 (1) Underwood, Gale, J. Am. Chem. Soc. 56, 2117-2120 (1934). (2) Cross, Ann. 189, 3 (1877). (3) Kohlrausch, Koppl, Monatsh. 63, 268 (1933). (4) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929). (5) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925). (6) Sherrill, J. Am. Chem. Soc. 52, 1985-1988 (1930). (7) Sabatier, Mailhe, Compt. rend. 169, 124 (1919). (8) Ssolonina, Cent. 1898, II 888. (9) Wertyporoch, Ber. 66, 737-738 (1933). (10) Vogel, J. Chem. Soc. 1943, 638, 640.

(11) Houben, Boedler, Fischer, Ber. 69, 1768, 1777 (1936). (12) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934).

3: 8264 METHYL
$$d_1l_{-\alpha}$$
-CHLORO- n -VALERATE C₆H₁₁O₂Cl Beil. II - 302 CH₃.CH₂.CH₂.CH₂.CH.COOCH₃ II₁--- II₂---

B.P. 160° at 764 mm. (1)

[For prepn. of \bar{C} from α -chloro-n-valeronitrile with MeOH + H₂SO₄ see (1).] 3:8264 (1) Henry, Bull. acad. roy. Belg. (3) 36, 241-262 (1898); Cent. 1898, I 194.

Cl

C4H7OCl

Beil. S.N. 25

3:8270 3-CHLOROBUTEN-2-OL-1

(2-Chlorobuten-2-ol-4;
$$\gamma$$
-chlorocrotonyl alcohol)

B.P. 161-162° (1)

92-93° at 50 mm. (2)

92° at 50 mm. (3) (4)

78.5-79° at 25 mm. (1)

67-67.5° at 12 mm. (5)

56.5° at 9 mm. (6)

CH₃—C=CH—CH₂OH

$$D_4^{20} = 1.1139 (1) \quad n_D^{20} = 1.4678 \quad (1)$$

1.1128 (2)

1.4649 (2)

$$D_4^{17} = 1.1172 (5) \quad n_C^{17} = 1.4654 \quad (5)$$

$$D_4^{15} = 1.1185 (1) \quad n_D^{15} = 1.4698 \quad (1)$$

[For prepn. of \bar{C} from 1,3-dichlorobutene-2 (3:5550) by hydrolysis with steam (6), or aq. alk. (4) (6), or aq. K_2CO_3 (2), aq. Na_2CO_3 (70-80% yield (3)) or $CaCO_3$ (5) see indic. refs.; note that the ether corresp. to \bar{C} (see below) is always formed as a by-product (4) and also that alc. KOH does not yield \bar{C} but the corresponding ethers (see below); for prepn. of \bar{C} from 1-bromo-3-chlorobutene-3 ("chloroprene hydrobromide") by refluxing 2 hrs. with aq. Na_2CO_3 (80% yield) see (1).]

C refluxed with 16% H₂SO₄ yields (2) methyl vinyl ketone.

Ethers of \tilde{C} . Di-(3-chlorobuten-2-yl-1) ether: from \tilde{C} in aq. KOH by addn. of 1 mole 1,3-dichlorobutene-2 (3:5550) (80-90% yield (3)) (4); b.p. 142° at 50 mm., (3) (4) $D_{20}^{20} = 1.171$ (3), 1.1171 (4); $n_D^{20} = 1.4860$ (3) (4).

Methyl 3-chlorobuten-2-yl-1 ether: from 1,3-dichlorobutene-2 (3:5550) with MeOH + alk. (7), b.p. 125-126° (7).

Ethyl 3-chlorobuten-2-yl-1 ether: from 1,3-dichlorobutene-2 (3:5550) with excess conc. alk. EtOH (80-90% yield (3)) (4) (7); b.p. 143° (3) (4), $88-89^{\circ}$ at 129 mm. (7), $62-64^{\circ}$ at 40 mm. (3) (4); $D_2^{40} = 0.9788$ (7), $D_{20}^{20} = 0.9729$ (3) (4); $n_D^{20} = 1.4392$ (7), 1.4382 (3) (4).

Phenyl 3-chlorobuten-2-yl-1 ether: from 1,3-dichlorobutene-2 (3:5550) with alk. + phenol (7); b.p. 94° at 1 mm., $D_4^{20} = 1.1080$, $n_D^{20} = 1.5378$ (7).

Esters of \bar{C} . 3-Chlorobuten-2-yl-1 acetate: from \bar{C} with AcCl (1); b.p. 80.5-81.5° at 25 mm. $D_4^{20} = 1.1029$, $n_D^{20} = 1.4495$ (1).

 \bar{C} readily adds Br₂ yielding (1) 2,3-dibromo-3-chlorobutanol-1, b.p. 111-112.5° at 10 mm., $D_4^{20} = 2.0058$, $n_D^{20} = 1.5544$ (1).

- **3-Chlorobuten-2-yl-1** N- $(\alpha$ -naphthyl)carbamate: cryst. from lgr., m.p. 107-108° (5).
- 3-Chlorobuten-2-vl-1 3.5-dinitrobenzoate: m.p. 72-73° (6).

3:8270 (1) Petrov, J. Gen. Chem. (U.S.S.R.) 10, 1418-1424 (1940); C.A. 35, 3593 (1941). (2) Churbakov, J. Gen. Chem. (U.S.S.R.) 10, 977-980 (1940); C.A. 35, 2469 (1941). (3) Klebanskii, Chevuichalova, Sintet. Kauchuk 1935, No. 6, 16-21; Cent. 1936, I 1975; C.A. 30, 1024 (1936). (4) Klebanskii, Tzyurikh, Dolgopol'skii, Bull. acad. sci. (U.S.S.R.) 1935, No. 2, 189-226; Cent. 1935, II 3844; C.A. 30, 1259 (1936) (full English translation in Rubber Chem. Tech. 9, 383-408 (1936)). (5) Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 658-662 (1937); Cent. 1937, II 371; C.A. 31, 5754 (1937). (6) Collins (to du Pont), U.S. 2,192,299, Mar. 5, 1940; C.A. 34, 4392 (1940). (7) Berchet (to du Pont), U.S. 2,079,758, May 11, 1937; Cent. 1937, II 2597; C.A. 31, 4676 (1937).

CHa

C₇H₇Cl

Beil. V - 291

3:8275 m-CHLOROTOLUENE

B.P. F.P. 162.2° at 756.5 mm. (1)
$$-48.0^{\circ}$$
 (7) $D_4^{20} = 1.07218$ (9) $D_4^{18.7} = 1.0760$ (10) $D_4^{18.7} = 1.0797$ (10) $D_4^{18.9} = 1.0797$ (10) $D_4^{18.9} = 1.0797$ (10) $D_4^{18.9} = 1.0797$ (10) $D_4^{18.9} = 1.0797$ (10)

[For prepn. of \tilde{C} from *m*-toluidine [Beil. XII-853, XII₁-(397)] via diazotization and use of Cu₂Cl₂ reactn. (yields: 86% (46), 80% (11)) (12) (13) or CuH (35% yield (48)) see indic. refs.; from 3-chloro-4-aminotoluene [Beil. XII-989, XII₁-(436)] via diazotization followed by boilg. with alc. (60% yield (14)) or conversion to corresp. hydrazine and subsequent oxidn. with CuSO₄ (50% yield (15)) see indic. refs.; from 5-chloro-2-aminotoluene [Beil. XII-835] with alc. H₂SO₄ + ethyl nitrite (1) or by diazotization, reduction to the corresp. hydrazine, and oxidn. of latter with CuSO₄ (43–63% yield (15)) see indic. refs.: for formn. of \tilde{C} from 1-methylcyclohexanone-3 by conversion with PCl₅ to 3-chloro-1-methylcyclohexane-x, treatment with Br₂, and boilg. with quinoline see (16); from 3-chloro-1-methylcyclohexadiene-1,3 [Beil. V-116] by conv. to dibromide and boilg. with quinoline see (17), from *m*-cresol (1:1730) with PCl₅, or from tri-(*m*-tolyl) phosphate at 210° see (18): for study of formn. of \tilde{C} by partial rearr. with AlCl₃ of o-chlorotoluene (3:8245) or p-chlorotoluene (3:8287) see (2).]

 $[\bar{C} \text{ with } H_2 \text{ in pres. of } Pd/CaCO_3 \text{ in alc./alk. soln. loses all its chlorine as HCl (19); <math>\bar{C} \text{ with } H_2 \text{ in pres. of } Pt \text{ in AcOH loses } HCl, \text{ but no quant. data are given (20).}]$

[C with Cl₂ in pres. of Al/Hg yields (21) both 2,5-dichlorotoluene (3:6245) and 3,4-dichlorotoluene (3:6355) but no trace of any other isomers.]

[$\bar{\mathbb{C}}$ with Br₂ in CCl₄ at 60-80° in bright light (22) (23) or in CS₂ (23) or $\bar{\mathbb{C}}$ at 130° with Br₂ directly (24) gives (55% yield (22)) m-chlorobenzyl bromide, m.p. 15-15.5°, b.p. 103-105° at 8 mm. (22), b.p. 108-111° at 10 mm. (24), $D_{25}^{25} = 1.5652$ (22); $\bar{\mathbb{C}}$ with Br₂ in CCl₄ in pres. of Al/Hg (25) or $\bar{\mathbb{C}}$ with Br₂ in AcOH in pres. of HNO₃ or HNO₃/H₂SO₄ (26) gives both 6-bromo-3-chlorotoluene, b.p. 120-125° at 15 mm. (26), 100-103° at 15 mm. (25) (note disagreement!), and 4-bromo-3-chlorotoluene, b.p. 90-93° at 12 mm. (26).] — [$\bar{\mathbb{C}}$ with Br₂ in pres. of Be yields (27) x,y-dibromo-3-chlorotoluene, m.p. 96.5°.]

[\tilde{C} with AlCl₃ + HCl gas as directed undergoes partial rearr. (2) to both o-chlorotoluene (3:8245) and p-chlorotoluene (3:8287); for anal. of mixtures of the three isomers see (2).]

[Č with $AcCl + AlCl_3$ in CS_2 gives (60% yield (28)) 3-chloro-4-acetyltoluene (2-chloro-4-methylacetophenone), b.p. 260–262° at 760 mm. (28), b.p. 120–126° at 14 mm. (29), accompanied (29) by some of the isomeric 3-chloro-6-acetyltoluene (4-chloro-2-methylacetophenone), b.p. 120–122° at 14 mm. (29). — Č with chloroacetyl chloride (3:5235) + $AlCl_3$ in CS_2 gives (70% yield (33)) 3-chloro-6-(chloroacetyl)toluene (ω,4-dichloro-2-methylacetophenone, m.p. 90° (33). — Č with β-chloropropionyl chloride (3:5690) + $AlCl_3$ in CS_2 gives (87% yield (50)) (30) 3-chloro-6-(β-chloropropionyl)toluene which on ring closure with conc. H_2SO_4 gives (50) (30) 5-chloro-7-methylindanone-1, m.p. 71° (50) (30). — Č with biphenyl-4,4'-bis-(carboxylic acid chloride) + $AlCl_3$ yields (31) 4,4'-bis-(4-chloro-2-methylbenzoyl)-biphenyl (used in prepn. of bis-anthraquinonyl derivs.).]

[Č with trichloroacetonitrile + AlCl₃ as directed (32) yields 4-chloro-2-methylbenzoic acid (3:4700).]

[For study of system: C + SbCl₃ see (7).]

[\bar{C} with NH₃ + cat. as directed (34) (35) yields *m*-toluidine; \bar{C} with aq. NaOH in pres. of Cu at 300-400° under press. yields (51) mixt. of o-cresol (1:1400), *m*-cresol (1:1730), and *p*-cresol (1:1410).]

[\bar{C} on mononitration, e.g., with 4 pts. HNO₃ (D=1.52) at 0°, gives a mixt. contg. (36) cf. (37) (13) (38) 59% 3-chloro-6-nitrotoluene [Beil. V-327, V₁-(162)], m.p. 24.9°, + 32% 3-chloro-4-nitrotoluene [Beil. V-329, V₁-(163)], m.p. 24.2°, + 9% 3-chloro-2-nitrotoluene [Beil. V-327, V₁-(162)], m.p. 23.4°. — \bar{C} on dinitration, e.g., with mixt. of 2 wt. pts. HNO₃ (D=1.52) + 3 wt. pts. conc. H₂SO₄ at room temp. for 12–18 hrs. (13), gives (95.8% yield (13)) 3-chloro-4,6-dinitrotoluene [Beil. V-344, V₁-(168)], cryst. from alc. or lgr., m.p. 91° (13) (38) (39), 90–90.5° (52) (note that the isomeric 3-chloro-2,6-dinitrotoluene [Beil. V₁-(168)] (40), m.p. 77° (40), and 3-chloro-2,4-dinitrotoluene, m.p. 92° (41), are also known but prepd. by indirect means). — \bar{C} on trinitration, e.g., by refluxing with 3 pts. HNO₃ (49.4°Bé) + 3 pts. H₂SO₄ (66°Bé) at 160° (42), yields 3-chloro-2,4,6-trinitrotoluene [Beil. V-349], cryst. from C₆H₆ + lgr., m.p. 150–151° (52), 148.5° (42).]

[\bar{C} with Na followed by CO₂ as directed gives (yields: 88% (43A), 58% (43B)) *m*-toluic acid (1:0705), m.p. 110-111°, also obtd. in small yield (44) from \bar{C} + alc. KCN in pres. of NiCl₂, htd. in s.t. at 260-270° for 20 hrs.]

[\bar{C} with CrO_2Cl_2 gives a cpd. which with aq. gives (44.5% yield (45)) *m*-chlorobenzaldehyde (3:6475).]

 \tilde{C} on oxidn. with $K_2Cr_2O_7 + H_2SO_4$ (14), with 5% aq. KMnO₄ (11) (46) or with dil. HNO₃ in s.t. at 130-140° for 10 hrs. (15) gives (75% yield (46)) *m*-chlorobenzoic acid (3:4392).

3:8275 (1) Feitler, Z. physik. Chem. 4, 73-76 (1889). (2) Norris, Turner, J. Am. Chem. Soc. 61;
2128-2131 (1939). (3) Kohlrausch, Pongratz, Monatsh. 63, 441 (1934). (4) Stuckey, Saylor, J. Am. Chem. Soc. 62, 2923 (1940). (5) Wibaut, Rec. trav. chim. 32, 286 (1913). (6) Rule, McLean, J. Chem. Soc. 1931, 689. (7) Menschutkin, J. Russ. Phys.-Chem. Soc. 44, 1940 (1912);
Cent. 1913, I 805. (8) Haase, Ber. 26, 1053 (1893). (9) Seubert, Ber. 22, 2520, 2522 (1889).
(10) von Auwers, Ann. 422, 164 (1921).

(11) Bornwater, Holleman, Rec. trav. chim. 31, 223-224 (1912). (12) Wibaut, Rec. trav. chim. 32, 286 (1913). (13) Réverdin, Crépieux, Ber. 33, 2505-2507 (1900). (14) Wroblewski, Ann. 168, 200 (1873). (15) Wynne, J. Chem. Soc. 61, 1047-1049, 1058-1059 (1892). (16) Klages, Ber. 32, 2567-2569 (1899). (17) Klages, Knoevenagel, Ber. 27, 3021-3023 (1894). (18) Autenrieth, Geyer, Ber. 41, 156-157 (1908). (19) Busch, Stove, Ber. 49, 1069 (1916). (20) Willstatter, Hatt, Ber. 45, 1477 (1912).

Cohen, Dakin, J. Chem. Soc. 79, 1117-1118 (1901). (22) Jenkins, J. Am. Chem. Soc. 55, 2897 (1933). (23) Sampey, Fawcett, Morehead, J. Am. Chem. Soc. 62, 1839-1840 (1940). (24) Thomson, Stevens, J. Chem. Soc. 1932, 62. (25) Cohen, Smithells, J. Chem. Soc. 165, 1911-1912 (1914). (26) Varma, Sahay, J. Indian Chem. Soc. 11, 293-294 (1934). (27) Pajeau, Compt. rend. 262, 1796 (1936). (28) Ganguly, LeFevre, J. Chem. Soc. 1934, 851. (29) Mayer, Albert, Sohön, Ber. 65, 1297-1299 (1932). (30) Mayer (to I.G.), Ger. 515,110, Jan. 15, 1931; Cent. 1931, 11 908.

(31) I.G., Brit. 394,995, Aug. 3, 1933; Cent. 1933, II 2753. (32) Houben, Fischer, Ber. 64, 2649 (1931). (33) Kunckell, Ber. 41, 2648 (1908). (34) Federal Phosphorus Co., Brit. 370,774, May 5, 1932; Cent. 1932, II 1237. (35) Booth (to Swann Research, Inc.), U.S. 1,954,469, April 10, 1934; Cent. 1934, II 1846. (36) Wibaut, Rec. trav. chim. 32, 286-309 (1913). (37) Fry, J. Am. Chem. Soc. 38, 1327-1333 (1916). (38) Réverdin, Crépieux, Bull. soc. chim. (3) 23, 838-839 (1900). (39) Sane, Joshi, J. Indian. Chem. Soc. 5, 300 (1928). (40) Lindemann, Pabst, Ann. 462, 43 (1928).

(41) Brady, Bowman, J. Chem. Soc. 119, 896-897 (1921). (42) Réverdin, Dresel, Déletra,

Ber. 37, 2094-2095 (1904); Bull. soc. chim. (3) 31, 633 (1904). (43A) Morton, LeFevre, Hechenbleikner, J. Am. Chem. Soc. 58, 754-755 (1936). (43B) Morton, Stevens, J. Am. Chem. Soc. 53, 4031-4032 (1931). (44) Siebodzinski, J. prakt. Chem. (2) 143, 119 (1935). (45) Law, Perkin, J. Chem. Soc. 93, 1636 (1908). (46) Koopal, Rec. trav. chim. 34, 144 (1915). (47) Huntress, Carten, J. Am. Chem. Soc. 62, 512-513 (1940). (48) Neogi, Mitra, J. Chem. Soc. 1928, 1332. (49) I.G., Brit. 281,290, Nov. 22, 1927; French 644,319, Oct. 5, 1928; Cent. 1929, II 352. (50) Mayer, Müller, Ber. 60, 2281-2283 (1927).

(51) Britton (to Dow Chem. Co.), U.S. 1,996,744, April 9, 1935; Cent. 1935, II 1962. (52) Qvist, Moilanen, Acta Acad. Aboensis, Math. et Phys. 14, No. 3, 9 pp. (1943); Cent. 1943, II 1268-

1269; C.A. 38, 5491 (1944).

```
3-CHLOROPROPANOL-1
3:8285
                                              CH<sub>2</sub>.CH<sub>2</sub>.CH<sub>2</sub>OH
                                                                      C<sub>3</sub>H<sub>7</sub>OCl
                                                                                    Beil. I - 356
            (Trimethylene chloro-
                                                                                           I<sub>1</sub>-(180)
            hydrin, y-chloro-n-
                                                                                           I<sub>2</sub>-(370)
            propyl alcohol)
  B.P.
                                                       D_4^{20} = 1.1318 \quad (9)
                                                                               n_{\rm D}^{20} = 1.44693 (2)
  160-162° cor.
                                    (1) (10)
  160.0-160.3° at 734.1 mm.
                                    (2)
                                                               1.1309 (2)
                                                                                      1.4469 (9)
  158.6-161.0° at
                        734 mm.
                                                               1.1262 (7)
                                                                                      1.448
                                                                                                  (7)
  158-159°
                                    (4)
                                                       D_4^{18} = 1.129 \quad (10)
  74-76°
                          23 mm.
                                   (5)
  66.0-66.2°
                   at
                          16 mm.
                                    (6)
  63-64°
                          16 mm. (7)
                   at
  64-66°
                   at
                          14 mm. (77)
  60-64°
                   at
                          10 mm. (8)
  53°
                           6 mm. (2)
                   at
```

Colorless oil with agreeable odor; undergoes partial decompn. on distn. at ord. press. — Very sol. aq. but not miscible with it.

[For prepn. of \bar{C} from propanediol-1,3 (trimethylene glycol) (1:6490) with HCl gas (50-60% yield (8)) (4) (7) (11) (12) (13) (1), with conc. HCl (yield: 34% (14), 28% (15), 15% (16)) (some 1,3-dichloropropane and other prods. are also formed), with SOCl₂ (50-60% yield (77)), or with S_2Cl_2 (yields: 68% (5), 60% (16)) (17) see indic. refs.; for formn. of \bar{C} from γ -chloro-n-propyl acetate (see below) by alcoholysis with MeOH/HCl (85% yield (18)) or from γ -chloro-n-propyl trichloroacetate (9) by hydrol. with aq. KOH at 35° (9) see indic. refs.; for manuf. from ethylene + formaldehyde + HCl + ZnCl₂ see (19).]

 \bar{C} on oxidn. with conc. HNO₃ gives (yields: 78-79% (20), 54-56% (21), 30-40% (13)) β -chloropropionic acid (3:0460) (note that the presumably intermediate β -chloropropionaldehyde (3:5576) is best obtd. by other means).

[\bar{C} with HBr gas (22), on distn. with 48% HBr (yield: 75–85% (22), 40% (11)), with HBr + H₂SO₄ (yield: 89% (23)), or with PBr₃ (94% yield (11)) gives 1-bromo-3-chloropropane (trimethylene chlorobromide) [Beil. I-109, I₁-(36), I₂-(75)], b.p. 142–145°, D_{25}^{25} = 1.4718 (24), n_{25}^{25} = 1.4732 (24); for study of rate of reactn. of \bar{C} with HBr in phenol see (25).]

[\bar{C} refluxed with $\frac{1}{2}$ wt. conc. H₂SO₄ gives (10–15% yield (26)) bis-(γ -chloro-n-propyl) ether, b.p. 215° at 745 mm., $D_{20}^{20} = 1.140$ (26). — \bar{C} with SO₂Cl₂ gives (68% yield (27)) γ -chloro-n-propyl chlorosulfonate, b.p. 85° at 4 mm., $D_{20}^{02} = 1.456$ (27). — \bar{C} with SOCl₂ gives (70% yield (27)) sym.-bis-(γ -chloro-n-propyl) sulfite, b.p. 161–162° at 13 mm., $D_{10}^{10} = 1.313$ (27).]

[$\bar{\mathbf{C}}$ with COCl₂ (3:5000) directly (28) or in toluene (29) gives (43% yield (29)) γ -chloro-n-propyl chloroformate (3:6895); $\bar{\mathbf{C}}$ with trichloroacetic acid (3:1150) gives (57% yield (9)) γ -chloro-n-propyl trichloroacetate, b.p. 107° at 8 mm., $D_4^{15} = 1.4732$, $n_D^{15} = 1.4830$ (9); for formn, of other esters (as derivs.) see below.]

[Other reactns. involving only the OH group of \tilde{C} include the following: \tilde{C} with acetylene + BF₃ + HgO gives (38% yield (30)) ethylidene bis-(γ -chloro-n-propyl)acetal, b.p. 127-129° at 14 mm. (30); \tilde{C} with benzonitrile + HCl gas in ether gives (31) γ -chloro-n-propyl iminobenzoate hydrochloride; \tilde{C} with β -acetobromglucose + Ag₂CO₃ yields (32) tetra-acetyl- β -d-(γ -chloro-n-propyl)glucoside, m.p. 74° (for extension to prepn. of corresp. xyloside, galactoside, and lactoside see (32)).]

[Č with solid KOH loses HCl on htg. giving (16) (7) (10) (1) 1,3-epoxypropane (trimethylene oxide) [Beil. XVII-6, XVII₁-(3)], b.p. 47.8° at 760 mm., $D_4^{25} = 0.8930$, $n_D^{24} = 1.3897$ (16) (for study of rate of reactn. see (33)).]

[\bar{C} with NaOEt in abs. alc. reacts vigorously giving (38% yield (34)) ethyl γ -hydroxy-n-propyl ether (trimethylene glycol monoethyl ether) [Beil. I-476, I₁-(247)], b.p. 160-161° (34), 162.1-162.2°, $D_4^{20} = 0.91691$, $n_D^{20} = 1.41666$ (35), accompanied by some trimethylene glycol diethyl ether, b.p. 140° (34). — \bar{C} with NaSH as directed gives (70-80% yield (34)) γ -hydroxy-n-propyl mercaptan, b.p. 85-90° at 15 mm. (Hg mercaptide = Hg (SCH₂CH₂-CH₂OH)₂, pl. from butanol, m.p. 132-134° (36). — \bar{C} with aq. Na₂S gives (36) bis-(γ -hydroxy-n-propyl) sulfide, visc. oil which could be neither distd. nor crystd. but which with phenyl isocyanate gave the corresp. bis-(phenylcarbamate), m.p. 146-148° (36). — \bar{C} with NaSCH₃ in ether gives (76% yield (42)) γ -hydroxy-n-propyl methyl sulfide, b.p. 105-105.5° at 30 mm. (42). — \bar{C} with benzyl mercaptan in alc. gives (88% yield (43)) benzyl γ -hydroxy-n-propyl sulfide, b.p. 185° at 19 mm. (43).]

[\bar{C} in alk. medium reacts with phenols yielding corresp. subst. alcohols; e.g., \bar{C} with phenol + alc. NaOEt (75% yield (37)) or \bar{C} + phenol + aq. NaOH (80% yield (38) (39)) gives 3-phenoxypropanol-1, b.p. 158-160° at 25 mm., $n_D^{2D} = 1.491$ (37) which with ZnCl₂ at 215° loses aq. and ring-closes (37) to chromane [Beil. XVII-52, XVII₁-(22)]; for corresp. reactn. with o-cresol (40), with m-cresol (41), p-cresol (41), β -naphthol (40), or resorcinol (40) see indic. refs.]

[$\bar{\mathbf{C}}$ with prim. or sec. amines splits out HCl yielding corresp. subst. aminoalcohols: e.g., for reactn. of $\bar{\mathbf{C}}$ with aniline + anhydrous Na₂CO₃ giving (67.5% yield) 3-(N-phenylamino)propanol-1 (N-(γ-hydroxy-n-propyl)aniline), b.p. 192° at 30 mm., $D_{20}^{20} = 1.063$, $n_{20}^{20} = 1.502$, see (44); for analogous reactn. of $\bar{\mathbf{C}}$ with p-toluidine see (45); for $\bar{\mathbf{C}}$ with actetrahydro-β-naphthylamine see (46); for $\bar{\mathbf{C}}$ with various sym. aliphatic sec. amines see (47) (55); for $\bar{\mathbf{C}}$ with morpholine giving (75% yield) 3-(morpholino)propanol-1, b.p. 147–149° at 21 mm., $n_{20}^{20} = 1.4743$, $n_{20}^{20} = 1.4762$, see (76); for $\bar{\mathbf{C}}$ with piperidine see (48) (56).] — [$\bar{\mathbf{C}}$ with ter-amines yields corresp. quat. ammon. salts: e.g., $\bar{\mathbf{C}}$ with (CH₃)₃N in C₆H₆ in s.t. at 100° for 8 hrs. gives (92% yield (49)) γ-homocholine chloride, m.p. 173° (49); $\bar{\mathbf{C}}$ with pyridine gives (85% yield (50)) γ-hydroxy-n-propyl pyridinium chloride, oil.] — [For reactn. of $\bar{\mathbf{C}}$ with arsanlic acid (p-aminobenzenearsonic acid) (51), with p-hydroxy-benzenearsonic acid (52), with ethyl β-methylaminopropionate (53), or with various carbazole derivs. (54) see indic. refs.]

[Č with 1 mole thiourea htd. at 120–125° yields (57) S-(γ -hydroxy-n-propyl)isothiourea hydrochloride, cryst. from butanol, m.p. 130° (57); Č with dry sodium p-toluenesulfonamide htd. at 160–170° for 18 hrs. yields (58) N-(γ -hydroxy-n-propyl)-p-toluenesulfonamide as an oil.]

[For study of rate of reactn. of \bar{C} with KI in acetone at 35° and 45° see (39); for reactn. of \bar{C} with Na₃AsO₃ see (5).]

⁻⁻⁻⁻ γ-Chloro-n-propyl acetate [Beil. II₁-(48), II₂-(139)]: liq., b.p. 168-169° (59), 165-166° (60), 88-90° at 22 mm. (61), 66° at 14 mm. (17), 62-63° at 10 mm. (7) $D_{21}^{21} = 1.1105$ (7); $n_D^{21} = 1.431$ (7). [From \ddot{C} + AcCl (yields: 90% (60), 87% (16)) (7) (62), from 1,3-dichloropropane (3:5450) with AgOAc (53% yield (61)), or from

- trimethylene glycol (1:6490) with $Ao_2O + S_2Cl_2$ (68% yield (17)).]—[This acetate with solid KOH loses HOAc giving (16) (7) (61) 2,3-epoxypropane (trimethylene oxide) (see above).]
- —— γ -Chloro-n-propyl benzoate: oil, b.p. 154-156° at 22 mm. (31), 155-156° at 15 mm. (4), 133-134° at 2 mm. (39), $D_4^{22} = 1.1672$ (31), $n_D^{20} = 1.5136$ (31). [From $\ddot{\mathbf{C}}$ + BzCl (yields: 84% (39), 75% (4)) or from γ -chloro-n-propyl iminobenzoate hydrochloride (see above) by hydrol. (31).] [For reactn. of this ester with pyrrolidine (63), pyrroline (63), piperidine (56), subst. piperidines (64) (65) (68), hydrogenated quinolines (66), or with N-methyl-phenyl-alkylamines (67) see indic. refs.]
- —— γ -Chloro-n-propyl p-nitrobenzoate: oil, b.p. 168.5–169.5° at 2 mm., $D_{25}^{25} = 1.3222$, $n_{D}^{25} = 1.54736$ (67). [From $\tilde{C} + p$ -nitrobenzoyl chloride on htg. (67).]
- \bigcirc γ -Chloro-n-propyl 3,5-dinitrobenzoate: colorless pl. from lt. pet., m.p. 77° (17). [From $\bar{C} + 3,5$ -dinitrobenzoyl chloride (17).]
- γ-Chloro-n-propyl hydrogen phthalate: unreported.
- ---- γ-Chloro-n-propyl hydrogen 3-nitrophthalate: unreported.
 - —— γ-Chloro-n-propyl benzenesulfonate: unreported.
- ---- γ-Chloro-n-propyl p-toluenesulfonate: oil, b.p. $216-219^{\circ}$ at 17 mm. (69), $188-192^{\circ}$ at 5 mm. (24), $D_4^{20} = 1.2674$ (69), $D_2^{25} = 1.2396$ (24), $D_D^{20} = 1.5230$ (69), $D_D^{21} = 1.5225$ (24). [From $\bar{C} + p$ -toluenesulfonyl chloride on htg. (69) or with aq. NaOH at 15° (50-55% yield (24)).]—[For reactn. of this ester with RMgX cpds. see (69) (24), with various sodium acetylenes see (70).]
- γ-Chloro-n-propyl carbamate: pearly cryst. from hot. aq., m.p. 62° (29). [From C with urea nitrate (2 moles) on htg. at 130-135° (16% yield (29)) or from γ-chloro-n-propyl chloroformate (3:6010) with conc. aq. NH₄OH (29).]
- —— γ-Chloro-n-propyl N-(phenyl)carbamate: ndls. from alc., m.p. 38° (29), m.p. 35-36° (28), b.p. 190° at 3.5 mm. (28). [From C̄ + phenyl isocyanate at 150° (29) or from γ-chloro-n-propyl chloroformate (3:6010) with aniline (29).]
- \bigcirc γ -Chloro-n-propyl N-(α -naphthyl)carbamate. cryst. from hot lgr., m.p. 76° (71) (17), 76.5° (9), 75.5–76.5° (28). [From $\ddot{C} + \alpha$ -naphthyl isocyanate (71).]
- ① $N-(\gamma-Hydroxy-n-propyl)$ phthalimide [3-(N-phthalimido)propanol-1] [Beil. XXI-472]: cryst. from aq., m.p. 75°-(72), 74° (73), 88° (74). [From \bar{C} + K phthalimide at 190° (73); also indirectly as cited in other indicated refs.]
- N-(γ-Hydroxy-n-propyl)tetrachlorophthalimide [3-(N-tetrachlorophthalimido)propanol-1)]: pr. from acetone, m.p. 165–166° (75). [From C with K tetrachlorophthalimide as directed (75).]
- 3:8285 (1) Reboul, Ann. chim. (5) 14, 493-496 (1878). (2) Karvonen, Ann. Acad. Sci. Fennicae A-3, No. 7, 1-103; Cent. 1912, II 1271; C.A. 14, 2175-2176 (1920); Ann. Acad. Sci. Fennicae A-5, No. 6, 120. (3) Kohlrausch, Ypsilanti, Z. physik. Chem. B-32, 414 (1936). (4) Zaki, J. Chem. Soc. 1930, 2271. (5) Gough, King, J. Chem. Soc. 1928, 2439. (6) Smyth, Walls, J. Am. Chem. Soc. 54, 2263 (1932). (7) Lespieau, Bull. soc. chim. (5) 7, 254-255 (1940). (8) Marvel, Calvery, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 533-535 (1941); (1st ed.), 519-521 (1932); 8, 112-115 (1928). (9) Gayler, Waddle, J. Am. Chem. Soc. 63, 3358-3359 (1941). (10) Ipatov, J. Russ. Phys.-Chem. Soc. 46, 64 (1914); Cent. 1914, I 2161.
- (11) Cloke, Anderson, Lachmann, Smith, J. Am. Chem. Soc. 53, 2793-2794 (1931). (12) Smith, Wode, Widhe, Z. physik. Chem. 130, 164 (1927). (13) Rojahn, Ber. 54, 3116-3117 (1921). (14) Hultman, Davis, Clarke, J. Am. Chem. Soc. 43, 369-370 (1921). (15) Norris, Mulliken, J. Am. Chem. Soc. 42, 2095-2096 (1920). (16) Derick, Bissell, J. Am. Chem. Soc. 38, 2481-2486 (1916). (17) Bennett, Heathcoat, J. Chem. Soc. 1929, 269-271. (18) Henry, Bull. acad. roy. Belg. 1906, 732-740 (1907); Cent. 1907, I 1314. (19) I.G., Brit. 465,467, June 3, 1937; French 812,292, May 4, 1937; Cent. 1937, II 1445. (20) Powell, Huntress, Hershberg, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 168-169 (1941).
 - (21) Powell, Org. Syntheses, Coll. Vol. 1 (1st. ed.), 162-163 (1932); 8, 58-59 (1928); J. Am. Chem.

Soc. 46, 2879 (1924). (22) Allen, Org. Syntheses, Coll. Vol. 2 (2nd ed.), 157, Note 2 (1941); Coll. Vol. 1 (1st ed.), 150-151, Note 2 (1932); 8, 53, Note 2 (1928). (23) Kamm, Marvel, J. Am. Chem. Soc. 42, 307 (1920). (24) Rossander, Marvel, J. Am. Chem. Soc. 50, 1493-1494 (1928). (25) Bennett, Reynolds, J. Chem. Soc. 1935, 134. (26) Kamm, Newcomb, J. Am. Chem. Soc. 43, 2228-2229 (1921). (27) Levaillant, Compt. rend. 197, 336 (1933). (28) Pierce, Adams, J. Am. Chem. Soc. 45, 791-793 (1923). (29) Dox, Yoder, J. Am. Chem. Soc. 45, 725 (1923). (30) Nieuwland, Vogt, Foohey, J. Am. Chem. Soc. 52, 1020-1022 (1930).

(31) Cloke, Keniston, J. Am. Chem. Soc. 60, 129-130 (1938). (32) Coles, Dodds, Bergeim, J. Am. Chem. Soc. 60, 1021-1022 (1938). (33) Petrenko-Kritschenko, Konschin, Ann. 342, 56 (1905). (34) Rojahn, Lemme, Arch. Pharm. 263, 617, 619 (1925). (35) Karvonen, Ann. Acad. Sci. Fennicae A-10, No. 9, p. 7. (36) Bennett, Hock, J. Chem. Soc. 127, 2673 (1925). (37) Rindfusz, J. Am. Chem. Soc. 41, 668-669 (1919). (38) Powell, J. Am. Chem. Soc. 45, 2709-2710 (1923). (39) Kirner, J. Am. Chem. Soc. 48, 2745-2751 (1926). (40) Rindfusz, Ginnings.

Harnack, J. Am. Chem. Soc. 42, 160-165 (1920).

(41) Powell, Johnson, J. Am. Chem. Soc. 46, 2862-2863 (1924). (42) Kirner, J. Am. Chem. Soc. 50, 2452 (1928). (43) Rothstein, J. Chem. Soc. 1934, 686. (44) Rindfusz, Harnack, J. Am. Chem. Soc. 42, 1723 (1920). (45) Davis, Brewster, Blair, Thompson, J. Am. Chem. Soc. 44, 2640-2641 (1922). (46) Coles, Lott, J. Am. Chem. Soc. 58, 1989 (1936). (47) Burnett, Jenkins, Peet, Dreger, Adams, J. Am. Chem. Soc. 59, 2249-2250 (1937). (48) Brill, J. Am. Chem. Soc. 47, 1135 (1925). (49) Major, Cline, J. Am. Chem. Soc. 54, 244-247 (1932). (50) Barnes, Adams, J. Am. Chem. Soc. 49, 1312 (1927).

(51) Hamilton, J. Am. Chem. Soc. 45, 2752 (1923). (52) Sweet, Hamilton, J. Am. Chem. Soc. 56, 2411 (1934). (53) McElvain, J. Am. Chem. Soc. 46, 1726 (1924). (54) Burtner, Lehmann, J. Am. Chem. Soc. 52, 529-530 (1940). (55) K. D. Campbell, B. K. Campbell, Proc. Induana Acad. Sci. 49, 101-104 (1939); C.A. 35, 5460 (1941). (56) McElvain, J. Am. Chem. Soc. 49, 2838 (1927). (57) Ohn, Davis, J. Am. Chem. Soc. 52, 3323 (1930). (58) Peacock, Givan, J. Chem. Soc. 1937, 1470. (59) Conant, Kirner, Hussey, J. Am. Chem. Soc. 47, 498-499 (1925).

(60) Bogert, Slocum, J. Am. Chem. Soc. 46, 766 (1924).

3:8287 p-CHLOROTOLUENE

(61) Bermejo, Aranda, Anales soc. españ. fis quím. 27, 798-800 (1929); Cent. 1930, I 2382. (62) Blicke, Blake, J. Am. Chem. Soc. 53, 1018 (1931). (63) Andrews, McElvain, J. Am. Chem. Soc. 51, 890-891 (1929). (64) Bailey, McElvain, J. Am. Chem. Soc. 52, 1637-1638 (1930). (65) Walters, McElvain, J. Am. Chem. Soc. 55, 4625-4626 (1933). (66) Bailey, McElvain, J. Am. Chem. Soc. 52, 4015-4016 (1930). (67) Cope, McElvain, J. Am. Chem. Soc. 53, 1589-1590 (1931). (68) McElvain, U.S. 1,784,903, Dec. 16, 1930, Cent. 1931, I 1789; C.A. 25, 1037 (1931). (69) Gilman, Beaber, J. Am. Chem. Soc. 45, 842 (1923). (70) Johnson, Schwartz, Jacobs, J. Am. Chem. Soc. 60, 1882-1884 (1938).

(71) Bickel, French, J. Am. Chem. Soc. 48, 747-749 (1926).
(72) Gabriel, Ber. 38, 633 (1905).
(73) Gardner, Haenni, J. Am. Chem. Soc. 53, 2766-2767 (1931).
(74) Garelli, Racciu, Att. accad. sci. Torino, Classe sci. fis. mat. nat. 69, 358-363 (1934); Cent. 1934, II 2823.
(75) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934).
(76) Cheney, Bywater, J. Am. Chem. Scc. 64, 970 (1942).
(77) Rovira, Halasz, Compt. rend. 212, 644 (1941).

C7H7Cl

Beil. V - 292

V₁-(150) V_{2} -(226) B.P. M.P. $D_4^{25} = 1.065$ $+7.8^{\circ}$ 163.5° cor. 764 mm. (1) (8) (16) $n_{\rm D}^{25} = 1.51895$ (9) $D_4^{24.35} = 1.0651$ (21) 760 mm. (2) 7.5° (14) (15) (16) 162.4° (3) $n_{\rm D}^{24 \ 35} = 1.51925 (21)$ 162.3° at 756.4 mm. $\langle 4 \rangle$ 7.4° (17)(4) $D_4^{20} = 1.0700$ 162.0-162.2° cor. (5) 7.15-7.30° (7) 162-163° (6) 7.1° (18)1.06974 (17) 161.98-161.99° at 760 mm. 7° (6) (19) (7) 1.069 $n_{\rm D}^{20} = 1.521$ 161.7-162.2° cor.at 759.9 mm. (8) 6.86° (12)(21)at 760 mm. 6.85° (20) 161.5-161.9° (9) See also 161.0-161.4° (10)Note 3. $n_{\rm D}^{19} = 1.5223$ 160.6-161.2° See also Note 2. (11)162.1° u.c. at 755 mm. (12)

55.57°	at	16 mm.	(3)	$n_{\rm D}^{18} = 1.5221$	(12)
54.28°	at	15 mm.	(3)	See also Note 4.	
52.86°	at	14 mm.	(3)		
48°	at	12 mm.	(13)		
45.5°	at	12 mm.	(14)		
44°	at	10 mm.	(15)		

See also Note 1.

Note 1. For further data on b.p. of C at 16 pressures from 74-764 mm. see (4).

Note 2. For effect of press. on m.p. see (20).

Note 3. For data on D_4^t from $t = 25^\circ$ to $t = 160^\circ$ see (16) (4); note also $D_{20}^{20} = 1.0714$ (8).

Note 4. For $n_{\rm D}^{19}/{\rm compn}$. data on system: $\bar{\rm C}$ + o-chlorotoluene (3:8245) see (22).

 \bar{C} with aq. forms a const.-boilg. mixt., b.p. 95° (use in sepn. of \bar{C} from polychlorotoluenes (23)). — For f.p./compn. data on system: \bar{C} + o-chlorotoluene (3:8245) (eutectic, f.p. -49.8°, contg. 27 wt. % \bar{C}) see (8) (147); for D_{20}^{20} /compn. data (8) and for n_{D}^{10} /compn. data (22) on this system see indic. refs. — For f.p./compn. data on systems of \bar{C} with p-bromotoluene or with p-fluorotoluene see (19). — For data on const.-boilg. mixts. of \bar{C} with various org. cpds. see Beil. V₂-(227). — For cryoscopic constant (i.e., lowering of f.p. per mole solute per 1000 g. \bar{C}) viz., 5.53 (12), 5.6 (24), 5.97 (25), see indic. refs.; for use in detn. of \bar{C} in mixt. with o-chlorotoluene (3:8245) and m-chlorotoluene (3:8275) see (25).

[For prepn. of \bar{C} from p-toludine via diazotization in HCl and warming the resultant solution as such (yields: 60% (26), 40-44% (27)) (28) or in pres. of Cu₂Cl₂ (yields: 95% (33), 88-89% (29), 81% (31), 70-79% (30), 63.5% (32)) [for study of kinetics of this reaction see (34) (35)], or in pres. of Cu powder (63.8% yield (36)), or in pres. of CuH (64% yield (37)), or by electrolysis between Cu electrodes in pres. of CuCl₂ (38) see indic. refs.; for prepn. of \bar{C} from p-toluidine via diazotization, conversion to solid p-toluenediazonium chloride, and subsequent warming with C_6H_6 + AlCl₃ (39), or via diazotization, conversion of diazonium salt to its cpd. with PbCl₄, and subsequent htg. of latter in naphthalene at 150° (40), see indic. refs.]

[For formn. of \tilde{C} (usually together with other prods.) from toluene (1:7405) with Cl₂ (70) in pres. of Fe in diffuse light in cold (8) (gives mixt. contg. 42% \tilde{C} + 58% o-chlorotoluene (3:8245) (8) (22)), or in pres. of I₂ (22) (41) (42), or in pres. of PbCl₂ (8), SbCl₅ (41), MoCl₅ (43) (28) (44), or Al/Hg (45); for formn. of \tilde{C} from toluene by electrolysis in strong HCl (46) or in AcOH/conc. HCl in dark (47) see indic. refs.; for formn. of \tilde{C} from toluene with SO₂Cl₂ at 160° (48), with SO₂Cl₂ in pres. of various cat. in dark (49), with SO₂Cl₂ + AlCl₃ + S₂Cl₂ at 70° (50), with pyrosulfuryl chloride + AlCl₃ at 0° (51), with HCl + HNO₃ at 100° (52), with n-butyl chlorosulfonate + AlCl₃ (6.2% yield (53)), with anhydrous FeCl₃ after refluxing 1½ hrs. (65% yield (54)), or with NCl₃ (55) see indic. refs.]

[For formn. of \tilde{C} from o-chlorotoluene (3:8245) or m-chlorotoluene (3:8275) by partial rearr. with AlCl₃ + HCl gas see (25); from tetra-(p-tolyl)tin with Cl₂ in CHCl₃ (85% yield (6)) or from tri-(p-tolyl) stibine dichloride on htg. under 5-7 mm. press. at 60-65° (56) (note that at 160-200° di-p-tolylstibine chloride is formed (56)) or from tri-(p-tolyl)-phosphite dichloride by htg. at 200-210° (57) see indic. refs.; from p-tolyl MgBr in ether with Cl₂ (58) or with benzenesulfonyl chloride (59) see indic. refs.; from p-toluenediazopiperidide with conc. HCl see (60); from p-chlorobenzaldehyde (3:0765) on elec. reduction in acid soln. with Cu cathode see (61); from chlorobenzene (3:7903) via condensation with CH₂O + HCl to p-chlorobenzyl chloride (3:0220) and subsequent reductn. with Zn + NaOH see (62).]

[Č on pyrolysis over red-hot Pt yields (63) mainly 4,4'-dichlorodibenzyl (1,2-bis-(p-chlorophenyl)ethane [Beil. V-600, V_1 -(281), V_2 -(507)], colorless lfts. from alc., m.p. 112°, accompanied by a very small amt. 4,4'-dichlorostilbene (1,2-bis-(p-chlorophenyl)ethylene) [Beil. V_1 -(304), V_2 -(539)], ndls. from alc., m.p. 170°.]

[\bar{C} with H₂ in pres. of Pd/CaCO₃ (64) or reduced Ni (65) in alc./alk. soln. loses all its halogen as HCl; \bar{C} with Na in liq. NH₃ as directed (66) yields toluene and other prods.; \bar{C} with HI + P in s.t. at 302° for 5 hrs. gives (80% yield (67)) toluene.]

 $\bar{\mathbb{C}}$ on oxidn. with 3 pts. KMnO₄ in dil. aq. soln. under reflux for 4–5 hrs. (68) (51), or with CrO₃ (42), or with dil. HNO₃, e.g., with 6 pts. of dil. HNO₃ (1 vol. conc. HNO₃ + 2 vols. aq.) at 145° for 1½ hrs. (69) or at 115–120° for 5–6 hrs. (70), yields p-chlorobenzoic acid (3:4940), m.p. 243° (for use in quant. estn. of $\bar{\mathbb{C}}$ in pres. of toluene, benzyl chloride, and o-chlorotoluene see (70)). — Note that with HNO₃ $\bar{\mathbb{C}}$ is more rapidly oxidized than o-chlorotoluene, m-chlorotoluene, or the various dichlorotoluenes but more slowly than p-bromotoluene (69). — $\bar{\mathbb{C}}$ on oxidn. with air at 260° in pres. of Na₂CO₃ and under press. (71), or on vapor-phase oxidn. over suitable cat. (72), or on electrolytic oxidn. in dil. Na₂CO₃ soln. at 60° (73) cf. (74), or even on very long stdg. (2 years) with $\bar{\mathbb{I}}_2$ + aq. in sunlight (75) gives p-chlorobenzoic acid. — $\bar{\mathbb{C}}$ with N₂O₄ yields (76) p-chlorobenzoic acid accompanied by nitration prods.

[\bar{C} with chromyl chloride (CrO₂Cl₂) yields an addn. prod. which with aq. gives in good yield (77) p-chlorobenzaldehyde (3:0765). — \bar{C} with air in aq. susp. of FeO.OH + cat. at 235-240° and 50-60 atm. press. gives (78) a mixt. of p-chlorobenzaldehyde (3:0765) + p-chlorobenzoic acid (3:4940).]

[$\bar{\mathbb{C}}$ with Cl₂ or on htg. with PbCl₄.2NH₄Cl or with SO₂Cl₂ in pres. of dibenzoyl peroxide in dark yields p-chlorobenzyl chloride (3:0220), q.v. for relevant refs. — $\bar{\mathbb{C}}$ with 2 moles Cl₂ in pres. of 5% PCl₅ at 160–170° gives (79) (80) p-chlorobenzal (di)chloride (3:6700). — $\bar{\mathbb{C}}$ with 3 moles Cl₂ at high temp. in u.v. light (81) cf. (82) or with 3 moles Cl₂ (83) in pres. of FeCl₃ (84) or of PCl₅ (85) (86) gives (93% yield (85)) p-chlorobenzotrichloride (3:6825) q.v. — $\bar{\mathbb{C}}$ with Cl₂ (1 mole) in pres. of 1% Fe or 40% PbCl₂ at 20° gives (65% yield (87)) a mixt. comprising 58.4% 2,4-dichlorotoluene (3:6290) + 41.6% 3,4-dichlorotoluene (3:6355).]

[\bar{C} with Br₂ at 130° (88) or at 160° (89) (90) or in pres. of dibenzoyl peroxide in dark at 100° (91) gives (21% yield (90)) exclusively (91) p-chlorobenzyl bromide [Beil. V-307, V₂-(239)], cryst. from MeOH, m.p. 62-63° (88), ndls. from 85% alc., m.p. 50° (90), 51° (79), 48.5° (89); for study of rate of side-chain bromination of \bar{C} in CS₂ at 57° see (92). — \bar{C} with 2 moles Br₂ in pres. of BeBr₂ (93) or in AcOH + fumg. HNO₃ + fumg. H₂SO₄ (94) gives p-chlorobenzal (di)bromide, m.p. 99° (93).]

[C with AlCl₃ + HCl gas as directed (25) undergoes partial rearr. to both o-chlorotoluene (3:8245) and m-chlorotoluene (3:8275); for anal. of mixts. of the three isomers see (25).]

[\bar{C} with AcCl (95) or better Ac₂O (96) (97) + AlCl₃ in CS₂ (98) gives (yields: 85% in 4 hrs. (97), 65% (98), 34% in 2 hrs. (96)) 2-chloro-5-methylacetophenone [Beil. VII-307], b.p. 245.8-246.0° at 760.1 mm. (96), $n_2^{25} = 1.5419$ (96). — \bar{C} with β -chloropropionyl chloride (3:5690) + AlCl₃ in CS₂ gives (87% yield (99)) (100) 4-chloro-3-(β -chloropropionyl)toluene, oil, which on ring closure with conc. H₂SO₄ gives (72% yield (99)) (100) 7-chloro-4-methylindanone-1, cryst. from MeOH, m.p. 128° (99) (100). — \bar{C} with trichloroacetonitrile + AlCl₃ (4 moles) at 80-90° satd. with HCl gas for 2 days gives only 5% yield (101) of a mixt. of 2-chloro-5-methyl- and 5-chloro-2-methyl- ω , ω , ω -trichloroacetophenones.]

[Č with oxalyl (di)chloride (3:5060) + AlCl₃ in CS₂ for 20 hrs. at room temp. gives (40% yield (102)) 2-chloro-5-methylbenzoic acid (6-chloro-3-methylbenzoic acid) (3:4615), cryst. from aq., m.p. 163-166° (102), accompanied by some dichlorodimethyl-benzophenone, m.p. 70°, whose structure was not detd. — Č with fumaryl (di)chloride (3:5875) + AlCl₃

in CS₂ at 50-60° for 2 hrs. gives (25% yield {103}) bis-1,2-(2-chloro-5-methylbenzoyl)-ethylene, pale yel. cryst. from alc., m.p. 158° (103).]

[$\ddot{\mathbf{C}}$ with benzoyl chloride + AlCl₃ in CS₂ gives (50% yield (98)) (104) (105) 2-chloro-5-methylbenzophenone (6-chloro-3-methylbenzophenone) [Beil. VII₁-(235)], cryst. from AcOH, m.p. 35–36° (98) (104) (105), together with 5-chloro-2-methyl-(3-chloro-6-methyl)-benzophenone [Beil. VII₁-(235)], oil, b.p. 210° at 30 mm. (106). — $\ddot{\mathbf{C}}$ with o-chlorobenzoyl chloride (3:6640) + AlCl₃ in CS₂ gives (106) 5,2'-dichloro-2-methylbenzophenone [Beil. VII₁-(235)], oil, b.p. 225° at 12 mm. (106).]

[C with phthalic anhydride (1:0725) + AlCl₃ gives (62.5% yield on the phthalic anhydride (107)) o-(2-chloro-5-methylbenzoyl) benzoic acid, ndls. from C₆H₆, m.p. 164-165° (107), 165° (108), which with conc. H₂SO₄ at 75° for 4 hrs. (108) or with 8 pts. fumg. H₂SO₄ (20% SO₃) (107) ring-closes to give (yields: 93% (107), 85% (108)) 1-chloro-4-methylanthraquinone [Beil. VII-809, VII₁-(421)], yel. ndls. from AcOH or alc., m.p. 164° (107) (108). — Note that the structure of the above keto acid, m.p. 164-165°, has been definitely established (109) as shown and that it is not the isomeric o-(5-chloro-2-methylbenzoyl)-benzoic acid, which appears to be still unreported. — For reactn. of C with 3,6-dichloro-phthalic anhydride (3:4860) (110) or with pyromellitic anhydride (111) in pres. of AlCl₃ see indic. refs.]

[\bar{C} does not (112) react with bis-(chloromethyl) ether (3:5245), but \bar{C} with formalin + conc. HCl yields (62) 4-chloro-3-(chloromethyl)toluene since on reductn. with Zn + NaOH the prod. gives 4-chloro-1,3-dimethylbenzene (3:8665). — \bar{C} with aq. vapor + CO over suitable cat. at 300-400° yields (113) p-toluic acid (1:0795). — \bar{C} with NH₃ + CO over suitable cat. as directed (114) yields p-toluidine (see also below). — \bar{C} with S₂Cl₂ + AlCl₃ in CS₂ gives (115) 4,5-dichloro-1,8-dimethylthianthrene, m.p. 195-197° (115).]

[\bar{C} with Li in ether gives (63% yield (116)) p-tolyllithium; \bar{C} with Li at 150° followed by treatment with aq. gives (117) toluene + 4,4'-dimethylbiphenyl. — \bar{C} with Na in C₆H₆ treated with CO₂ at ord. temp. (118) (119) or at 50° and 500 lbs. press. (120) cf. (121) gives (yields: 95% (120), 76% (121)) p-toluic acid (1:0795), m.p. 178°. — \bar{C} with Na treated with benzophenone as directed (122) yields diphenyl-p-tolyl-carbinol [Beil. VI-722, VI₁-(355)], m.p. 72-73°.]

[C on hydrolysis with aq. vapor over silica gel contg. 3% finely divided Ni at 380° (123), or with aq. vapor over cat. at 480° (124), or with aq. Na₂CO₃ in pres. of Cu at 300° under press. (125), or with 15–20% aq. NaOH at 300° (126) gives (80% yield (123)) p-cresol (1:1410). Note, however, claim (127) that C when hydrolyzed with 15% aq. NaOH in pres. of Cu for 2 hrs. at 315–320° yields prod. contg. not only p-cresol (1:1410) but also m-cresol (1:1730) (for extensive study of hydrolysis of C as means of prepn. of m-cresol see (147)). — C with H₂S at 700° over suitable cat. yields (128) thio-p-cresol (p-tolyl-mercaptan).]

[C with aq. NH₄OH + CuO at 150-250° under press. (129) or C + aq. NH₄OH + Cu salts + various anti acids at 225-230° under press. (130) (131) yields p-toluidine and/or di-p-tolylamine. — C with KNH₂ in liq. NH₃ (132) or Na in liq. NH₃ (66) yields p toluidine. — Note that C does not react with aq. sodium sulfanilate + Na₂CO₃ (dif. from benzyl chloride (3:8535) and use in sepn. of C from latter (8)).]

[\bar{C} on mononitration yields a mixt. contg. both 4-chloro-2-nitrotoluene [Beil. V-327, V₁-(162), V₂-(251)], m.p. 38.2° (133), 37-38° (10), 37° (29) (22), b.p. 239.5-240° at 718 mm. (134), 115.5° at 11 mm. (22) (easily volatile with steam, but not reacting with piperidine even after 8 hrs. at 100° (10)), and 4-chloro-3-nitrotoluene [Beil. V-329, V₂-(252)], m.p. 7° (135), 5.8° (133), b.p. 260° at 745 mm. (135), 118° at 11 mm. (22) (reacts readily with piperidine at 100° (10)); e.g., \bar{C} added in 2 equal portions to 3 wt. pts. HNO₃ (D = 1.5) at 0° gives 88% yield of mixt. contg. 58.8% 4-chloro-2-nitrotoluene + 41.2% 4-chloro-3-

nitrotoluene (10). — For further studies of mononitration of \bar{C} with HNO₃ + H₂SO₄ or with HNO₃ + Ac₂O + P₂O₅ see (29) (136), for influence of temperature (at -15° proportion of 4-chloro-2-nitrotoluene is slightly increased) see (10) (133).]

 \bar{C} on direct dinitration, e.g., with 3 wt. pts. fumg. HNO₃ (D=1.47), gives (134) a prod. now regarded (137) as 4-chloro-2,6-dinitrotoluene [Beil. V-344], yel. ndls. from ether, m.p. 76° (134), 76–77° (137). — [The three other possible dinitro-4-chlorotoluenes are now all known but have been prepd. indirectly; viz., 4-chloro-2,3-dinitrotoluene, lemon-yel. pr. from C₆H₆ + {lt. pet., m.p. 106.5° (138); 4-chloro-2,5-dinitrotoluene [Beil. V-344, V₁-(168), V₂-(263)], yel. pr. from lgr., m.p. 107°; and 4-chloro-3,5-dinitrotoluene [Beil. V-345, V₁-(169), V₂-(264)], pale yel. ndls. from alc., m.p. 115–116° (139), 116° (140).]

[C on monosulfonation, e.g., by htg. with 3 pts. 100% H₂SO₄ at 100° (141) (142) cf. (143) (28), yields mainly 4-chlorotoluenesulfonic acid-2 [Beil. XI-88] (corresp. sulfonyl chloride (144), m.p. 24° (142), see also below; corresp. sulfonamide, m.p. 145° (144), 142° (142), see also below; corresp. sulfonamilide, m.p. 144° (142)), accompanied by some 4-chlorotoluenesulfonic acid-3 [Beil. XI-95] (corresp. sulfonyl chloride, m.p. 56° (142), corresp. sulfonamide, m.p. 156° (142), corresp. sulfonamilide, m.p. 188° (142)). — C sulfonates much less readily than the isomeric o-chlorotoluene (3:8245); for use of this means of separation of C from the latter see (8) (145).]

◆ 4-Chlorotoluenesulfonamide-2 (5-chloro-2-methylbenzenesulfonamide-1): cryst. from dil. alc., m.p. 142-143° u.c. (146). [From C with ClSO₃H in CHCl₃ as directed (146) followed by conversion of the intermediate 4-chlorotoluenesulfonyl chloride-2 cryst. from pet. ether, m.p. 21°, to the sulfonamide with (NH₄)₂CO₃ or NH₄OH (146).]

Sugden, J. Chem. Soc. 125, 1175 (1924).
 Lecat, Rec. trav. chim. 46, 245 (1927).
 von Rechenberg, J. prakt. Chem. (2) 101, 117 (1920).
 Feitler, Z. physik. Chem. 4, 78-79 (1889).
 Perkin, J. Chem. Soc. 69, 1203 (1896).
 Bost, Baker, J. Am. Chem. Soc. 55, 1112 (1933).
 Stuckey, Saylor, J. Am. Chem. Soc. 62, 2923 (1940).
 Wahl, Normand, Vermeylen, Bull. scc. chim. (4) 31, 570-583 (1922); Compt. rend. 174, 948 (1922).
 Mathews, J. Am. Chem. Soc. 49, 570 (1926).
 Shaw, Turner, J. Chem. Soc. 1932, 1884-1888.

(11) Kohlrausch, Pongratz, Monalsh. 63, 441 (1934). {12} Bell, Baughan, Vaughan-Jackson, J. Chem. Soc. 1934, 1970-1971. {13} Paulsen, Monalsh. 72, 256 (1939). {14} Rule, McLean, J. Chem. Soc. 1931, 689. {15} van Scherpenzeel, Rec. trav. chim. 20, 155 (1901). {16} Jaeger, Z. anorg. allgem. Chem. 101, 126 (1917). {17} Seubert, Ber. 22, 2520, 2524 (1889). {18} Meharg, Allen, J. Am. Chem. Soc. 54, 2921 (1932). {19} L. Klemm, W. Klemm, G. Schiemann, Z. physik. Chem. A-165, 384, 386 (1933). {20} Block, Z. physik. Chem. 82, 408, 410 (1913).

(21) von Auwers, Frühling, Ann. 422, 164, 168 (1921). (22) Gindraux, Helv. Chim. Acta 12, 923-932 (1929). (23) Buchheim (to Chem. Fabrik von Heyden), Ger. 616, 596, Aug. 1, 1935; Cent. 1935, II 3703. (24) von Auwers, Z. physik. Chem. 42, 515 (1902). (25) Norris, Turner, J. Am. Chem. Soc. 61, 2128-2131 (1939). (26) Holleman, Beckmann, Rec. trav. chim. 23, 239 (1904). (27) Gaslorowski, Wayss, Ber. 18, 1939 (1885). (28) Hübert, Majert, Ber. 6, 760, 794 (1873). (29) Hodgson, J. Soc. Dyers Colourists 41, 328-329 (1925). (30) Marvel, McElvain, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 170-172 (1941); (1st ed.), 163-166 (1932); 3, 33-35 (1923).

(31) Erdmann, Ann. 272, 141–147 (1892). (32) Sandmeyer, Ber. 17, 2651 (1884). (33) Heller, Z. angew. Chem. 23, 389–392 (1910). (34) Heller, Tischner, Ber. 44, 250–255 (1911). (35) Waentig, Thomas, Ber. 46, 3933–3937 (1913). (36) Gattermann, Ber. 23, 1221 (1890). (37) Neogi, Mitra, J. Chem. Soc. 1928, 1332. (38) Votocek, Zenisek, Z. Elektrochem. 5, 486 (1898). (39) Möhlau, Berger, Ber. 26, 1998 (1893). (40) Sakellarios, Ber. 56, 2539 (1923).

(41) Wertyporoch, Ann. 493, 163 (1932). (42) Beilstein, Geitner, Ann. 139, 334-337 (1868). (43) Aronheim, Dietrich, Ber. 8, 1402 (1875). (44) Seelig, Ann. 237, 130 (1887). (45) Cohen, Dakin, J. Chem. Soc. 79, 1119-1120 (1901). (46) Cohen, Dawson, Crosland, J. Chem. Soc. 87, 1034-1037 (1905). (47) Fichter, Glanzstein, Ber. 49, 2481-2485 (1916). (48) Töhl, Eberhard, Ber. 26, 2942 (1893). (49) O. Silberrad, C. A. Silberrad, B. Parke, J. Chem. Soc. 127, 1724-1731 (1925). (50) O. Silberrad, J. Chem. Soc. 127, 2680 (1925).

(51) Steinkopf, Buchheim, Ber. 54, 2963-2968 (1921). (52) Datta, Fernandes, J. Am. Chem. Soc. 38, 1010-1011 (1914). (53) Barkenbus, Hopkins, Allen, J. Am. Chem. Soc. 61, 2453 (1939). (54) Dangyan, J. Gen. Chem. (U.S.S.R.), 8, 1780-1783 (1938); Cent. 1939, I 4928; C.A. 33, 4967 (1939). (55) Stoll, Bull. soc. chim. Belg. 38, 77-91 (1929). (56) Goddard, Yaraley,

J. Chem. Soc. 1928, 720. (57) Autenrieth, Geyer, Ber. 41, 155-156 (1908). (58) Datta, Mitter,
J. Am. Chem. Soc. 41, 292 (1919). (59) Gilman, Fothergill. J. Am. Chem. Soc. 51, 3506 (1929).
(60) Wallach, Ann. 235, 247 (1886).

(61) Law, J. Chem. Soc. 99, 1114 (1911).
(62) Tschunkur, Eichler (to I.G.), Ger. 509,149, Oct. 8, 1933, Cent. 1931, I 360.
(63) Meyer, Hofmann, Monatsh. 38, 151-152 (1917).
(64) Busch, Stöve, Ber. 49, 1069 (1916).
(65) Kelber, Ber. 50, 309 (1917).
(66) Kraus, White, J. Am. Chem. Soc. 45, 774 (1923).
(67) Klages, Liecke, J. prakt. Chem. (2) 61, 322 (1900).
(68) Emmerling, Ber. 8, 880-881 (1875).
(69) Cohen, Miller, J. Chem. Soc. 85, 174-179, 1626, 1630 (1904).

(70) Cohen, Dawson, Blockey, Woodmansey, J. Chem. Soc. 97, 1623-1636 (1910).

(71) Schrader, Ges. Abhandl. Kenntn. Kohle 4, 325 (1920), Cent. 1921, I 537; C.A. 15, 2850 (1921). (72) Charlot, Bull. soc. chim. (4) 53, 575 (1933); Ann. chim. (11) 2, 470 (1934). (73) Fichter, Adler, Helv. Chim. Acta 9, 281-282 (1926). (74) Dunbrook, Lowy, Trans. Am. Electrochem. Soc. 45 (Preprint), 1924; Cent. 1924, II 2838; C.A. 18, 1088 (1924). (75) O. Silberrad, J. Chem. Soc. 125, 2196-2197 (1924). (76) Schaarschmidt, Smolla, Ber. 57, 34 (1924). (77) Law, Perkin, J. Chem. Soc. 93, 1636 (1908). (78) I.G., Brit. 331,100, July 17, 1930; Cent. 1939, II 2186: French 676,826, Feb. 27, 1930; Cent. 1930, I 3881. (79) Shoesmith, Slater, J. Chem. Soc. 1926, 218-219. (80) McEwen, Org. Syntheses, Coll. Vol. 2 (1 st ed.), 133-135 (1943); 12, 12-14 (1933).

(81) Maryott, Hobbs, Gross, J. Am. Chem. Soc. 62, 2321 (1940). (82) Kenner, Witham, J. Chem. Soc. 97, 1963 (1910). (83) Britton (to Dow Chem. Co.), U.S. 1,878,463, Sept. 20, 1932; Cent. 1933, I 311. (84) Scottish Dyes, Ltd. & Bangham & Thomas, Brit. 308,231, April 18, 1929; Cent. 1929, II 1348. (85) Booth, Elsey, Burchfield, J. Chem. Soc. 57, 2068 (1935). (86) I.G., French 798,727, May 25, 1936; Cent. 1936, II 3360. (87) Wahl, Bull. soc. chim. (5) 4, 344-349 (1937); Compt. rend. 202, 2161-2163 (1936). (88) Thomson, Stevens, J. Chem. Soc. 1932, 62. (89) Jackson, Field, Ber. 11, 904-905 (1878). (90) Oxford, Robinson, J. Chem. Soc. 1927, 2241. (91) Kharasch, Margolis, White, Mayo, J. Am. Chem. Soc. 59, 1405 (1937). (92) Sampey,

Kharasch, Margolis, White, Mayo, J. Am. Chem. Soc. 59, 1405 (1937).
 Sampey, Fawcett, Morehead, J. Am. Chem. Soc. 62, 1839-1840 (1940).
 Pajeau, Compt. rend. 202, 1796 (1936).
 Yayama, Sahay, J. Indian Chem. Soc. 11, 293-294 (1934).
 Chem. 46, 26-27 (1892).
 Allen, Bridgess, J. Am. Chem. Soc. 49, 1846 (1927).
 Allen, Normington, Wilson, Can. J. Research 11, 387 (1934).
 Mayer, Freund, Ber. 55, 2052-2053 (1922).
 Mayer, Muller, Ber. 60, 2281 (1927).
 Mayer (to I.G.), Ger. 515,110, Jan. 15, 1931; Cent. 1931, II 908.

(101) Houben, Fischer, Ber. 64, 2648-2649 (1931). (102) Scholl, Meyer, Keller, Ann. 513, 298 (1934). (103) Conant, Lutz, J. Am. Chem. Soc. 47, 891 (1925). (104) Heller, Ber. 46, 1500-1501 (1913). (105) de Diesbach, Dobbelmann, Helv. Chim. Acta 14, 374 (1931). (106) A.G.F.A., Ger. 267,271, Nov. 12, 1913; Cent 1913, II 2014. (107) Heller, Schülke, Ber. 41, 3634-3635 (1908). (108) Dougherty, Gleason, J. Am. Chem. Soc. 52, 1025, 1027 (1930). (109) Reilly, Drumm, J. Chem. Soc. 1927, 2814. (110) Keimatsu, Hirano, Yoshimi, J. Pharm. Soc. Japan 59, 95-98 (1930); Cent. 1930, II 2384.

(111) de Diesbach, Schmidt, Helv. Chim. Acta 7, 650 (1924).
(112) Stephen, Short, Gladding, J. Chem. Soc. 117, 513 (1920).
(113) Dieterle, Eschenbach, Ger. 537,610, Nov. 6, 1931; Cent.
1932, I 1156-1157.
(114) Dieterle, Eschenbach, Arch. Pharm. 265, 195 (1927).
(115) Ray, J. Chem. Soc. 119, 1963-1964 (1921).
(116) Gilman, Zoellner, Selby, J. Am. Chem. Soc. 55, 1255 (1933).
(117) Spencer, Price, J. Chem. Soc. 97, 388 (1910).
(118) I.G., French 736, 428, Nov.
23, 1932; Cent. 1933, II 2193.
(119) I.G., Austrian 148,984, Mar. 25, 1937; Cent. 1937, II 1082.

(120) Morton, Le Fevre, Hechenbleikner, J. Am. Chem. Soc. 58, 755 (1936).

(121) Morton, Stevens, J. Am. Chem. Soc. 53, 4032 (1931). (122) Imperial Chem. Ind., Ltd. & Coffey, Brit. 325,933, March 27, 1930; Cent. 1930, II 2695: French 687,316, Aug. 7, 1930; Cent. 1930, II 3851. (123) I.G., Brit. 308,220, May 15, 1929; Cent. 1930, II 1772. (124) F. Raschig Co., French 698,341, Jan. 29, 1931; Cent. 1931, II 1491. (125) Britton (to Dow Chem. Co.), U.S. 1,959,283, May 15, 1934; Cent. 1934, II 1688. (126) Meyer, Bergius, Ber. 47, 3159 (1914). (127) Meharg, Allen, J. Am. Chem. Soc. 54, 2920-2922 (1932). (128) Ohse (to Chem. Fabrik von Heyden), Ger. 497,570, May 8, 1930; Cent. 1930, II 622. (129) Williams (to Dow Chem. Co.), U.S. 1,775,360, Sept. 9, 1930; Cent. 1931, II 1195. (130) Federal Phosphorus Co., Brit. 370,774, May 5, 1932; Cent. 1932, II 1237.

(131) Booth (to Swann Research, Inc.), U.S. 1,954,469, April 10, 1934; Cent. 1934, II 1846. (132) Bergstrom, Wright, Chandler, Gilkey, J. Org. Chem. 1, 174-175 (1936). (133) Holleman, van den Arend, Rec. trav. chim. 28, 418-423, 496 (1909). (134) Goldschmidt, Hönig, Ber. 19, 2438-2440 (1886). (135) Gattermann, Kaiser, Ber. 18, 2600 (1885). (136) Hodgson, Anderson, J. Chem. Soc. 125, 2195-2196 (1924). (137) Cohen, McCandlish, J. Chem. Soc. 87, 1265-1266 (1905). (138) Kenner, Tod, Witham, J. Chem. Soc. 127, 12348 (1925). (139) Borsche, Fiedler,

Ber. 46, 2118-2121 (1913). (140) Borsche, Feske, Ber. 60, 159 (1927).

(141) Wynne, J. Chem. Soc. 61, 1078-1082 (1892). (142) Wynne, Bruce, J. Chem. Soc. 78,

Beil. II - 250

61.5°

3:8290 ETHYL β-CHLOROPROPIONATE

at 15 mm. (7)

760-762, 772-773 (1898). (143) Vogt, Henninger, Ann. 165, 363-365 (1873). (144) DeRoode, Am. Chem. J. 13, 225 (1891). (145) Wahl, Brit. 159,837, March 31, 1921; French 524,587, Sept. 6, 1921; Swiss 96,185, Sept. 16, 1932; Ger. 376,634, June 5, 1923; Cent. 1921, IV 124. (146) Huntress, Carten, J. Am. Chem. Soc. 62, 512-513 (1940). (147) Shreve, Marsel, Ind. Eng. Chem. 38, 254-261 (1946).

C₅H₉O₂Cl

CICH₂.CH₂.CO.O.C₂H₅
$$\Pi_{1}$$
-(111) Π_{2} -(227)

B.P. 162–163° at 765 mm. (1) D_{4}^{20} = 1.1086 (5) n_{D}^{20} = 1.42537 (5) 162-163° at 760 mm. (3) 162° (4) D_{4}^{15} = 1.1141 (2) n_{D}^{15} = 1.4284 (2) 161.4–161.8° at 758 mm. (5) 161° (6) 80° at 29 mm. (2)

[For prepn. of \tilde{C} from β -chloropropionic acid (3:0460) by esterification with EtOH + HCl (59% yield (6)) (4) or H₂SO₄ (1) see indicated refs.; from β -chloropropionyl chloride (3:5690) + EtOH see (1); from acrylic acid chloride (3:7153) + EtOH see (4) (7); from ethyl acrylate (1:3071) + HCl see (2); from acrylonitrile + HCl to β -chloropropionitrile followed by reactn. with EtOH see (8); from ethyl lactate (1:3303) + SOCl₂ + pyridine (95% yield (9)) see (9).]

C with 20% alc. NaOH at room temp. (10) or htd. at 95-100° with 10 pts. conc. H_2SO_4 (11) gives (90% yield (10)) ethyl acrylate (1:3071), b.p. 101°.

Č refluxed with NaI in acetone gives (yield: 81% (12), 75-80% (13)) ethyl β -iodopropionate, b.p. $183-185^{\circ}$ at 760 mm. (13). [For study of rate of reactn. with KI in acetone see (6).] [Note also that β -iodopropionic acid with alc. HCl (as in its esterification) gives some ethyl β -chloropropionate (14).]

 \bar{C} on catalytic hydrogenation as specified (7) takes up only a little H_2 [dif. from ethyl α -chloropropionate which gives quant. ethyl propionate].

[For reactns. of C with CH₃MgI (15), C₂H₅MgBr (16), and other RMgX cpds. (17) see indicated refs.]

3:8290 (1) Henry, Compt. rend. 100, 115 (1885); J. prakt. Chem. (2) 31, 127 (1885). (2) Moureu, Murat, Tampier, Ann. chim. (9) 15, 239 (1921). (3) Robinson, Watt, J. Chem. Soc. 1934, 1539. (4) Moureu, Ann. chim. (7) 2, 171-172 (1894). (5) Karvonen, Ann. Acad. Sci. Fennicae A-10, No. 4, 31; Cent. 1919, III 808. (6) Conant, Kirner, J. Am. Chem. Soc. 46, 243, 249 (1924). (7) Paal, Müller-Lobecle, Ber. 64, 2145, 2147 (1931). (8) I.G., Brit. 352,802, Aug. 6, 1931; Cent. 1931, II 2658. (9) Darsen, Compt. rend. 152, 1601 (1911). (10) Rohn, Haas, Ger. 546,141, March 12, 1932; Cent. 1933, I 2642.

Brit. 351,518, July 23, 1931; Cent. 1931, II 1923. (12) Baker, J. Chem. Soc. 1933, 216.
 Borsche, Ann. 526, 16 (1936). (14) Flürscheim, J. prakt. Chem. (2) 68, 346 (1903). (15) Bennett, Philip, J. Chem. Soc. 1928, 1937-1942. (16) Moureu, Barrett, Bull. soc. chim. (4) 29, 994-996 (1921). (17) Weizmann, Bergmann, J. Chem. Soc. 1936, 401-402. (18) Schjanberg, Z. physik. Chem. A-173, 231 (1935).

3:8295-3:8305

 $\begin{array}{ll} \textbf{TE} & \textbf{C}_{5}\textbf{H}_{9}\textbf{O}_{2}\textbf{C} \textbf{I} \\ \textbf{n-C}_{3}\textbf{H}_{7}\textbf{O}.\textbf{CO}.\textbf{CH}_{2}\textbf{C} \textbf{I} \end{array}$

Beil. II - 198 II₁-(89) II₂---

B.P. 162.9° (1) $D_4^{20} = 1.1033$ (6) $n_D^{20} = 1.4261$ (6) $162.8-163.2^{\circ}$ (2) 1.1050 (2) 1.4256 (2) $162.3-162.5^{\circ}$ at 777.5 mm. (3)

162.3-162.5° at 777.5 mm. (3) 161-162° at 765 mm. (4) 161° at 740 mm. (5)

3:8295 (1) Cheng, Z. physik. Chem. B-24, 307 (1934). (2) Drushel, Hill, Am. J. Sci. (4) 30, 72-78 (1910); C.A. 4, 2438 (1910). (3) Schiff, Z. physik. Chem. 1, 378 (1887). (4) Henry, Compt. rend. 100, 115 (1885). (5) Schreiner, Ann. 197, 8 (1879). (6) Schjanberg, Z. physik. Chem. A-172, 228 (1935).

3:8300 2,3-DICHLOROHEXANE Cl Cl
$$C_6H_{12}Cl_2$$
 Beil. I - 144 I_1 — $CH_3.CH_2.CH_2$ — C — C — CH_3 I_4 — I_{2} —(109) H H D₁₁ = 1.0527 (1)

[For prepn. of C from 2,3-epoxyhexane with PCl₅ see (1) (2).]

Č is not attacked by solid KOH but with alc. KOH yields (1) a chlorohexane, b.p. 122° (1).

3:8300 (1) Henry, Bull. soc. chim. (2) 41, 363 (1884). (2) Henry, Compt. rend. 97, 262 (1883).

3: 8305
$$d$$
, l - β -METHYL- n -CAPROYL CHLORIDE $C_7H_{13}OCl$ Beil. II — (sec.-Amyl-(2)-acetyl chloride) CH₃.CH₂.CH₂.CH₂.CH₂.CH₂.CH₂.CH₃. Cl II₂-(298)

B.P.
$$163-164^{\circ}$$
 at 751 mm. (1) $D_4^{20} = 0.967$ (1) $159-161^{\circ}$ at 733 mm. (2)

[For prepn. of C from methyl-n-propyl-acetic acid [Beil. II₁-(146)] (1) (2) with PCl₃ (1) or SOCl₂ (87% yield (2)) see indic. refs.]

[\bar{C} with n-propyl zinc iodide in toluene gives (70% yield (2)) 6-methylnonanone-4, b.p. 192-193° at 715 mm. (2).]

C on hydrolysis yields (1) β-methyl-n-caproic acid, [Beil. II₁-(146)] (1) (2), b.p. 215-216° (3), 212-213° at 755 mm. (1), 207-209° u.c. at 728 mm. (2).

 \oplus β -Methyl-n-caproamide: m.p. 97° (1), 99° (4). [From \tilde{C} + excess conc. aq. NH₄OH (1).]

3:8305 (1) Dewael, Weckering, Bull. soc. chim. Belg. 33, 496-497 (1924). (2) Karrer, Shibata, Wettstein, Jacubowicz, Helv. Chim. Acta 13, 1302-1303 (1930). (3) Ciamician, Silber, Ber. 46, 3080 (1913). (4) Bayer & Co., Ger. 228,667, Nov. 15, 1910; Cent. 1910, II 1789.

3:8307-3:8315

3: 8307 ETHYL
$$d,l-\alpha$$
-CHLORO- n -BUTYRATE $C_6H_{11}O_2Cl$ Beil. II-277 CH₃.CH₂.CH.COOC₂H₅ II₁— II₂— Cl

B.P. 163-164° at 760 mm. (1) $D_-^{13} = 1.056$ (1) $n_-^{-} = 1.42430$ (1) $D_-^{17.5} = 1.063$ (2)

[For prepn. of \bar{C} from α -chloro-n-butyronitrile with EtOH (2) or with EtOH + HCl (1) see indic. refs.; for formn. of \bar{C} from ethyl n-butyrate (1:3127) with SO₂Cl₂ + dibenzoyl peroxide in CCl₄ (10% \bar{C} + 50% β - and 40% γ -isomers (3)) see (3).]

[For use of C in Reformatsky reactn. see (4).]

For the amide corresp. to \bar{C} see α -chloro-n-butyric acid (3:9130).

3:8367 (1) Henry, Bull. acad. roy. Belg. (3) **35,** 507-520 (1898); Cent. **1898**, I 273. **(2)** Markownikow, Ann. **153**, 241 (1870). **(3)** Price, Schwarcz, J. Am. Chem. Soc. **62**, 2854-2895 (1940). **(4)** Nieuwland, Daly, J. Am. Chem. Soc. **53**, 1842-1846 (1931).

3:8310 γ -CHLORO-n-PROPYL ACETATE $C_5H_9O_2Cl$ Beil. II — (1-Acetoxy-3-chloropropane; $ClCH_2.CH_2.CH_2.O.CO.CH_3$ II₁-(58) VI - 1281 II₂-(139)

B.P.
$$165-166^{\circ}$$
 (1) $D_4^{21} = 1.1105$ (7) $n_D^{21} = 1.431$ (7) $168-173^{\circ}$ (2) $163-165^{\circ}$ at 747 mm. (3) $160-166^{\circ}$ (4) $88-90^{\circ}$ at 22 mm. (5) 66° at 14 mm. (6) $62-63^{\circ}$ at 10 mm. (7)

[For prepn. of \tilde{C} from trimethylene chlorohydrin (3:8285) + AcCl see (7) (2) (1); from trimethylene dichloride (3:5450) + AgOAc see (5); from trimethylene glycol (1:6490) + Ac2O + S₂Cl₂ (68% yield) see (6); from trimethylene chlorobromide + KOAc + AcOH see (3) (8).]

 \bar{C} htd. with KOH + 8% aq. at 100-110° yields (1) (7) trimethylene oxide [Beil. XVII-6], b.p. 48.2° at 761 mm., $D_4^{18}=0.9038, n_D^{20}=1.392$ (7).

3:8310 (1) Bogert, Slocum, J. Am. Chem. Soc. 46, 766 (1924). (2) Blicke, Blake, J. Am. Chem. Soc. 53, 1018 (1931). (3) Henry, Bull. acad. roy. Belg. (3) 32, 261 (1896). (4) Derick, Bissel, J. Am. Chem. Soc. 38, 2483 (1916). (5) Bermejo, Gomez Aranda, Anales soc. españ. fie. quím. 27, 798-800 (1929); Cent. 1930, I 2382. (6) Bennett, Heathcoat, J. Chem. Soc. 1929, 271. (7) Lespieau, Bull. soc. chim. (5) 7, 254 (1940). (8) Henry, Bull. acad. roy. Belg. 1906, 738, Note.

[For prepn. of \tilde{C} from 3,4-dimethylhexanediol-3,4 [Beil. I-492, I₁-(256), I₂-(558)] by saturation with HCl gas in presence of P₂O₅ see (1).]

3:8315 (1) Frumins, Bull. acad. roy. Belg. 1909, 1151-1157; Cent. 1910, I 1001; C.A. 5, 1096 (1911).

3: 8325 ETHYL
$$\beta$$
-CHLOROISOCROTONATE $C_6H_9O_2Cl$ Beil. II - 417
 CH_3-C-Cl II₁-(190)
 $C_7H_5OOC-C-H$ II₂-(397)

B.P. (contd.)
165.6-167.2° (1) 60° at 15 mm. (7)
$$D_4^{20} = 1.088$$
 (8)
164° (13) 56-57° at 13 mm. (8) (9) 1.087 (7)
161.4° (2) 54° at 14 mm. (10) 1.086 (11)
159-161° (3) 50° at 10 mm. (11) $n_D^{18.7} = 1.4538$ (7)
157-158° at 740 mm. (4) $D_4^{18.7} = 1.0924$ (3)
155-156° (5) $n_D^{17.7} = 1.45423$ (3)
154-157° (6) $D_4^{17.7} = 1.0920$ (11)

[See also ethyl β -chlorocrotonate (3:8538).]

Note the lack of accord regarding the b.p. of \bar{C} especially at ordinary pressures; this is presumably attributable to more or less contamination with the stereoisomeric ester (3:8538).

[For prepn. of \tilde{C} from β -chloroisocrotonic acid (3:1300) in EtOH with dry HCl gas (yields: 100% (4), 65% (12)) (2) (5) or a little conc. H₂SO₄ (yield 65% (6)) (8) (11) see indic. refs.]

[For prepn. of \bar{C} from ethyl acetoacetate (1:1710) with PCl_5 in C_6H_6 followed by refluxing with a little I_2 see {13} (1); note, however, that this method has subsequently (6) been regarded as unsatisfactory for the prepn. of pure \bar{C} although it suffices to give (40–50% yields (14)) a mixt. of \bar{C} with its stereoisomer (3:8538) which for many purposes is adequate.]

[\bar{C} (2 moles) with K₂S (1½ moles) in 5 vols. abs. EtOH refluxed for 5 hrs. (note that the stereoisomer (3:8538) requires 16) gives (53% yield (14)) diethyl β , β -thiodicrotonate, S(—C(CH₃)=CH.COOC₂H₅)₂, b.p. 150-153° at 4 mm. (14), accompanied by some ethyl β -mercaptocrotonate (see below).]

 $[\bar{C}]$ with alc. NaSH as directed gives (55-60% yield crude prod. (15)) ethyl β -mercaptocrotonate; note that this prod. is apparently a mixt. of the two geom. stereoisomeric thioenols together with the keto form, viz., ethyl thioacetoacetate, CH₃.CS.CH₂.COOC₂H₅; for details see (15); note also that ethyl β -chlorocrotonate (3:8538) by the same treatment gives the same result so that a mixt. of the esters can be employed as initial material.]

 $[\bar{C}]$ with alkali derivs. of alcohols, phenols, mercaptans, etc., splits out alkali halide yielding corresp. ethyl β -substituted crotonates: e.g., \bar{C} with NaOEt in ether gives (5) ethyl β -ethoxycrotonate [Beil. III-373, III₁-(135), III₂-(254)], m.p. 29.5° (5); \bar{C} with Na allylate gives (6) ethyl β -allyloxycrotonate; \bar{C} with Na cinnamylate gives (6) ethyl β -cinnamyloxycrotonate; \bar{C} with Na phenolate gives (16) ethyl β -phenoxycrotonate, b.p. 152° at 18 mm. (16); note that in the three preceding cases either \bar{C} or its stereoisomer (3:8538) yields the same result.]

[Č with Na salt of ethyl mercaptan gives (12) ethyl β -ethylmercaptoisocrotonate, b.p. 127–129° at 16 mm. (12); Č with Na salt of benzyl mercaptan gives (75% yield (12)) a mixt. of ethyl β -benzylmercaptocrotonate, m.p. 64.5° (12), and ethyl β -benzylmercaptoisocrotonate (consts. not given).]

[Č with diethyl sodiomalonate gives (9) cf. (17) cis diethyl α-carbethoxy-β-methylglutaconate, (C₂H₅OOC)₂CH.C(CH₃)=CH.COOC₂H₅ [Beil. II-853], b.p. 164-165° at 12 mm.,

 $D_4^{20} = 1.0884$, $n_D^{20} = 1.4579$ (9); cf. behavior of stereoisomeric ethyl β -chlorocrotonate (3:8538).

 $\ddot{\mathbf{C}}$ with hydrazine hydrate in abs. alc. splits out HCl and EtOH with consequent ring closure yielding (18) 5-methylpyrazolone-3 [Beil. XXIV-19, XXIV₁-(189)], m.p. 215° (18); note that same prod. is also obtd. from methyl β -chloroisocrotonate (3:8028).

Č (1 mole) with phenylhydrazine (1 mole) at 100° for 6–8 hrs. gives by ring closure mainly (4) 3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-20, XXIV₁-(190)], pr. from aq., m.p. 127°, accompanied by small amts. of 4-benzeneazo-3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-328, XXIV₁-(319)], m.p. 155–156°, and 3,3'-dimethyl-1,1'-diphenyl-bis pyrazolone-5,5' [Beil. XXVI-484], dec. at high temp. without melting. — Note that with excess phenylhydrazine (2–4 moles) only traces of the 3-methyl-1-phenylpyrazolone-5 are formed while the amt. of the other two (less desirable) prods. is greatly increased (4).

3:8325 (1) Kohlrausch, Pongratz, Z. physik. Chem. 27, 193 (1934). (2) Geuther, Frolich, Zeit. für Chemie 1869, 273. (3) Eisenlohr, Ber. 44, 3208 (1911). (4) Autenrieth, Ber. 29, 1654-1664 (1896). (5) Koll, Ann. 249, 323-324 (1888). (6) Lauer, Kilburn, J. Am. Chem. Soc. 59, 2587 (1937). (7) von Auwers, Ber. 56, 724 (1923). (8) von Auwers, Ber. 45, 2807-2808 (1912). (9) Gidvani, Kon, Wright, J. Chem. Soc. 1932, 1034-1035. (10) Errera, Lepingle, Bull. sci. acad. roy. Belg. (5) 11, 150-153 (1925); Cent. 1925, II 897; C.A. 19, 3057 (1925).

(11) von Auwers, Ann. 432, 62 (1923). (12) Scheibler, Voss, Ber. 53, 381-382, 387-388 (1920). (13) Thomas-Mamert, Bull. soc. chm. (3) 13, 70-71 (1895). (14) Scheibler, Bube, Ber. 48, 1449-1451 (1915). (15) Scheibler, Topouzada, Schulze, J. prakt. Chem. (2) 124, 7-12 (1930). (16) Ruhemann, Wragg, J. Chem. Soc. 79, 1190 (1901). (17) Fichter, Schwab, Ann. 348, 251-256 (1906). (18) Freri, Gazz. chim. ital. 66, 25 (1936); Cent. 1936, II 621; C.A. 30, 6387 (1936).

72° at 13 mm. (2) 62–63° at 14 mm. (3)

[For prepn. of \bar{C} from methyl β -chloropropionate (3:5765) (3) or from ethyl β -chloropropionate (3:8290) (1) (53% yield (2)) with MeMgBr see indic. refs.]

Č with fumg. HCl at room temp. yields (1) 2,4-dichloro-2-methylbutane (3:8105).

 \bar{C} mixed with 3 pts. dry powdered KOH and htd. at 130-180° gives (43% yield (2)) by loss of HCl and ring closure 2,4-epoxy-2-methylbutane (α,α -dimethyltrimethylene oxide), b.p. 71° at 750 mm., $D_4^{20} = 0.8279$ (2).

 $\ddot{\mathbf{C}}$ with specially dried K phthalimide htd. in a s.t. 8 hrs. at 169°, finally 3½ hrs. at 218°, yields (3) (by metathesis and loss of H₂O) N-(2-methylbuten-2-yl-4)phthalimide, m.p. 99° (3).

3:8335 (1) Henry, Bull. soc. chim. Belg. 20, 152-156 (1906); Cent. 1906, II 1178; Compt. rend. 142, 133 (1906). (2) Bennett, Philip, J. Chem. Soc. 1928, 1938. (3) Späth, Spitzy, Ber. 58, 2276-2277 (1925).

3: 8340 3-CHLORO-2-METHYLPROPEN-2-OL-1 CH₃ C₄H₇OCl Beil. I-448
$$(\gamma$$
-Chloro- β -methyl-allyl alcohol)

CH₂—C=CH
OH
Cl

High-boilg. (cis?)

B.P.
167-167.5° (1)
166-168° cor. (2)
163-164° (3)

Low-boilg. (trans?)

B.P.
160-162° cor. (2)

 $D_4^{25} = 1.1262$ (2)
 $D_4^{20} = 1.1243$ (1)
 $D_6^{20} = 1.4677$ (1)

 $D_7^{25} = 1.1290$ (2)
 $D_7^{25} = 1.1290$ (2)
 $D_7^{25} = 1.4737$ (2)

[For prepn. of \bar{C} (mixt. of both forms) from 1,2,3-trichloro-2-methylpropane (3:5885) in 84% yield by hydrolysis with excess 5% aq. NaOH see (2) (4); for prepn. of \bar{C} from 1,3-dichloro-2-methylpropene-1 (3:5590) by hydrolysis with aq. alk. (4), with aq. Na₂CO₃ (3), or aq. + CaCO₃ (1) see indic. refs. Note that by virtue of allylic transposition 1,3-dichloro-2-methylpropene-1 (3:5590) may frequently yield derivatives of its synionic isomer, 1,1-dichloro-2-methylpropene-2 (3:7480).]

 \bar{C} with excess AcOH + conc. HCl gives (60% yield (2)) 1-chloro-2-methylpropen-2-yl-1 acetate, b.p. $167-174^{\circ}$ at 748 mm. (2), $176-178^{\circ}$ at 784 mm. (1).

 \bar{C} on treatment with acids as specified (5) gives 3-chloro-2-methylpropanal-1 (β -chloro-isobutyraldehyde) (3:9112).

- ① 1-Chloro-2-methylpropen-2-yl-1 3,5-dinitrobenzoate: from high-boilg. form of C;
 m.p. 63.8-64.5° (2); from low-boilg. form of C; m.p. 94.4-95.8° (2).
- 1-Chloro-2-methylpropen-2-yl-1 N-phenylcarbamate: from high-boilg. form of C; m.p. 81-82° (1).

3:8340 (1) Tishchenko. J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4223; C.A. 33, 4190 (1939). (2) Rogers, Nelson, J. Am. Chem. Soc. 58, 1030 (1936). (3) Pogorshelski, J. Russ. Phys.-Chem. Soc. 36, 1129-1184 (1904); Cent. 1905, I 668. (4) Nelson, Rogers (to Purdue Research Foundation), U.S. 2,061,519, Nov. 17, 1936; Cent. 1937, I 2682; C.A. 31, 711 (1937). (5) N. V. de Bataafsche Petroleum Maatschappij, French 763,286. Apr. 26, 1934; Cent. 1934, II 1531.

B.P. 167-168° (1)
$$D_{16}^{16} = 0.8923$$
 (2) $n_{D}^{16} = 1.4424$ (2)

Some doubt exists as to whether this material is in fact C, 2-chloro-octene-1, or a mixture of both.

[For prepn. of C from octanone-2 (n-hexyl-methyl ketone) (1:5490) with PCl₅ followed by distillation (1) or treatment with alkali (2) see indic. refs.]

Č with alc. KOH yields (1) octyne-1 (n-hexylacetylene) (1:8105) or octyne-2 (n-amylmethyl-acetylene) (1:8120).

[\tilde{C} on protracted (16 days') standing with benzoyl hydrogen peroxide in ether yields (2) 2-chloro-2,3-epoxyoctane, b.p. 81-82° at 21 mm., $D_4^{16} = 0.9609$, $n_D^- = 1.4359$ (2).]

3:8345 (1) Béhal, Ann. chim. (6) 15, 277-278 (1888). (2) Prileshaiev, Ber. 59, 197-198 (1926).

3:8346 2-CHLORO-OCTENE-1
$$CH_3$$
— $(CH_2)_{\delta}$ — C = CH_2 $C_8H_{18}Cl$ Beil. I-221 I_1 — I_2 —
B.P. 168-170° (1) $D_0^0 = 0.9274$ (2) 167-168° (2)

[For prepn. of \tilde{C} from (β -chloro- β -n-hexylvinyl)arsonic acid by htg. at 175° (1) or from octanone-2 (1:5490) with PCl₅ (2) see indic. refs.]

[Note that the structure of \tilde{C} has not been unequivocally demonstrated, and it may be 2-chloro-octene-2 (3:8345).]

3:8346 (1) Fusco, Cottignoli, Farm. ital. 11, 89-91 (1943); Cent. 1943, II 2285; C.A. 38, 6054 (1944). (2) Béhal, Ann. chim. (6) 15, 277-278 (1888).

B.P. 167.5° at 760 mm. (2)
$$D_{20}^{20} = 1.062$$
 (2) $n_{\rm D}^{19} = 1.4251$ (1) $D_{15}^{15} = 1.055$ (1)

[For prepn. from butene-2 + chloroacetic ac. (3:1370) + $ZnCl_2$ see (1).] [For study of insecticidal action of vapor of \bar{C} see (2).]

3:8350 (1) Aldoschin, J. Gen. Chem. (U.S.S.R.) 8, 1385-1389 (1938); Cent. 1939, II 2223; C.A. 33, 4194 (1939). (2) Roark, Cotton, Ind. Eng. Chem. 20, 512-514 (1928).

B.P. 167-168° at 767 mm. (1)
$$D_4^{20} = 0.9677$$
 (1)

[For prepn. of \bar{C} from γ -methyl-n-caproic acid (1:1136) with PCl₃ see (1).] [The dextrorotatory isomer of \bar{C} , b.p. 80° at 50 mm. (2), has been prepared from the dextrorotatory acid + SOCl₂.]

 $\ddot{\mathbf{C}}$ on hydrolysis yields γ -methyl-n-caproic acid (1:1136) q.v. (for the amide, anilide, and other derivatives corresponding to $\ddot{\mathbf{C}}$ see 1:1136).

3:8355 (1) Dewael, Weckering, Bull. soc. chim. Belg. 33, 501-502 (1924). (2) Levene, Rothen, Marker, J. Biol. Chem. 115, 261-262 (1936).

3:8360 d,l-1,4-DICHLORO-2-METHYLBUTANE
$$C_5H_{10}Cl_2$$
 Beil. I — Cl Cl I_1 — I_2 — CH_2 — CH_2 — CH_3 CH_3

B.P. 168-169° at 760 mm. (calcd.) (1)
$$D_4^{24.5} = 1.1003$$
 (1) $n_D^{21} = 1.4562$ (1)

[For formn. of \bar{C} from 2-methylbutane (isopentane) (1:8500) with Cl_2 (together with 2,3-dichloro-2-methylbutane (3:7975) and 2,4-dichloro-2-methylbutane (3:8105)) see (3); for formn. of \bar{C} (together with other products) from dextrorotatory 1-chloro-2-methylbutane (act.-amyl chloride) by chlorination with SO_2Cl_2 + benzoyl peroxide see (1); for formn. of \bar{C} (together with other products) from 4-chloro-2-methylbutane (isoamyl chloride) (3:7365) + Cl_2 in light see (2).] [The dextrorotatory form of \bar{C} has been obtd. (4) from N_1N' -dibenzoyl-2-methyltetramethylenediamine with PCl_5 .]

C on boilg. with AgOAc gives (3) a diacetate which upon saponification and subsequent oxidn. gives (3) methylsuccinic acid [Beil. II-637; II₁-(274)], m.p. 112°.

3:8360 (1) Brown, Kharasch, Chao, J. Am. Chem. Soc. 62, 3437-3439 (1940). (2) Perkin, J. Soc. Chem. Ind. 31, 616-624 (1912); Cent. 1912, II (1912). (3) Davydova, Papkina, Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 1992-1994 (1937); Cent. 1939, I 2397; C.A. 32, 482 (1938). (4) von Braun, Jostes, Ber. 59, 1095-1096 (1926).

3:8365
$$\delta$$
-METHYL- n -CAPROYL CHLORIDE $C_7H_{13}OCl$ Beil. II - 342 (Isoheptanoyl chloride; isoamylacetyl CH_3 . CH.CH₂.CH₂.CH₂.CH₂.C II₁— chloride) CH_3 CH_3 CH_4

B.P. 168-169° at 739 mm. (1)

[For prepn. of \bar{C} from isoamylacetic acid [Beil. II-342, II₁-(146)] with PCl₃ (1) or with SOCl₂ (2) see indic. refs.]

[$\bar{\mathbf{C}}$ with McOH yields methyl isoheptanoate, b.p. 166-167.5° cor. (3); $\bar{\mathbf{C}}$ with EtOH yields ethyl isoheptanoate, b.p. 181.5-182.5° cor. (3), 182.7° cor. at 750 mm. (4); for reactn. of $\bar{\mathbf{C}}$ with benzyl alc., phenylethyl alc., phenylpropyl alc., geraniol, and terpineol to give corresp. esters see (5).]

C on hydrolysis yields isoamylacetic acid (see above), b.p. 216° cor. at 762 mm. (4).

- (4), 102-103° (6).
- D Isoamylacet-anilide: cryst. from ether + pet. ether, m.p. 74-75° (7), 75° (6).
- D Isoamyl acet-p-toluidide: ndls. from dil. alc., m.p. 75° (8).

3:8365 (1) Ponzio, de Gaspari, Gazz. chim. ital. 28, II 277 (1898). (2) Staudinger, Muntwyler, Kupfer, Helv. Chim. Acta 5, 761 (1922). (3) Poetsch, Ann. 218, 68-70 (1883). (4) Levene, Allen, J. Biol. Chem. 27, 442 (1916). (5) Rothstein, Bull. sec. chim. (4) 53, 1106-1107 (1938). (6) Wallach, Ann. 408, 190 (1915). (7) Fournier, Bull. sec. chim. (4) 5, 925 (1909). (8) Fichter, Rosenberger, J. prakt. Chem. (2) 74, 324 (1906).

[For prepn. of \bar{C} from 2-ethylhexanol-1 (1:6248) with SOCl₂ + dimethylaniline see (1).] 3:8376 (1) Weizmann, Bergmann, Haskelberg, Chemistry & Industry 56, 589 (1937).

3: 8373 ETHYL
$$d$$
, l - s -CHLORO- n -BUTYRATE $C_0H_{11}O_2Cl$ Beil. II - 277 CH_3 . CH. CH. CH_2 . COOC₂H₅ II₁-(124) II₂-(253) Cl

B.P. 169.5° (1) $D_4^{20} = 1.0542$ (6) $n_D^{20} = 1.4253$ (2) 1.68-169° at 745.4 mm. (3) 1.4247 (6) 1.4248 (3) 168-169° at 741 mm. (4) 65-65.5° at 15 mm. (5)

[For prepn. of \bar{C} from ethyl *n*-butyrate (1:3127) with SO₂Cl₂ + dibenzoyl peroxide in CCl₄ (50% \bar{C} together with 10% α - and 40% γ -isomers) see (2); from β -chloro-*n*-butyric acid (3:0035) with EtOH + HCl see (4); from β -chloro-*n*-butyronitrile with EtOH + HCl or ethyl crotonate (1:3196) with HCl see (7) (9); from crotonic acid (1:0425) + EtOH + HCl see (3); from crotonyl chloride (3:7693) with EtOH see (8); from ethyl acetoacetate (1:1710) with Zn/Hg + alc. HCl (together with other prods.) see (10).]

 \bar{C} on htg. at 70-80° in s.t. with 9 vols. conc. alc. NH₃ yields (12) (13) (10) β -amino-n-butyramide [Beil. IV-412], sirup (chloroplatinate, pale yel. ndls. from alc., % Pt. 31.78 (10) (12)).

 \tilde{C} on hydrolysis (e.g., with aq. KOH (11)) yields EtOH (1:6130) and crotonic acid (1:0425), m.p. 72°, together with a little β -hydroxy-n-butyric acid.

3:8373 (1) Weidel, Roithner, Monatsh. 17, 188 (1896). (2) Price, Schwarcz, J. Am. Chem. Soc. 62, 2894-2895 (1940). (3) Brühl, Ann. 203, 27-28 (1880). (4) Balbiano, Ber. 10, 1749 (1887). (5) Loven, Johansson, Ber. 48, 1256 (1915). (6) Schjanberg, Z. physik. Chem. A-172, 232 (1935). (7) Henry, Bull. acad. roy Belg. (3) 35, 507-520 (1898); Cent. 1898, II 273. (8) Henry, Bull. acad. roy. Belg. (3) 36, 31-54 (1898); Cent. 1898, II 663. (9) Pinner, Ber. 17, 2008 (1884). (10) Steinkopf, Wolfram, Ann. 430, 141 (1923).

(11) Balbiano, Ber. 11, 348 (1878). (12) Balbiano, Ber. 13, 312 (1880); Gazz. chim. ital. 10, 137 (1880). (13) Scheibler, Magasanik, Ber. 48, 1812 (1915).

3:8375 ISOBUTYL CHLOROACETATE
$$C_0H_{11}O_2Cl$$
 Beil. II - 198 $(CH_3)_2CH.CH_2O.CO.CH_2Cl$ II₁-(89) II_2 —

B.P. 170° at 760 mm. (1) $D_4^{20} = 1.0612$ (2) $n_D^{20} = 1.4255$ (2) $D_4^{15} = 1.0675$ (1)

Colorless liq. with agreeable odor; insol. aq.; sol. alc., ether.

[For prepn. from isobutyl alc. (1:6165) + chloroacetic ac. (3:1370) + conc. H_2SO_4 see (1).]

For study of hydrol. by dil. aq. halogen acids see (3).

3:8375 (1) Steinlen, Bull. acad. roy. Belg. (3) 34, 103 (1897); Cent. 1897, II 659. (2) Schjanberg, Z. physik. Chem. A-172, 228 (1935). (3) Drushel, Hill, Am. J. Sci. (4) 30, 72-78 (1910); C.A. 4, 2438 (1910).

3:8378-3:8380

3:8378
$$d$$
, l -2-CHLORO-OCTANE $(n$ -Hexyl-methyl-carbinyl chloride) Cl I_1 — I_2 -(124) I_3 — I_4 -(124) I_4 -(124) I_5 -(124) I_6

[For prepn. of \tilde{C} from octanol-2 (n-hexyl-methyl-carbinol) (1:6245) with HCl (4) (5), with PCl₅ (4) (6), or with SOCl₂ in pyridine (3) see indic. refs.; for prepn. of \tilde{C} from octene-1 + HCl + AlCl₃ see (7).] [The large amt. of work on the opt. act. isomers of \tilde{C} cannot be discussed here; see Beil. I₁-(60), I₂-(124) and subsequent literature incl. (8).]

[For study of rate of reactn. of C with KI in acetone see (2).]

3:8378 (1) Perkin, J. prakt. Chem. (2) 31, 495 (1885). (2) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925). (3) McKenzie, Tudhope, J. Biol. Chem. 62, 554 (1924/25). (4) Bouis, Ann. 92, 398 (1854). (5) Malbot, Bull. soc. chim. (3) 3, 69 (1890). (6) Dachauer, Ann. 166, 270 (1858). (7) Webb (to Carbide and Carbon Chem. Corp.), U.S. 1,560,625, Nov. 10, 1925; Cent. 1926, I 1713; C.A. 20, 51 (1926). (8) Gerrard, J. Chem. Soc. 1944, 85-90; 1945, 106-112.

3:8380 d,l-1,2-DICHLOROHEXANE Cl Cl
$$C_6H_{12}Cl_2$$
 Beil. I - 144 I_1 — $CH_3.CH_2.CH_2.CH_2$ — CH_2 I_1 — I_2 — I_2 — I_2 — I_3 — I_4

[For prepn. of \bar{C} from hexene-1 (1:8255) + Cl_2 see (1).]

3:8380 (1) Brochet, Bull. soc. chim. (3) 7, 569 (1892).

CHAPTER XIX

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 2. D_4^{20} less than 1.1500

(3:8500-3:8999)

3:850	0 <i>d,l-</i> 1-CH	d,l-1-CHLOROPENTANOL-3 (β-Chloroethyl-ethyl-carbinol)			C ₅ H ₁₁ OCl CH ₃ .CH ₂ .CH.CH ₂ .CH ₂		Beil. I — I ₁ -(194)		
	(\$-Chlore								
				ОН]	2-(4	21)
B.P.	173°	at 760 mm.	(1)	$D_4^{25} =$	1.0327	(2)	$n_{\rm D}^{25}=1.4$	466	(3)
	100°	at 60 mm.	(1)		1.035	(3)	1.4	448	(2)
	77.0-77.5°	at 20 mm.	(2)						
	70-71°	at 10 mm.	(3)						

Liquid with weak odor resembling that of allyl alcohol. — Sparingly sol. cold aq.; sol. hot aq.

[For prepn. of C from β-chloropropionaldehyde (3:5576) with EtMgBr see (1) (2) (3).] [C with AcCl yields (1) 3-acetoxy-1-chloropentane, b.p. 89° at 15 mm. (1), while C htd. 4 hrs. at 160-170° with KOAc yields (4) 1-acetoxypentanol-3, b.p. 113-114° at 12 mm. (4); C with BzCl yields (1) 3-benzoxy-1-chloropentane, b.p. 168° at 15 mm. (1), while C htd. to 180° for 10 hrs. with NaOBz + KI yields (4) 1-benzoxypentanol-3, b.p. 181° at 20 mm., 171° at 11 mm. (4).]

[For reactn. of C with alk. Na₃AsO₃ see (3).]

[\bar{C} with COCl₂ yields (5) the corresp. chloroformate, b.p. 95° at 18 mm., which with excess NH₃ gives β -chloroethyl-ethyl-carbinyl carbamate, m.p. 68° (5).]

3:8560 (1) Fourneau, Ramart-Lucas, Bull. soc. chim. (4) 25, 366-368 (1919). (2) Lespieau, Bull. soc. chim. (5) 7, 254-258 (1940); C.A. 34, 5414 (1940). (3) Backer, Bolt, Rec. trav. chim. 54, 70 (1935). (4) Fourneau, Ramart-Lucas, Bull. soc. chim. (4) 27, 554-556 (1920). (5) Puyal, Montagne, Bull. soc. chim. (4) 27, 859 (1920).

3:8510 1-CHLORO-4-ETHYLHEXENE-3
$$C_8H_{15}Cl$$
 Beil. I — Cl $CH_2.CH_3$ I_1 — I_2 —(201) $CH_2.CH_2.CH_3$ I_2 —(201) B.P. 173° (1) $D_2^{40} = 0.9102$ (1) $n_D^{20} = 1.4524$ (1)

[For prepn. of $\tilde{\mathbf{C}}$ from 6-chlorohexanone-3 (γ -chloro-n-propyl ethyl ketone) [Beil. I₁-(355), I₂-(747)] with excess EtMgBr see (1).] $\tilde{\mathbf{C}}$ adds Br₂.

3:8519 (1) De Boosere, Bull. soc. chim. Belg. 32, 35-39 (1923).

Colorless strongly refractive liquid rapidly decomposed in strong light (7).—Č is stronger lachrymator than BzCl (2).

[For prepn. of \bar{C} from furoic acid (1:0475) with PCl₅ (poor yields (3) (4) (6)), with excess PCl₅ in dry CHCl₃ as specified (100% yield (6)) (8), with PCl₅ (77% yield (5)), with SOCl₂ (100% (2), 79% (1), 60% (3)), with SOCl₂ in C₆H₆ (89.5% yield (7)), or with phosgene (9) see indic. refs.

[$\bar{\mathbf{C}}$ with MeOH yields methyl furoate (1:3452), b.p. 180.5° at 750 mm., 76° at 20 mm., $D_4^{20}=1.1792,~n_D^{20}=1.4875$ (10); $\bar{\mathbf{C}}$ with EtOH yields ethyl furoate (1:2082), b.p. 197°, m.p. 34°; $\bar{\mathbf{C}}$ with furfuryl alc. (1:6425) yields (11) furfuryl furoate, dimorphous cryst., m.p. 27.5° and 19 5°, b.p. 122° at 2 mm. (11); for study of reactn. of $\bar{\mathbf{C}}$ with cellulose see (12).]

[C with phenol yields (2) phenyl furoate, m.p. 41 5° (2).]

[\tilde{C} with C_6H_6 + AlCl₃ yields (13) (14) α -furyl phenyl ketone [Beil. XVII-348; XVII₁-(186)], b.p. 282-284°; \tilde{C} with toluene + AlCl₃ gives (80% yield (15)) α -furyl p-tolyl ketone, m.p. 41-42°, b.p. 180-183° at 23 mm. (15).]

[For study of reactn. of C with Cl₂ (16) or Br₂ (17) see indic. refs.]

Č with pyridine in ether or Č with Na or Ag furoate yields (18) furoic anhydride, ndls. from alc., m.p. 73° (18).

 \bar{C} on hydrolysis (rate of reactn. even with boilg. aq. slower than BzCl (6)) yields furoic acid (1:0475), m.p. 133-134° (for the amide, anilide, p-toluidide, and other derivatives corresp. to \bar{C} see 1:0475).

3:8515 (1) Bogert, Stull. J. Am. Chem. Soc. 48, 252 (1925). (2) Baum, Ber. 37, 2951 (1904), (3) Gelissen, van Roon, Rec. trav. chim. 43, 361 (1924). (4) Liès-Bodart, Ann. 100, 327 (1856); Compt. rend. 43, 393 (1856). (5) Reichstein, Morsman, Helv. Chim. Acta 17, 1122 (1934). (6) Frankland, Aston, J. Chem. Soc. 79, 516-517 (1901). (7) Hartmann, Dickey, Ind. Eng. Chem. 24, 151-152 (1932). (8) Chavanne, Compt. rend. 134, 1439 (1902). (9) Meuser (to Dominion Rubber Co.), Canadian 373,516, May 3, 1938; Cent. 1938, II 3609; C.A. 32, 5003 (1938). (10) Price, Chapin, Goldman, Krebs, Shafer, J. Am. Chem. Soc. 63, 1859 (1941).

(11) Zanetti, J. Am. Chem. Soc. 47, 1452-1453 (1925). (12) Kobe, Montonna, J. Am. Chem. Soc. 53, 1889-1891 (1931). (13) Marquis, Bull. soc. chim. (3) 23, 33 (1900); Ann. chim. (8) 4, 276-277 (1905). (14) Gilman, Hewlett, Iowa State Coll. J. Sci. 4, 27-33 (1929); Cent. 1931, II 428; C.A. 24, 1640 (1930). (15) Borsche, Leditsche, Ann. 529, 110 (1937). (16) Hewlett, Iowa State Coll. J. Sci. 6, 439-445 (1932); Cent. 1933, I 942; C.A. 27, 979-980 (1933). (17) Shepard, Winslow, Johnson, J. Am. Chem. Soc. 52, 2083-2090 (1930). (18) Baum, Ber. 34, 2505 (1901).

B.P. 173-175° at 745 mm. (1)
$$D_4^{20} = 1.0259$$
 (1) $n_D^{20} = 1.4489$ (1) 58-59° at 12 mm. (1)

[For prepn. of \bar{C} from allyl chloride (3:7035) with 2-methylpropane (isobutane) + AlCl₃ at -10° (13-15% yield accompanied by 35-40% yield of 5-chloro-2,3-dimethylpentane (3:8153)), or with ter-butyl chloride (3:7045) + AlCl₃ at -10° to -20° , see (1).] [\bar{C} with isobutane + AlCl₃ gives (1) a mixt. of products including ter-butyl chloride (3:7045), 5-chloro-2,3-dimethylpentane (3:8153), etc.]

C with Zn dust + alc. reacts only very slowly under reflux but in s.t. at 120° gives (45% yield (1)) 4,4-dimethylpentene-1 (1:8285), b.p. 71.8° (1).

3:8516 (1) Schmerling, J. Am. Chem. Soc. 67, 1438-1441 (1945).

3:8517 METHYL
$$\gamma$$
-CHLORO- n -BUTYRATE $C_5H_9O_2Cl$ Beil. II -278 CH_2 .CH $_2$.COOCH $_3$ II $_1$ — II_2 —

B.P. 175-176° at 764 mm. (1) $D_-^{14} = 1.1268$ (1) $n_D^{20} = 1.4324$ (4) 173-174° (2) 172-174° at 749 mm. (3) $D_-^{10} = 1.1894$ (2) 102-105° at 58 mm. (3) 90° at 45 mm. (4) 55-56° at 7 mm. (5)

[For prepn. of \bar{C} from γ -chloro-n-butyronitrile with MeOH + HCl (80% yield (4)) (2) see indic. refs.; from γ -methoxy-n-butyric acid (3) by htg. with SOCl₂ for 6 hrs. (86% yield (3)) or by htg. γ -methoxy-n-butyryl chloride (84% yield (3)) see (3); from γ -hydroxy-n-butyronitrile with MeOH + HCl see (5).]

Č on 48-hr. reflux with alc. KOH gives (67.5% yield (3)) γ -butyrolactone (1:5070), b.p. 206°.

[C refluxed 8 hrs. with NaI in acetone gives (3) methyl γ-iodo-n-butyrate, b.p. 80-83° at 11 mm. (3); C with 4 moles MeMgCl in ether yields (4) 5-chloro-2-methylpentanol-2.

Č on hydrolysis by boilg. 6 hrs. with conc. HCl gives (32% yield (3)) γ -chloro-n-butyric acid (3:0020) q.v.

For the amide, anilide, p-toluidide, and other derivatives corresp. to \bar{C} see γ -chloro-n-butyric acid (3:0020).

8:8517 (1) Henry, Bull. acad. roy. Belg. (3) 35, 507-520 (1898); Cent. 1898, II 273. (2) Henry, Bull. soc. chim. (2) 45, 341 (1886). (3) Blicke, Wright, Zienty, J. Am. Chem. Soc. 63, 2489 (1941).
 (4) B. K. Campbell, K. N. Campbell, J. Am. Chem. Soc. 60, 1375 (1938). (5) Palomaa, Ber. 75, 339 (1942).

3:8518 ETHYL d.J-\a-CHLORO-\a-METHYL-n-BUTYRATE C7H12O2Cl Beil. II-306

$$\begin{array}{c} \text{CH}_3 & \textbf{II}_1 \\ \text{CH}_3.\text{CH}_2 & \textbf{COOC}_2\textbf{H}_5 \end{array}$$

B.P. 175° at 747 mm. (1)
$$D_{-}^{14} = 1.069 (1)$$
 $n_{-}^{11} = 1.43683 (1)$

Oily liq.; insol. aq.; sol. alc., ether.

[For prepn. of \tilde{C} from α -chloro- α -methyl-n-butyronitrile with EtOH + HCl see (1).] For the corresp. acid, α -chloro- α -methyl-n-butyric acid see 3:8718.

3:8518 (1) Servais, Rec. trav. chim. 20, 60 (1901).

3:8520 n-HEPTANOYL CHLORIDE
$$CH_3(CH_2)_5$$
. $C=O$ $C_7H_{13}OCl$ Beil. II - 340 (Enanthoyl chloride) II₁...

B.P. F.P.
$$-83.8^{\circ}$$
 (1) $D_4^{25} = 0.95694$ (1) . . 175.0° (2) $174-175^{\circ}$ (3) $D_4^{20} = 0.96170$ (1) 77° at 23 mm. (4) $74-75^{\circ}$ at 19 mm. (5) $D_4^{15} = 0.96645$ (1) $n_D^{15} = 1.43447$ (2) $59-61^{\circ}$ at 11 mm. (6) 0.9669 (2) 56° at 8 mm. (7)

[For prepn. of \bar{C} from heptanoic acid (enanthic acid) (1:1140) with PCl₅ (2) (51% yield (8)), with PCl₅ (75% yield (1)), with PCl₅ + ZnCl₂ (89% yield (8)), or with SOCl₂ (yield 98.5% (6), 80% (8)) see indic. refs.]

[For reactn. of \bar{C} with various higher alcohols see (9), with various acylureas see (10), with vanilylamine see (11) (5), with sodium *n*-heptylate to yield *n*-heptylic anhydride (1:1165), b.p. 258°, see (1) (2).]

[\bar{C} with AlCl₃ + phenol yields (12) 48% o-(n-heptanoyl)phenol, b.p. 172-174° at 20 mm. (13), 155-156° at 10 mm. (12), m.p. 24° (13), +9.8° (12), D_{-}^{24} = 1.0110 (12), $n_{D}^{25.5}$ = 1.5209 (12) (phenylhydrazone, m.p. 91-92° (13), semicarbazone, m.p. 162° (12)), and 41% p-(n-heptanoyl)phenol, m.p. 93-94° (13), 91-91.5° (12), b.p. 220° at 15 mm. (13) (acetate, m.p. 46.5° (12), benzoate, m.p. 96.5-97° (12), 92-93° (13)).]

[\bar{C} on warming with NaN₃ in C₆H₆ yields (14) n-hexyl isocyanate, b.p. 163-164° (14), and/or (15) n-hexylamine HCl + N,N'-di-n-hexylurea, m.p. 58-59° (15).]

[C in ether treated with diazomethane as directed (7) yields 1-chlorooctanone-2, b.p. 91-96° at 10 mm. (7).]

 \tilde{C} on hydrolysis yields *n*-heptanoic (enanthic) acid (1:1140) q.v. (for the amine, anilide, *p*-toluidide, and other derivatives corresp. to \tilde{C} see 1:1140).

3:8520 (1) Deffet, Bull. soc. chim. Belg. 40, 389-394 (1931). (2) Lumsden, J. Chem. Soc. 87, 92-93 (1905). (3) Freundler, Bull. soc. chim. (3) 13, 833 (1895). (4) Krafit, Ber. 19, 2987 (1886). (5) Ford-Moore, Phillips, Rec. trav. chim. 53, 855 (1934). (6) Fierz-David, Kuster, Helv. Chim. Acta 22, 86-89 (1939). (7) Späth, Lorenz, Ber. 74, 599-603 (1941). (8) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (9) Rothstein, Bull. soc. chim. (4) 53, 1106-1107 (1933). (10) Stoughton, J. Org. Chem. 2, 514-521 (1938).

(11) Nelson, J. Am. Chem. Soc. 41, 2124 (1919). (12) Sandulesco, Girard, Bull. soc. chim. (4) 47, 1305-1310 (1930). (13) Coulthard, Marshall, Pyman, J. Chem. Soc. 1936, 280-291.

(14) Schroeter, Ber. 42, 3358 (1909). (15) Nelles, Ber. 65, 1346-1347 (1932).

3:8523 ETHYL
$$\alpha$$
-CHLOROCROTONATE $C_0H_0O_2Cl$ Beil. II - 415 III_1 -(189) III_2 -(395) Cl—C—COOC $_2H_5$ B.P. (contd.)
176-178° (1) 85° at 35 mm. (3) $D_4^{20.1} = 1.1086$ (8) 175-177° (2) 67-68° at 15 mm. (2) $n_D^{20.1} = 1.45303$ (8) 176° at 760 mm. (3) 72° at 14 mm. (8) $D_4^{20} = 1.109$ (8) 176° (4) 61° at 10 mm. (9) 1.102 (9) 175-176° cor. (5) $D_4^{19.8} = 1.1133$ (6) $n_D^{19.8} = 1.45378$ (6) $D_4^{14.3} = 1.1073$ (9)

[See also ethyl α -chloroisocrotonate (3:9368).]

[For prepn. of \tilde{C} from α -chlorocrotonic acid (3:2760) in EtOH with dry HCl gas (4) (5) (8) or with conc. H₂SO₄ (9) see indic. refs.; from α -chloroisocrotonic acid (3:1615) in EtOH with conc. H₂SO₄ at 100° (note isomerization) see (9); from the ethyl ester of the lower-melting (63°) α,β -dichloro-n-butyric acid (3:1375) in EtOH with KCN (1 mole) for 10 min. (75% yield) see (3); from ethyl α,α,β -trichloro-n-butyrate (3:6380) with Zn in moist ether (100% yield) see (10); from α,α,β -trichloro-n-butyraldehyde (butylchloral) (3:5910) (1) as hydrate (3) or cyanohydrin (3) in EtOH with KCN (2 moles) below 15° (85% yield (3)) see indic. refs.; from ethyl α -chloro- α -vinylacetate (2) by isomerization of the double bond with NaOAc/AcOH under reflux 30-40 hrs. see (2).]

[C with Al/Hg in alc. gives (11) crotonic acid (1:0425), m.p. 72°.]

 \bar{C} with diazomethane in dry ether does not react (12); however, upon addn. of a drop of water addition of CH₂N₂ to unsatd. linkage takes place with elimination of HCl (on distillation) yielding (12) ethyl 4-methylpyrazole-3-(5)carboxylate [Beil. XXV-117], m.p. 156-157° (12).

[\overline{C} with piperidine (3 moles) in abs. alc. stood 3 hrs. then neutralized, etc., (13) gives (by reactn. of 1 piperidine with the halogen and addition of a second molecule of piperidine to the unsatd. linkage (or vice versa)) (63% yield (13)) ethyl α,β -di-piperidino-n-butyrate, viscous oil, insol. aq., b.p. 181–183° at 14 mm.]

3:8523 (1) Wallach, Ann. 173, 301 (1874). (2) Rambaud, Bull. soc. chim. (5) 1, 1353-1354 (1934). (3) Chattaway, Irving, J. Chem. Soc. 1929, 1043-1045. (4) Sarnow, Ann. 164, 101 (1872). (5) Perkin, J. Chem. Soc. 65, 424 (1894). (6) Eisenlohr, Ber. 44, 3208 (1911). (7) Roberts, J. Chem. Soc. 1938, 779. (8) von Auwers, Ber. 45, 2806 (1912). (9) von Auwers, Ann. 432, 61 (1923). (10) Michael, Schulthess, J. prakt. Chem. (2) 43, 595 (1891).

(11) Wislicenus, J. prakt. Chem. (2) 54, 59-60 (1896). (12) von Auwers, König, Ann. 496, 31,

41 (1932). (13) Roberts, J. Chem. Soc. 1938, 963-964.

d,l-form

B.P.

62.0-62.5° at 12 mm. (2)

 $D_4^{25} = 1.0431 \quad (1)$

$$D_4^{12} = 1.0529$$
 (2) $n_C^{12} = 1.4495$ (2) $D_4^0 = 1.0675$ (1)

meso-form

B.P.

177.8-178.2° cor. at 751.8 mm. (1) 18.7° (

18.7° (1)
$$D_4^{25} = 1.0459 \quad (1)$$

[For prepn. of \bar{C} (presumably mixt. of both diastereoisomers) from hexadiene-1,5 (biallyl) (1:8045) by shaking with 5 vols. conc. HCl for 120 hrs. at room temp. (57% yield accompanied by 23% 5-chlorohexene-1 (3:7665)) see (1); from 2,5-dimethyltetrahydrofuran [Beil. XVII-14] on protracted treatment with HCl gas + ZnCl₂ (8% yield (3)) see (3).]

[For sepn. of meso- from d_i -form by cooling to -50° see (1).]

[For behavior of \bar{C} on treatment with N/10 ag. alc. KOH see (2).]

3:8525 (1) Cortese, J. Am. Chem. Soc. 52, 1519-1520 (1930). (2) Tishchenko, J. Gen. Chem. (U.S.S.R.) 9, 1380-1388 (1939); C.A. 34, 1611 (1940). (3) Fried, Kleene, J. Am. Chem. Soc. 63, 2691 (1941).

3:8528 ETHYL d,l-
$$\alpha$$
-CHLORO-ISOVALERATE $C_7H_{13}O_2Cl$ Beil. II - 316 (Ethyl α -chloro- β -methyl- n -butyrate) CH_3 — CH — CH — $COOC_2H_5$ II₁— II₂— II₂—

B.P. 177-179° at 756 mm. (1)
$$D_{-}^{13.2} = 1.021$$
 (1) $n_{-}^{11} = 1.42951$ (1)

Oil with odor like peppermint.

[For prepn. of \bar{C} from α -chloro-isovaleric acid (3:0050) with EtOH + H₂SO₄ see (1); for formn. from ethyl α -diazo-isovalerate with HCl see (2).]

3:8528 (1) Servais, Rec. trav. chim. 20, 54 (1901). (2) Curtius, J. prakt. Chem. (2) 125, 254 (1930).

B.P. 178.2-179° at 727 mm. (1)
$$D_4^{20} = 1.0704$$
 (4) $n_D^{20} = 1.4301$ (4) 176.7° (2) 94° at 38 mm. (3)

Colorless mobile liq. with fragrant odor. — Insol. aq., misc. with alc. or ether (5). [For prepn. (97% yield (3)) from n-butyl_alc. (1:6180) + chloroacetic ac. (3:1370) see (3).]

[For study of insecticidal action of vapor of \bar{C} see (6).]

3:8530 (1) Gustus, Stevens, J. Am. Chem. Soc. 55, 384-385 (1933). (2) Cheng, Z. physik. Chem. B-24, 307 (1934). (3) Liston, Dehn, J. Am. Chem. Soc. 60, 1264-1265 (1938). (4) Schjanberg, Z. physik. Chem. A-172, 228 (1935). (5) Gehring, Bull. soc. chim. (2) 46, 147 (1886). (6) Roark, Cotton, Ind. Eng. Chem. 20, 512-514 (1928).

3:8535		oro	CHLORI toluene; luene)	IDE	,	CH ₂	CI	C7	H ₇ Cl	_	- 292 -(151) -(227)
B.P.						F.P.					
179.35	°	at	760 m	m. ((1)	-37.5° (23) D	30 =	1.08977	(24)	
179.3°		at	760 m	m.	(2)	-39.0° (1)	_	1.08815	(28)	
179° c	or.			((3)	-39.2° (24	.)		1.08699		
179°		at	749 m	m.	(4)	-39.7° (7) D	$_{4}^{25} =$	1.09460	(24)	
	179.0°	at	766 m		(5)	-41.2° (25			1.100	(29)	
178.5	179°				(6)	-43.2° (26	i)		$n_{\rm D}^{25}=1$	l.5363	(21)
178.5°		at	754 m	m.	(7)	-48.0° (27	D	$^{20}_{4} =$	1.09943	(24)	
178.0-	-178.5°			((8)				$n_{\mathrm{D}}^{20} = 1$	1. 5391 (3	1) (32)
177.5-	178°	at	755 m	m. (14	2)				$n_{\rm D}^{17.4} = 1$	L.5391	(33)
177.0-	-177.5°	u.c	: .		(9)		D_4^1	5.4 _	$ \begin{array}{l} 1.1138 \\ n_{\rm D}^{154} = 1 \end{array} $	(30)	
175.2-	178.3°			(2	28)						(30)
175-1	75.2°	at	769.3 m	m. (1	(0)		D	$Q_4^{15} =$	1.10426		
174.0-	174.8°			(2	(85			_		1.54124	(24)
173° d	ec.			(1	11)		D) <u> </u>		(34)	
172°		at	730 m	m. (1	2)				$n_{\rm D}^7 = 1$	1.5415	(34)
141°		at	261 m	m. (1	3)						
128°		at	163 m	m. (1	3)		S	ee als	o Note 2.		
118°		at	111 m	m. (1	3)				See also	Note 3.	
106.2°		at	92 m	m. (1	4)					_	
103°		at	76.1 m	m. (1	4)	Note 1.					
96-99	•	at	62 m	m. (1	15)	(34) stated	to dec	compo	se so rea	adily on l	neating
100°		at	59 m		13)	that precise		of bo	oiling poir	at at 760	mm. is
93.3°		at	47.8 m	m. (1	4)	impracticable	e.				
89.9°		at	40 m		4)						
83.6°		at	28.64 m	-	4)						
81.5~8	2°	at	28 m	•	6)	Note 2.					
81.8°		at	26.74 m	•	4)	lowers densit				or of ox	idation
78.2°		at	22.1 m		4)	products rais	ses den	nsity (24).		
73.9°		at	17 m	-	4)						
66-67 °		at	16 m	-	7)						_
70.4-7		at	15 m		1)	Note 3.	Values	of n	for mix	xtures of	C with
64.0-6	4.2°	at	12 m		.8)	benzal (di)c					$n_{\rm D}^{20} =$
66°		at	11 m	-	3)	1.5502) are l	inear	with o	compositi	on (31).	
61-62°		at	11 m	•	9)				•		
63.0°		at	8.2 m	-	4)						
57-58°		at	8 m	-	(0)						
56-58°		at	4-5 m	•	1)						
51-52°		at	4 m	n. (2	2)						

See also Note 1.

[See also benzal (di)chloride (3:6327) and benzotrichloride (3:6540).]

Colorless liq. with penetrating odor; vapor of \bar{C} is irritating to eyes. — Insol. aq., volatile with steam. — Insol. cold conc. H_2SO_4 , but soon reacts evolving HCl. \bar{C} dissolves below -20° in equal vol. pet. ether (35).

Binary systems containing \bar{C} . \bar{C} + toluene: for b.p. and vapor press. relations see (36). - \bar{C} + anisole: for f.p./composition data see (25). - \bar{C} + N-methylaniline: for f.p./composition data see (25).

 \bar{C} with benzaldehyde (1:0195) forms a const.-boilg. mixt., b.p. 177.9° at 760 mm., contg. 50 wt. % \bar{C} (37-a). — \bar{C} with n-butyric acid (1:1035) forms a const.-boilg. mixt., b.p. 160.8° at 760 mm., contg. 35 wt. % \bar{C} (38). — \bar{C} with isobutyric acid (1:1030) forms a const.-boilg. mixt., b.p. 153.5° at 760 mm., contg. 20 wt. % \bar{C} (38). — \bar{C} with n-caproic acid (1:1130) forms a const.-boilg. mixt., b.p. 179.0° at 760 mm., contg. 97 wt. % \bar{C} (38).

 \bar{C} with chloroacetic acid (3:1370) forms a const.-boilg. mixt., b.p. 172° at 760 mm., contg. 72 wt. % \bar{C} (38-b). — \bar{C} with " α -dichlorohydrin" (1,3-dichloropropanol-2) (3:5985) forms a const.-boilg. mixt., b.p. 168.9° at 760 mm., contg. 43 wt. % (2)

PREPARATION OF C

From benzene. The prepn. of \bar{C} from benzene (1:7400) by direct introduction of the —CH₂Cl group (chloromethylation) has been much studied especially in recent years. Chloromethylation may be effected with paraformaldehyde (1:0080), formalin (1:0145), chloromethyl methyl ether (3:7085), or bis-(chloromethyl) ether (3:5245), each in the pres. of ZnCl₂ and frequently also of HCl gas. For a general review of the process of chloromethylation see (39) and subsequent articles (32) (40) (41). Various by-products of the reaction are formed, notably ω, ω' -dichloro-p-xylene (3:2825) and diphenylmethane (1:7120). For study of further chloromethylation of \bar{C} to various poly-(chloromethyl)-benzenes see (41).

[For prepn. of \bar{C} from C_6H_6 (1:7400) by chloromethylation with paraformaldehyde (1:0080) + $ZnCl_2$ + HCl (yields: 80% (42), 73.5% (40), 70% (32), 36% (42)) (39), with formalin (1:0145) + $ZnCl_2$ + HCl (yields: 70.5% (40), 57% (44)) (45) (39) (48), or with chloromethyl methyl ether (3:7085) (40) (43) (46) (47) or bis-(chloromethyl) ether (3:5245) (40) (43) see indic. refs.]

From toluene. [For prepn. of C from toluene (1:7405) by chlorination with SO₂Cl₂ in pres. of dibenzoyl peroxide (75-80% yield (15)), with SO₂Cl₂ (for study of effect of catalysts see (83) (84)) below 130° (49) (50), with SO₂Cl₂ in pres. of acetyl chloride (51), with Cl₂ (52) (53) (for study of catalysts see (85)) in vapor phase (54) (55) (61) in light (56) (57) (58) (59) (60) (62), with Cl₂ in pres. of Pb + PCl₃ (63), with NOCl at 150° (64) or 350° (65), with NCl₃ (66), or with ter-butyl hypochlorite (3:7165) (62% yield (67)) see indic. refs.]

From benzyl alcohol. [For prepn. of \bar{C} from benzyl alcohol (1:6480) with HCl gas (68), with conc. aq. HCl at 60° (70–100% yield (69)) (70) in C_6H_6 (study of kinetics at 60° (71)), with conc. HCl + ZnCl₂ in cold (100% yield (72)), with PCl₃ + ZnCl₂ (60% yield (72)), with SOCl₂ (100% yield (73)) in C_6H_6 (85% yield (72)) or in N,N-dimethylaniline (26% yield (72)), or with AlCl₃ in pet. eth. above 40° (74) see indic. refs.]

From other miscellaneous sources. [For formn. of \bar{C} from benzyl chloroformate (3:9565) on htg. (75) (76), from benzyl benzoate (1:4422) with 5 moles SO_2Cl_2 (77), from dibenzyl ether (1:7640) or other benzyl ethers with PCl_5 (78), from dibenzyl disulfide with excess SO_2Cl_2 in C_6H_6 at 37-39° (79), from benzylamine with NOCl in ether at -15° (80) or with aqua regia (81), or from tetrabenzylhydrazine with conc. HCl on htg. (82) see indic. refs.]

CHEMICAL BEHAVIOR OF C

Determination of C. Many methods for detn. of C have been employed and no complete listing can be given here; the following examples, however, may be helpful. [For detn. of C by boilg, with alc. AgNO₃ and weighing pptd. AgCl see (85) cf. (83); for detn. of C in

C₆H₆ by addn. of excess standard AgNO₃ in isopropyl alc., htg. several hrs., and excess AgNO₃ titrated with standard aq. NaCl see (71); for methods of detn. of C in pres. of benzal (di)chloride (3:6327) or benzatichloride (3:6540) see (86) (87).]

Pyrolysis of C. [C on boiling (34) (88) gradually dec. with evoln. of HCl. — C over glowing Pt wire gives (89) (90) much stilbene (1:7250) accompanied (91) by small amounts of toluene (1:7405) and dibenzyl (1:7149).]

Resinification of \tilde{C} . \tilde{C} under the influence of various catalysts condenses with itself evolving HCl and yielding a material of composition $(C_7H_6)_n$; this material is often (though incorrectly) designated as polymeric \tilde{C} . Because of the indefinite character of the product and the voluminous and diffuse character of the literature, no exhaustive review will here be attempted. However, for extensive reviews of this reaction see (92) (93); for studies of catalysts for this type of reaction see also (94) (95) (96) (97).

Reduction of \bar{C} . $[\bar{C}$ with H_2 in pres. of Pd/BaCO₃ (98) or Ni (99) in alc. KOH loses all its halogen as HCl (use in quant. detn.), but the corresp. org. reduction prod. has not been characterized. — \bar{C} with H_2 in pres. of colloidal Pd in alc. gives (76% yield (100)) toluene (1:7405). — \bar{C} with EtOH + Zn dust on boilg. gives (101) cf. (102) toluene (1:7405) + benzyl ethyl ether (1:7530). — \bar{C} in EtOH/KOH with hydrazine hydrate in pres. of Pd boiled for 1 hr. gives (29% yield (103)) dibenzyl (1:7149); note that in conc. soln. only traces of dibenzyl are formed (103) cf. (104) and the principal prod. is N_1N_2 -dibenzyl-hydrazine [Beil. XV-533, XV₁-(164)] accompanied by some benzyl ethyl ether (1:7530).]

Oxidation of C. C upon oxidn. yields either benzoic acid or benzaldehyde according to circumstances.

[\bar{C} with air at 160° over Ni cat. (105), with O₂ in u.v. light (106), or with CrO₃/H₂SO₄ at 95–98° for 1½ hrs. (note that β -chloroethylbenzene (3:8712) is stable under these conditions (1071) cf. (53), gives benzoic acid (1:0715). — \bar{C} with conc. aq. alk. at 250–280° and at 300–500 lb./sq. in. press. gives (80–90% yield (108)) benzoic acid (1:0715).]

[Č with equimolal amt. SeO₂ refluxed without solv. for 3 hrs. (109), with CrO₂Cl₂ followed by aq. (110), with hot very dil. HNO₃ (111) (112), with hot 14% aq. Pb(NO₃)₂ (111), with boilg. aq. Ca(NO₃)₂ (112), with boilg. aq. Na₂Cr₂O₇ + Na₂CO₃ (113), with boilg. aq. or alc. hexamethylenetetramine (114) (115), with air at 160° over Ni cat. (105), or with steam + air at 360–480° over V₂O₅ on pumice (116) (117) gives benzaldehyde (1:0195); naturally any over-oxidn. gives also some benzoic acid (1:0715).]

[Note that auto-ignition temp. of C on Pt in air at ord. press. is 627° (118).]

Substitution of \bar{C} . Chlorination. [\bar{C} with NOCl at 150° gives (64) benzal (di)chloride (3:6327). — \bar{C} with aq. PbCl₄.2NH₄Cl on boilg. gives (119) benzal (di)chloride (3:6327) + benzotrichloride (3:6540). — \bar{C} with Cl₂ in pres. of I₂ at 30–40° gives (120) cf. (121) both o-chlorobenzyl chloride (3:6400) and p-chlorobenzyl chloride (3:0220). — Note that \bar{C} with Cl₂ in sunlight (122) undergoes both substitution and addition and that only isolatable prod. was benzal (di)chloride hexachloride, m.p. 153°.]

Bromination. [\bar{C} with Br₂ at 100° gives (123) cf. (124) a mixt. of benzyl bromide, benzal chlorobromide, and benzal (di) bromide. — \bar{C} with Br₂ + BeBr₂ in ether gives (125) p-bromobenzyl bromide. — \bar{C} with Br₂ in pres. of I₂ gives (126) (127) a mixt. of p-bromobenzyl bromide and p-bromobenzyl chloride.]

Sulfonation. [Presumably because of facile hydrolysis or resinification of \tilde{C} with conc. H_2SO_4 , its direct sulfonation has not been reported. However, p-sulfobenzyl chloride (ω -chlorotoluene-p-sulfonic acid) [Beil. XI₁-(30)] has been prepd. (e.g., (128) (129)) from sodium salt of p-toluenesulfonic acid by chlorination.]

Nitration. \bar{C} on mononitration gives a mixt. of o-nitrobenzyl chloride [Beil. V-327, V₁-(162), V₂-(252)], m.p. 49-50° (130), 49.5° (17), 48-48.5° (131), 48-49° (132), 47.9° (133) (143), m-nitrobenzyl chloride [Beil. V-329, V₁-(163), V₂-(252)], m.p. 45-46° (130),

45.5° (17) (131) (134), 44.9° (143), 44.8° (133), and p-nitrobenzyl chloride [Beil. V-329, V₁-(163), V₂-(253)], cryst. from alc., m.p. 72.5° (17) (131) (134), 72.4° (133), 71-72° (130), 71.95° (143), 71° (53). — [For earlier studies of this mononitration of \bar{C} see (53) (135) (136) (137) (138) (139) and especially (140). — Subsequent studies of this mononitration with conc. HNO₃ in acetic anhydride gives (133) 40.9% o-, 4.2% m-, and 54.9% p-nitrobenzyl chlorides (cf. (141) (142) (144)). — For thermal anal. of various mixtures of these three nitrobenzyl chlorides see (133) (143). — For study of rate of nitration of \bar{C} in nitrobenzene soln. at 16-18° see (145). Note that p-nitrobenzyl chloride is a useful reagent for characterization of organic acids by conversion to the corresp. p-nitrobenzyl esters (146) (147); for transformation of p-nitrobenzyl chloride to p-nitrobenzyl bromide in alc. NaBr see (147) cf. (148).]

[Direct polynitration of \bar{C} has not been reported; however, p-nitrobenzyl chloride on further nitration with HNO_3/H_2SO_4 as directed (149) (150) gives 2,4-dinitrobenzyl chloride [Beil. V-344, V₂-(263)], tbls. from ether, m.p. 34° (150), 33-34° (149). — No other dinitrobenzyl chlorides and no trinitrobenzyl chlorides have been reported.]

Hydrolysis of C. C on hydrolysis by various means gives benzyl alcohol (1:6480) and HCl.

[\bar{C} with aq. on protracted boilg. (151) (86) in sunlight (154), with steam + cat. at 550–850° (155) cf. (156), with boilg. aq. K_2CO_3 (157) or alk.-earth carbonates at elev. temps. (158) (159), with hot aq. suspension of PbO (111), with boilg. aq. Na_2CO_3 , NaOH, or their mixt. (160) (161), or with anhydrous formic acid (162) gives benzyl alcohol (1:6480).— For studies on kinetics of hydrolysis of \bar{C} in aq. (163) (169), in 95% EtOH at 30° and 40° (164) (165), in 50% acetone at 60° (166) cf. (167) (168) (170) (17), in dioxane (22), or in formic acid (170) see indic. refs.]

BEHAVIOR OF C WITH OTHER INORGANIC REACTANTS

With alkali sulfhydrates. [\bar{C} with alc. KSH (171) (172) or aq. NaSH (173) (174) (175) gives (75% yield (172)) benzyl mercaptan [Beil. VI-453, VI₁-(224), VI₂-(427)], b.p. 194-195° (171), 99° at 32 mm. (176), 75.8-76.2° at 10 mm. (11), $D_4^{25} = 0.8097$ (176), $n_D^{25} = 1.5729$ (176) (corresp. benzoate, m.p. 30° (177), 3,5-dinitrobenzoate, m.p. 119-120° (177), reaction prod. with 3-nitrophthalic anhydride, m.p. 136-137° (177), 2,4-dinitrophenyl thioether, m.p. 182.5° cor. (185)). Note that benzyl mercaptan with isotopic sulfur has been prepared (178) from \bar{C} via conversion to RMgCl and reaction with S³⁴.]

With alkali sulfides. [\bar{C} with alc. K_2S (171) or alc. Na_2S (179) gives (83% yield (179)) dibenzyl sulfide [Beil. VI-455, VI₁-(225), VI₂-(429)], tbls. from ether, CHCl₃, or alc., m.p. 49-50° (180), 49° (171) (179) (181) (corresp. sulfoxide [Beil. VI-456, VI₁-(226), VI₂-(429)], m.p. 135° (182), 133-134.6° (183), 132-133° (179); corresp. sulfone [Beil. VI-456, VI₁-(226), VI₂-(430)], m.p. 151° (184), 149.5-151° (183), 149.5-150° (179)).]

With alkali polysulfides. [\bar{C} with alc. Na₂S.9H₂O + S (186) (189) in C₆H₆ (187) cf. (188) gives dibenzyl disulfide [Beil. VI-465, VI₁-(229), VI₂-(437)], m.p. 74° (189), 72° (190), 71-72° (191), 70° (186) (corresp. disulfoxide [Beil. VI-466, VI₁-(230), VI₂-(438)], m.p. 108° (190) (192) cf. (209) (201) (210)).]

With salts of various sulfur acids. $[\bar{C}$ with conc. aq. K_2SO_3 (194) cf. (196) or Na_2SO_3 (195) in aq. alc. at 37° (197) (for study of rate at 40° see (16)) or at 190–200° under press. (98% yield (198)), or \bar{C} with aq. $Na_2SO_3/NaOH$ on boilg. (80% yield (199)) (192), gives corresp. salt of toluene- α -sulfonic acid (benzylsulfonic acid) [Beil. XI-116, XI₁-(32)]; for dimorphism of Na salt see (200) (corresp. sulfonyl chloride, m.p. 92–93° (201) (202), 92° (203); corresp. amide, m.p. 105° (203) (192), 104–105° (199), 102° (204); corresp. methyl ester, m.p. 61–62° (205)).]

[\bar{C} with Na₂S₂O₃ on boilg. in aq. alc. (206) or aq. (207) gives salt of S-benzylthiosulfuric acid [Beil. VI-439, VI₁-(230)] (corresp. quaternary salt, viz., benzyl-dimethyl-phenyl-ammonium S-benzylthiosulfate, from metathesis of benzyl-dimethyl-phenyl-ammonium chloride with sodium S-benzylthiosulfate, has m.p. 104° (208)).]

With salts of other inorganic acids. [\bar{C} with NaI in acetone (211) (212) or abs. MeOH (213), or \bar{C} with KI in acetone (214) or EtOH (215), gives (90% yield (211)) benzyl iodide [Beil. V-314, V₁-(157), V₂-(241)], m.p. 24° (211) (212), 27-30° (213), b.p. 97-98° at 11 mm. (216), 93° at 10 mm. (214). — For study of rate of reaction of \bar{C} with KI in acetone at 25° (19) (20), 30° (19), and 50° (19), or with NaI or LiI in acetone at 25° or 30° (19), see indic. refs.]

[Č with powdered AgNO₃ in dry ether 20 hrs. in cold, then at 70–75° for 5 hrs., gives (84% yield (219)) (220) benzyl nitrate [Beil. VI-439], explosive liquid, b.p. 106° at 20 mm. (219), 100–101° at 18 mm. (21), 43° at 0.5 mm. (220). — For study of kinetics of reaction of C with solid AgNO₃ (221) in pres. of inert diluents such as dry ether, CHCl₃, and CCl₄ (222) see indic. refs.; for study of kinetics of reaction of C with Hg(NO₃)₂ in aq. dioxane see (21).]

[Č with AgNO₂ (223) (224) (231) or better mercurous nitrate (225) gives ω -nitrotoluene (phenylnitromethane) [Beil. V-325, V₁-(161), V₂-(249)], b.p. 225-227° dec. (226) (227) cf. (228), 141-142° sl. dec. at 35 mm. (226), 135° at 25 mm. (229), 118-119° at 16 mm. (230), 110° at 8 mm. (231), 90-92° at 3 mm. (232); $D_1^{24.7} = 1.1540$ (233), $D_0^{20} = 1.1598$ (226); $n_{\rm He}^{24.7} = 1.5285$ (233), $n_{\rm D}^{20} = 1.5323$ (226); note, however, that phenylnitromethane is best prepd. in a different way, viz., from benzyl cyanide with methyl nitrate and alc./NaOEt (50-55% yield (232)). — Note that the isomeric benzyl nitrite [Beil. VI-439], unstable oil, b.p. 80-81° at 35 mm. (234), has been reported from benzyl alcohol (1:6480) with aq. NaNO₂ + H₂SO₄ (234).]

[Č with NaN₃ in alc. refluxed 6 hrs. gives (90% yield (234)) ω -azidotoluene (benzyl azide) [Beil. V-350, V₁-(174), V₂-(274)], oil, insol. aq. and volatile with either steam or ether, b.p. 108° at 23 mm. (235), 82.5° at 16.5 mm. (234), 74° cor. at 11 mm. (236); $D_{-}^{24.9} = 1.0655$ (237); $n_{D}^{24.9} = 1.53414$ (237).]

[For behavior of C with metallic evanides see below under organic acids.]

With ammonia. C with ammonia under various circumstances (see below) gives one (or more) of the following amines.

Benzylamine [Beil. XII-1013, XII₁-(445)], liq. with faint characteristic odor, misc. with aq. alc. ether: b.p. 184.5° cor. at 760 mm. (238), 184-186° cor. at 745 mm. (239), 184° at 767 mm. (240), 182° at 749 mm. (226), 181.5-182° at 740 mm. (241), 90° at 12 mm. (242); $D_4^{25} = 0.9812$ (243), $D_4^{20} = 0.9822$ (244); $n_D^{20} = 1.54015$ (226), $n_D^{10.5} = 1.54406$ (244) (corresp. B.HCl, m.p. 255.5-258° (245), 255-256° rap. htg. (226), 253° (246); B.PkOH, m.p. 195-199° (247), 194° (248); B.3,5-dinitrobenzoic acid, m.p. 210.0° cor. (249); B.2,4-dinitrobenzoic acid, m.p. 199.1-200.1° cor. (513); B.p-toluenesulfonic acid, m.p. 180.5-181.5° u.c. (250), 180° (251)). — Dibenzylamine [Beil. XII-1035, XII₁-(453)], oil, insol. aq., eas. sol. alc., ether; b.p. >300° dec. (252), 268-271° cor. at 250 mm. (238), 218-220° at 60 mm. (253), 215° \pm 1° at 39 mm. (254), 186° at 19 mm. (255), 172° at 14 mm. (256); f.p. -25.6° (254); $D_4^{25} = 1.024$ (255), 1.019 (257); $D_4^{21.6} = 1.0256$ (244); $n_D^{21.6} = 1.57432$ (244) (corresp. B.HCl, m.p. 256° (252), 255.5° (258); B.p-toluenesulfonic acid, m.p. 155.5-156.5° u.c. (250)). — Tribenzylamine [Beil. XII-1038, XII₁-(454)], solid, m.p. 92° (259) (260), 91° (256) (261) (262); b.p. 218-222° at 14 mm. (256), 230° at 13 mm. (259) (corresp. B.HCl, m.p. 227-228° (263), 221° (261); B.p-toluenesulfonic acid, m.p. 200.0-202.5° u.c. (250)).

[For formn. of mixts. of benzylamine, dibenzylamine, and tribenzylamine (properties given in preceding paragraph) from reaction of C with aq. NH₄OH at 80° for 8 days (264) or at 125° and 8 atm. press. (265) in pres. of cat. (266); from reaction of C with alc. NH₃ on

stdg. several days (268) (269) (270) or in s.t. at 100° (256) (267), with NH₃ in conc. aq. phenol in s.t. at 100° for 18 hrs. (271), with liq. NH₃ for 24 hrs. (256), or with 5 moles aq. (NH₄)₂CO₃ for 5-6 hrs. at 85-110° (160) see indic. refs.]

[For formn. of benzylamine from reaction of \tilde{C} with K phthalimide at 170–180° followed by hydrolysis of the N-benzylphthalimide (see below under \mathfrak{D} 's) with fumg. HCl at 200° for 2 hrs. (272) cf. (273) (274), with silver cyanate followed by hydrolysis with alkali (275) (276) cf. (268) (277), with acetamide followed by hydrolysis with alc. KOH (278), or with hexamethylenetetramine followed by hydrolysis with alc. HCl (279) see indic. refs.]

[For formn. of tribenzylamine from reaction of C with NaNH₂ at 120° for 24 hrs. see (261) (280).]

With hydroxylamine. [\bar{C} with NH₂OH.HCl + Na₂CO₃ in aq. alc. under reflux gives (281) (282) (283) (284) N,N-dibenzylhydroxylamine [Beil. XV-19, XV₁-(9)], m.p. 124° (284), 123-124° (285), 123° (281); note that the isomeric O,N-dibenzylhydroxylamine [Beil. XV-21], oil, b.p. 145-146° at 3 mm. (286), is obtd. indirectly. — \bar{C} with acetone oxime refluxed in 75% AcOH gives (287) (as the hydrochloride) N-benzylhydroxylamine [Beil. XV-17, XV₁-(8)], m.p. 57° (288), 56-58° (289) (\bar{B} .HCl, m.p. 110° (288)). — Various other benzylated hydroxylamines cannot be discussed here.]

With hydrazine. [\bar{C} with alc. 50% hydrazine hydrate under reflux gives (290) N,N-dibenzylhydrazine [Beil. XV-533, XV₁-(164)], m.p. 65° (\bar{B} .HCl, m.p. 202° (292), 200° (290)); note that the isomeric N,N'-dibenzylhydrazine [Beil. XV-534, XV₁-(166)], m.p. 47° (291) (\bar{B} .HCl, m.p. 225° (293)), is prepd. indirectly. — Various other benzylated hydrazines cannot be discussed here.]

With metals. Sodium. [\bar{C} with Na at 30° on stdg. gives (294) encrustation of NaCH₂-C₆H₅ [Beil. XVI₁-(589)]; the solid is wine red within 5 hrs., red-violet in 12 hrs., blue-violet in 36 hrs., and finally blue-black; and the sodium benzyl can be isolated as a blue-violet solid stable in air (294). — \bar{C} with Na at 100° (295) in a mixt. of C₆H₆ and toluene (296) or in toluene (297) gives dibenzyl (1:7149). — \bar{C} with Na in liq. NH₃ loses its halogen quantitatively (298) giving (50% yield (299)) dibenzyl (1:7149) accompanied by toluene and other products. — For study of free benzyl radical from \bar{C} with Na vapor in helium see (302).]

[\bar{C} with Cu powder in s.t. at 150-160° for 12 hrs. (300), or \bar{C} with Al powder (pretreated with H₂ at 500°) refluxed at 200° for 1 hr. (301), gives (60% yield (301)) dibenzyl (1:7149).] *Magnesium*. [\bar{C} as vapor passed over htd. Mg gives (303) magnesium allylide which with aq. yields methylacetylene ("allylene").]

[Č with Mg in dry ether gives (304) (305) (306) C₆H₅.CH₂MgCl: for study of optimum conditions (311) giving yields of 94.28% (307), 93.2% (308), 91.0-94.1% (309), 90.7-91.2% (310) see indic. refs.; for study of effect of nature of Mg (312), of use of ether/hydrocarbon mixts. as solvent (313), of stability toward long boilg. in ether or ether/benzene (314) see indic. refs.; for further examples of practical prepn. of C₆H₅.CH₂MgCl see (315) (316).—Note that some dibenzyl (1:7149) (e.g., 9.4% (317)) and di-p-tolyl (4,4'-dimethylbiphenyl) (318) are also formed and the yield of dibenzyl is greatly increased in pres. of cat. such as CuCl₂, HgBr₂, FeCl₃, FeBr₃ (319), or MoCl₅ (320).]

An exhaustive treatment of the behavior of C₆H₅.CH₂MgCl (hereafter called RMgCl) is far beyond the scope of this book, but the following examples will be useful and will serve as lead references; for further examples see Beil. XVI-939, XVI₁-(554) and subsequent literature.

[RMgCl with O_2 gives (80% yield (321)) cf. (322) benzyl alcohol (1:6480). — RMgCl (1 mole) gives (84% yield (323)) (324) (325) $C_6H_5CH_2HgCl$, m.p. 104° (323) (324) (326), but excess RMgCl with HgCl₂ gives (326) (325) (327) dibenzyl mercury, m.p. 111° (326). — RMgCl with SbCl₃ gives (328) tribenzylstilbene, m.p. 107-108°. — RMgCl with ClNH₂

gives (yields: 92% (329), 85% (212)) benzylamine (for constants see above under behavior of \bar{C} with NH₃) as hydrochloride; RMgCl with BrNH₂ gives (63% yield (330)) benzylamine. — RMgCl with NCl₃ gives (331) both benzylamine (32% yield) and dibenzylamine (7% yield). — RMgCl with SiF₄ gives (336) (C₆H₅.CH₂)₃SiF, m.p. 79°, accompanied by some (C₆H₅.CH₂)₄Si, m.p. 127.5°; the latter is also obtd. (20.7% yield (337)) from RMgCl with Na₂SiF₆.]

1166

RMgCl with organic reactants frequently (but not invariably) leads to products derived from o-tolyl MgCl and/or p-tolyl MgCl: for reviews on and studies of this rearr. of RMgCl see (332) (333) (334) (335). — RMgCl shows little if any tendency to act as a reducing agent in Grignard additions; for review of reducing action of many Grignard reagents (including C₆H₅.CH₂MgCl) see (338).

[RMgCl with CO at 120° under press. gives (60% yield (339)) 1,3-diphenylpropene-1 [Beil. V-643, V₁-(310), V₂-(552)]. — RMgCl with CO₂ gives (yields: 75-76% (310), 62.7% (335), 60% (340), 51% (318), 40% (333)) phenylacetic acid (1:0665).]

[RMgCl with trioxymethylene gives (50-55% yield (341)) (342) (343) o-tolylcarbinol (1:5922) (note rearr.), but RMgCl with acetaldehyde (as paraldehyde) gives (343) (335) the expected benzyl-methyl-carbinol [Beil. VI-503, VI₁-(251), VI₂-(472)]. — RMgCl with benzaldehyde gives according to conditions various prods. including benzyl-phenyl-carbinol (1:5958) (78% yield (344)) (345) (346), stilbene (1:7250) (25-35% yield (316)), and other products.]

[RMgBr with acetone gives (347) (343) benzyl-dimethyl-carbinol (1:5910). — RMgCl gives with diphenylketone (85% yield (349)) (348) benzyl-diphenyl-carbinol [Beil. VI-721, VI₁-(354), VI₂-(696)] easily dehydrated to (54–59% overall yield (316)) α,α,β -triphenyl-ethylene [Beil. V-722, V₁-(355), V₂-(630)].]

[RMgCl with ClCH₂OCH₃ (3:7085) according to circumstances gives either or both the "normal" prod. (350) (351) methyl β -phenylethyl ether [Beil. VI-479, VI₁-(238), VI₂-(449)] and the "abnormal" prod. (352) (353) methyl o-tolylcarbinyl ether [Beil. VI-484]. — RMgCl with ClCH₂O.CH₂CH₃ (3:7195) according to circumstances gives either or both the "normal" prod. (354) ethyl β -phenylethyl ether [Beil. VI₁-(450)] or the "abnormal" products (352) (332) ethyl o-tolyl ether [Beil. VI-484] and ethyl p-tolyl ether [Beil. VI-498].]

[RMgCl with methyl chloroformate (3:5075) gives some "abnormal" prod. (333).—RMgCl with ethyl chloroformate (3:7295) gives not only the "normal" tribenzylcarbinol [Beil. VI-723, VI₁-(356)] (355) and ethyl phenylacetate (1:3872) but also "abnormal" products (332) (333).]

[RMgCl with acetyl chloride (3:7065) gives (yields: 24% (333), 18% (335)) (332) the "abnormal" product, methyl o-tolyl ketone (o-methylacetophenone) (1:5224). — RMgCl with benzoyl chloride (3:6240) gives (333) the "abnormal" product, phenyl o-tolyl ketone [Beil. VII-439, VII₁-(234)].]

[RMgCl with benzenesulfonyl chloride gives (356) (357) benzyl phenyl sulfone [Beil. VI-455, VI₂-(428)] (2.9% yield (356)) cf. (357) and \bar{C} (60% yield (356)).]

RMgCl with alkyl p-toluenesulfonates gives hydrocarbons. — [E.g., RMgCl with methyl p-toluenesulfonate gives (40.9% yield (358)) ethylbenzene (1:7410), with ethyl p-toluenesulfonate (358) or diethyl sulfate (359) gives (yields: 100% (359), 38.3% (358)) n-propylbenzene (1:7450), with n-propyl p-toluenesulfonate gives (35.6% yield (358)) n-butylbenzene (1:7515), with n-butyl p-toluenesulfonate gives (yields: 67% (361), 50-59% (360), 24.6% (358)) n-amylbenzene (1:7549). — RMgCl with γ -chloro-n-propyl p-toluenesulfonate gives (42-50% yield (362)) ω -chloro-n-butylbenzene (δ -phenyl-n-butyl chloride) [Beil. V₁-(201), V₂-(317)].]

BEHAVIOR OF C WITH ORGANIC REACTANTS

With hydrocarbons. \bar{C} with benzene (1:7400) in pres. of widely varied condensing agts. gives diphenylmethane (1:7120), frequently accompanied by o-dibenzylbenzene [Beil. V-710, V₁-(351), V₂-(621)], m.p. 78-79°, and by p-dibenzylbenzene [Beil. V-711, V₁-(351), V₂-(621)], m.p. 86°. — [E.g., \bar{C} with benzene (1:7400) in pres. of Zn dust (363) (369), Cr powder (364), uranium dust at 100° for 4 hrs. (365), Al powder (preheated in H₂ at 500°) (301), Ti (393), Al/Hg (366) (367), Al + HgCl₂ (368), Al + HCl (368), AlCl₃ (369) (370), AlCl₃/nitrobenzene cpd. at 30° (372), NaCl.AlCl₃ at 15-20° (373), BeCl₂ at 100° for 6 hrs. (374), TiCl₄ (375), ZrCl₄ (376), SnCl₄/diethyl etherate (377), TlCl₃ (378), iron pyrites (97), Ag₂SO₄ (379), silver methionate (neutral silver salt of methanedisulfonic acid) (379), P₂O₅ (380), or HF in Cu bomb at 100° for 15 hrs. (381) gives (yields: 60-63% (368), 60% (372) (374), 56% (381), 52% (373), 49.5-52.5% (366), 40% (365), 38% (301), 35% (375), 30% (376), 22% (363)) diphenylmethane (1:7120).]

[\bar{C} with toluene (1:7405) in pres. of Zn dust (382) cf. (383) (384), Ti (393), AlCl₃ (369) (370) cf. (385) (386) (371), Al/Hg (367), FeCl₃ (385) (386), BeCl₂ at 110-125° (374), or MeMgI (387) gives p-benzyltoluene [Beil. V-607, V₁-(286), V₂-(511)], b.p. 279°.]

[\bar{C} with m-xylene (1:7420) in pres. of Zn dust (388), finely divided Cu (389), or BeCl₂ at 130-140° (374) gives (73.6% yield (384)) phenyl-m-xylyl-methane [Beil. V-615, V₁-(289), V₂-(518)], b.p. 295-296° cor. (388) (389).]

[Č with mesitylene (1:7455) refluxed 60 hrs. without cat. (391), or in pres. of AlCl₃ (390) at 98-100°, or BeCl₂ at 140-160° (374), gives (78% yield (374)) benzylmesitylene (phenyl-2,4,6-trimethylphenyl-methane) [Beil. V-619], m.p. 36-37° (390), 36° (374).]

[\overline{C} with biphenyl (1:7175) refluxed 3 hrs. without cat. (391), or in pres. of Zn dust at 100° (392), or of Ti (393) gives 4-benzylbiphenyl [Beil. V-708, V₂-(618)], m.p. 85° (392) (391).]

[\bar{C} with naphthalene (1:7200) refluxed 3 hrs. without cat. (391), or in pres. of Zn dust (394) (395), ZnCl₂ (396) at not over 125° (397), AlCl₃ (396) (398), Ti (393), or P₂O₅ at 200° (380) gives mainly 1-benzylnaphthalene [Beil. V-689, V₁-(341), V₂-(604)], m.p. 59° (corresp. picric acid addn. cpd., m.p. 100–101° (396) (400)), accompanied by some 2-benzylnaphthalene [Beil. V-690], m.p. 55–55.5° (398), 55.5° (399) (corresp. picric acid addn. cpd., m.p. 93° (396) (400)). — Note that using ZnCl₂ little 2-benzylnaphthalene is formed (398); also that polybenzylation may occur (399).]

With alcohols (or alcoholates). [\bar{C} with MeOH/KOH (401) or with MeOH/NaOMe (403) in s.t. at 120° (402) gives benzyl methyl ether (1:7475), b.p. 170–171° cor. (403), 170.5° cor. at 760 mm. (3), 170–171° at 759 mm. (377), 170.2–172.2° at 760 mm. (404); $D_4^{25} = 0.9745$ (405), 0.9594 (403), $D_4^{20} = 0.9649$ (403); $n_D^{25} = 1.4983$ (403), $n_D^{20} = 1.5031$ (405), 1.5008 (403) (corresp. picrate, m.p. 115–116° u.c. (406)). — \bar{C} with EtOH/KOH (401), EtOH/NaOEt (403) (377) (407), EtOH/LiOEt (407), or KOEt/liq. NH₃ (408) gives (yields: 81% (408), 63–77% (407)) benzyl ethyl ether (1:7530); b.p. 184.7–185.2° at 761 mm. (377), 184–186° cor. (403); $D_4^{25} = 0.9446$ (403), $D_4^{20} = 0.9490$ (409), 0.9478 (403); $n_D^{25} = 1.4934$ (403), $n_D^{20} = 1.4958$ (403), 1.4955 (409). — For studies of rate of reaction of \bar{C} with EtOH (410) (411) or with EtOH/NaOEt (412) see indic. refs.]

[\tilde{C} with n-PrOH/NaO-n-Pr gives (90-93% yield (413) (403)) benzyl n-propyl ether [Beil. VI-431, VI₁-(219), VI₂-(410)], b.p. 200-202° cor. (403), 68° at 9 mm. (413); $D_4^{25} = 0.9480$ (403), $D_4^{20} = 0.9535$ (403) cf. (413); $n_2^{25} = 1.4932$ (403), $n_2^{20} = 1.4953$ (403), 1.4905 (413); for study of rate at 50.6° see (414). — \tilde{C} with iso-PrOH/NaOisoPr gives (403) benzyl isopropyl ether, b.p. 192-194° cor.; $D_4^{25} = 0.9403$, $D_4^{20} = 0.9457$; $n_D^{25} = 1.4876$, $n_D^{20} = 1.4900$ (403).]

[For corresp. prepn. and constants for benzyl n-butyl ether (403) (417), benzyl sec-butyl ether (417), benzyl isobutyl ether (403), and benzyl isoamyl ether (403) see indic. refs.]

[\bar{C} with benzyl alc./NaOCH₂C₆H₅ in ether (415), with solid KOH at 180-200° (416), with conc. aq. NaOH at 90-120° (416), or with K benzylate in liq. NH₃ (408) gives dibenzyl ether (1:7640).]

With phenols (or phenolates). Č with phenols may react either with phenolic or nuclear hydrogen giving respectively benzyl aryl ethers or benzylated phenols; moreover, the former may, under appropriate conditions, be rearranged to the latter; examples of all these types of reaction are included below.

[\tilde{C} with K phenolate (111) (418) or Na phenolate (417) in boilg. alc., or \tilde{C} with phenol in boilg. alc. NaOMe or NaOEt (419) (420), boilg. aq. NaOH (160) (421), or boilg. acetone + K_2CO_3 (422) gives (73% yield (421)) benzyl phenyl ether [Beil. VI-432, VI₁-(220), VI₂-(411)], m.p. 39° (418) (420) (421) (422), 38-39° (401); b.p. 286-287° (401), 286-288° (419), 178-179° at 35 mm. (422), 124-125° at 4 mm. (417). — Note that although this prod. is completely stable to distn. (419) yet on htg. with ZnCl₂ or in dry HCl as directed (421) it undergoes rearr. (accompanied by some cleavage) giving 2-benzylphenol (1:1431), 4-benzylphenol (1:1485), 2,4-dibenzylphenol (see below), and other prods.]

 $\tilde{\mathbf{C}}$ under suitable conditions also effects nuclear benzylation of phenol yielding a mixt. of o-benzylphenol (1:1431) and p-benzylphenol (1:1485) (the latter usually predominating) accompanied by polybenzylphenols and other products. [E.g., $\tilde{\mathbf{C}}$ with phenol (1:1420) directly at 125° (423) or 150–180° (160), or in pres. of Cu powder at 115–120° (160), Ce at 120–130° (424), Ti (393), AlCl₃ in pet. ether (425), Zn at room temp. (426) (427) (428) (429) in solvent media such as C_6H_6 , toluene, CHCl₃, or EtOH (430), ZnCl₂ on warming (421) (431) (432), 38% HCl in s.t. at 100° (421), P_2O_5 (434) or PCl_5 (435) in toluene at 130–135°, or $\tilde{\mathbf{C}}$ with Na phenolate (or phenol + Na) in dry toluene (419) (436) (437) gives o-benzylphenol + p-benzylphenol (accompanied by other products). — For sepn. of the two benzylphenols by formn. of Na salt of latter in toluene see (438).]

Other phenols, cresols, naphthols, etc., behave analogously but cannot be discussed here. With phenol ethers. With phenol ethers (where no phenolic H atom is available for reaction) Č effects nuclear benzylation. [E.g., Č with methyl phenyl ether (anisole) (1:7445) refluxed 2-3 hrs. (391), or in pres. of Zn (439), Ti (393), Ce (424), W (365), AlCl₃ (440), or ZnCl₂ + dry HCl (421) gives (yields: 63% (393), 57% (424), 52.9% (365)) p-benzylanisole [Beil. VI-676, VI₁-(325), VI₂-(630)], b.p. 305-308° (425), 191-193° at 38 mm. (391), 172-174° at 10 mm. (421), 157-158° at 8 mm. (411), 133-135° at 4 mm. (425); m.p. 20-21° (441).]

[C with phenetole (1:7485) in pres. of Ti (393), U (365), or Ce (424) as directed gives (yields: 76% (393), 80% (365), 88% (424)) p-benzylphenetole [Beil. VI-676, VI₂-(630)], b.p. 317° (442), 315-317° (425), 217° at 37 mm. (442), 203° at 12 mm. (442), 171-173° at 12 mm. (425).]

With organic acids (or their salts). KCN or NaCN. [\bar{C} with alc. KCN (443) (444) (445) (446) in pres. of CuCN and in u.v. light (447), or \bar{C} with aq. alc. NaCN (160) (448), gives (yields: 80-90% (448), 70-76% (447), 70% (160)) benzyl cyanide (α -tolunitrile) (phenylacetonitrile) [Beil. IX-441, IX₁-(176)], b.p. 233-234° cor. (3), 231-232° at 755 mm. (449), 135-140° at 38 mm. (448), 118-119° at 20 mm. (450), 107-107.4° at 12 mm. (18); f.p. -24.6° (26), -26.5° (451); $D_4^{25} = 1.0125$ (452), $D_4^{20.2} = 1.0176$ (453), 1.0157 (454); $n_D^{25} = 1.52105$ (455), $n_D^{20.2} = 1.52422$ (453); for removal from this prod. of traces of benzyl isocyanide with aq. H₂SO₄ at 60° see (456).]

With salts of aliphatic acids. [C with Na formate + anhydrous formic acid in s.t. at 140° (402) gives benzyl formate (1:3596) q.v.]

[Č with KOAc in alc. (443) (457) (460) or benzyl acetate itself (458), or Č with Pb(OAc)₂ in AcOH (459), or Č with NaOAc in AcOH (461) cf. (160) or aq. at 115° (160), gives (80% yield (160)) benzyl acetate (1:3751) q.v.; for study of kinetics see (22).]

[\bar{C} with alc. K propionate (460) or with aq. Na propionate (160) gives benzyl propionate [Beil. VI-436, VI₁-(220), VI₂-(416)], b.p. 222°.]

 $[\bar{C} \text{ with alc. } \text{K } n\text{-butyrate (460), or aq. Na } n\text{-butyrate (160), gives benzyl } n\text{-butyrate (1:3977).}]$

C with salts of other aliphatic acids behaves similarly but detailed treatment will not be given here.

With salts of aromatic acids. [For extensive study of reaction of \bar{C} with NaOBz giving benzyl benzoate (1:4422) see (462) (629)]

With salts of enolic esters. [\tilde{C} with diethyl sodiomalonate gives (yields: 87% (463), 85% (464), 60% (471), 51–57% (465), 50% (470)) (466) diethyl benzylmalonate [Beil. IX-868, IX₁-(381)], b.p. 300° (466), 296–298° (467), 195° at 22 mm. (463), 163° at 14 mm. (468), 170° at 13 mm. (469), 169° at 12 mm. (470) (471), 158° at 8 mm. (472), 128–133° at 6 mm. (473), 145–155° at 5 mm. (465), 150–152° at 4 mm. (474), 140–140.5° at 1.5 mm. (474), 105–108° at 1 mm. (475) (476); $D_4^{20}=1.0750$ (468); $n_D^{20}=1.4872$ (468). This prod. on alk. hydrolysis (for study of kinetics see (477)) and subsequent acidification gives benzylmalonic acid [Beil. IX-868, IX₁-(381)], cryst. from ether, C_6H_6 , or CHCl₃/pet. ether, m.p. 120.6° (478), 120° (479), 120° dec. (468), 119–120° (480), 117–118° (472), 117° (466) (467); on htg. above its m.p. (480) this acid readily loses CO₂ yielding hydrocinnamic acid (1:0615), m.p. 48°.]

[\bar{C} with Na enolate of diethyl benzylmalonate (above) (482) (485), or \bar{C} with diethyl disodiomalonate (483), or \bar{C} with diethyl ethoxymagnesiomalonate (484), gives (yields: 85% (483), 84–87% (485)) diethyl dibenzylmalonate [Beil. IX-937, IX₁-(408)], b.p. 250° at 40 mm. (482), 256–257° at 38 mm. (486), 234–235° at 23 mm. (485), 224–226° at 15 mm. (484), 221° at 11 mm. (483), 192–193° at 2 mm. (487); m.p. 13–14° (486); $D_4^{20}=1.0930$ (482). Note that this prod. always accompanies the diethyl benzylmalonate of preceding paragraph. Diethyl dibenzylmalonate with alc. alk. hydrolyzes with great difficulty (488) (485) but gives dibenzylmalonic acid [Beil. IX-937, IX₁-(407)], m.p. 175° (485), 174° (488), which on htg. above its m.p. loses CO₂ giving dibenzylacetic acid (1:0668), m.p. 89°.]

[\bar{C} with ethyl sodioacetoacetate as directed (489) (490) (491), or \bar{C} with ethyl acetoacetate + BF₃ (492), gives (yields: 70% (491), 23% (492)) ethyl α -benzylacetoacetate [Beil. X-710], b.p. 283–284° u.c. (493), 276° (490), 157–158° at 14 mm. (494), 164–165° at 12 mm. (493), 163–165° at 12 mm. (491), 140–150° at 2–3 mm. (473) (corresp. 2,4-dinitrophenyl-hydrazone, m.p. 71.5° (473)). For ketonic cleavage of this prod. with 20% aq. NaOH (495) or aq. in s.t. at 250° (496) giving benzylacetone [Beil. VII-314, VII₁-(167)], b.p. 236°, see indic. refs.]

[\bar{C} with ethyl acctoacetate as directed (497) cf. (501) or \bar{C} with ethyl α -benzylacetoacetate (above) as directed (489) (493) (498) (499) gives (58% yield (497)) ethyl α , α -dibenzylacetoacetate [Beil. IX-771], m.p. 57° (493) (497) (500), b.p. 230-234° at 12 mm. (493) cf. (497). For ketonic cleavage of this prod. with HI/AcOH giving (80% yield) α , α -dibenzylacetone, b.p. 190-192° at 15 mm., see (497); for acid cleavage giving dibenzylacetic acid (1:0668) see (500) (501).]

With amines. With aliphatic primary amines. [\bar{C} with CH₃NH₂ (2 moles) as 33% soln. in abs. EtOH gives (546) cf. (554) N-methylbenzylamine [Beil. XII-1019, XII₁-(447)], oil, sol. aq., b.p. 184–186° (547) (554), 184–185° u.c. at 749 mm. (548), 184° (549) at 759 mm. (550), 180–181° cor. at 765.5 mm. (546), 180° at 760 mm. (551); $D_{18}^{18.5}$ = 0.9450 (552) (\bar{B} .HCl, 195° (554), 174–175° (546); \bar{B} .PkOH, m.p. 117–118° (532), 113–116° (553)). Note that this prod. is usually accompanied by some N-methyl-dibenzylamine [Beil. XII-1036, XII₁-(453)], b.p. 304–305° cor. at 765.5 mm. (546), 165° at 15 mm. (555), 161–162° at 12 mm. (556) (\bar{B} .HCl, m.p. 200–201° (556); \bar{B} .PkOH, m.p. 107° (5571), also obtd. from \bar{C} with N-methylbenzylamine (above) in pres. of NaOH at 145° for 4 hrs. (555).]

[Č with $C_2H_3NH_2$ in 33% aq. soln. with some alc. in s.t. at 110° gives (558) N-ethylbenzylamine [Beil. XII-1020, XII₁-(448)], oil, spar. sol. aq., b.p. 199° (539), 198° at 750 mm. (550), 194° cor. (558), 191-194° u.c. at 740 mm. (548); $D_{15}^{16.7} = 0.9350$ (552) (B.PkOH, m.p. 122-123° (559)), accompanied by N-ethyldibenzylamine [Beil. XII-1036], b.p. 306° cor. (558).]

With aromatic primary amines. [\bar{C} (1 mole) with aniline (2 moles) in s.t. at 160° for 24 hrs. (502), or htd. in open vessel at 140° (503), or in pres. of I₂ at 50° (504), in alc. (505) or aq. Na₂CO₃ (160), or \bar{C} (1 mole) with aniline (4 moles) in aq. NaHCO₃ at 90–95° (506), or \bar{C} with sodium anilide (from aniline + Na + Cu₂O) at 30–100° under press., (507) gives (yields: 85–87% (506), 56% (160), 49% (504)) N-benzylaniline (N-phenylbenzylamine) [Beil. XII-1023, XII₁-(449)], m.p. 39° (508), 37–38° (509), 37° (510), 36.5–36.8° cor. (503), 36.5° (511), 36° (506) (512); b.p. 306–307° at 759 mm. (509), 201–203° at 37 mm. (510), 178–180° at 12 mm. (506), 171.5° at 10 mm. (508); D_4^{65} = 1.0298 (503); n_D^{65} = 1.59562 (508) (\bar{B} .HCl, m.p. 214–216° (509), \bar{B} .3,5-dinitrobenzoic acid, m.p. 133.0° cor. (249), \bar{B} .2,4-dinitrobenzoic acid, m.p. 121.4–122.2° cor. (513), \bar{B} .p-toluenesulfonic acid, m.p. 148.3–148.8° cor. (250)); for method of sepn. of N-benzylaniline from N,N-dibenzylaniline (below) by reactn. with phthalic anhydride (1:0725) sec (514). — For studies of kinetics of reaction of \bar{C} with aniline in MeOH at 35° and 45° (515) or in EtOH at 35°, 40°, and 45° (516) cf. (4) see indic. refs.; for study of rearr. of N-benzylaniline to p-aminodiphenylmethane see (517).]

[\bar{C} with aniline on htg. cf. (503) (508) in pres of NaOH at 100° (518), anhydrous NaOAc + I_2 at 97° (504), NaNH₂ + Cu powder (519), benzyl alc. (520), or aq. Na₂CO₃ (160) gives N,N-dibenzylaniline (N-phenyldibenzylamine) [Beil. XII-1037, XII₁-(453)], m.p. 71-72° (521), 70° (522), 69.5° (508), 69° (520), 67° (518); b.p. 226° at 10 mm. (508); $D_4^{80} = 1.04436$; $n_D^{80} = 1.60647$ (508) (\bar{B} .HCl, pr. with 1 H₂O from alc (518), but m p unreported; \bar{B} .PkOH, m.p. 131-132° dec. (518); \bar{B} .3,5-dinitrobenzoic acid gives no cpd. (249); B.2,4-dinitrobenzoic acid gives no cpd. (513); \bar{B} .p-toluenesulfonic acid is oil (250); 2 \bar{B} .1,3,5-trinitrobenzene, m.p. 86-87° (523)). — For study of rearr. of N,N-dibenzylaniline hydrochloride to p-aminodiphenylmethane, 2,4-dibenzylaniline, and 2,4,6-tribenzylaniline see (524).]

Č with other aromatic primary amines behaves similarly but cannot be detailed here; however, for a number of cases see (508).

With aliphatic secondary amines. [\bar{C} with $(CH_3)_2NH$ in abs. alc. on stdg. (560) or under reflux (546) (561), or in C_6H_6 at 40–50° for 2 days (562), gives (80% yield (561)) N,N-dimethylbenzylamine [Beil. XII-1019, XII₁-(448)], oil, fairly sol. cold but less sol. hot aq., b.p. 183–184° cor. at 765.3 mm. (560), 180–181° at 749 mm. (540), 178–179° cor. (563), 177.8–178.2° cor. at 766 mm. (561), 178° u.c. (562), 98–99° at 24 mm. (564), 83.5–85.5° at 21 mm. (565), 66–67° at 15 mm. (566), $n_D^{20} = 1.5157$ (564) (\bar{B} .HCl, m.p. 175° (562) cf. (566); \bar{B} .PkOH, m.p. 94° (532), 94–95° (559)).]

[\bar{C} with $(C_2H_5)_2NH$ in s.t. at 100° gives (567) (568) N,N-diethylbenzylamine [Beil. XII-1021, XII₁-(448)], oil, spar. sol. aq., b.p. 212° (569), 211-212° (568) cor. (567), 209° (570) at 755 mm. (551), 96-98° at 17 mm. (564), 94° at 15 mm. (555) (\bar{B} .PkOH, m.p. 120-121° (571), 119° (566)).]

With aromatic secondary amines. [C htd. with N-methylaniline at 100° (521) (525) in pres. of aq. Na₂CO₃ (160), or C with N,N-dimethylaniline + I₂ at 150° (504), or C with mixt. of N-methylaniline and N,N-dimethylaniline at 150° (526), gives (yields: 92.5% (526), 60% (525), 41% (521)) N-benzyl-N-methylaniline (benzyl-methyl-phenylamine) [Beil. XII-1024, XII₁-(450)], b.p. 305-306° (527), 187-188° at 26 mm. (525), 177-178° at 18 mm. (528), 171° at 13 mm. (528), 162-163° at 8 mm. (504); $D_{2}^{26.5} = 1.0421$ (504), $D_{4}^{15} = 1.0475$ (528); $n_{2}^{26.5} = 1.6006$ (504), 1.6071 (528). (B.PkOH, m.p. 131° (529), 128-128.5° (504), 127° (525), 109° (530), 105-107° (531), 104° (532), 103.0-103.5° (533); note disagreement.)] [C htd. with N-ethylaniline (534) in toluene + Na₂CO₃ (535), or C with N,N-diethylaniline

iline + I₂ at 150° (504), or \tilde{C} with a mixt. of N-ethylaniline + N,N-diethylaniline at 150° (526), gives N-benzyl-N-ethylaniline (benzyl-ethyl-phenylamine) [Beil. XII-1026, XII₁-(450)], b.p. 285-286° sl. dec. at 710 mm. (534), 212-220° at 54 mm. (526), 185.5-186.5° at 22 mm. (535) (536), 173° at 12 mm. (528), 163-164° at 6 mm. (504); D_4^{15} = 1.0330 (528); n_D^{15} = 1.5975 (528) (\tilde{B} .PkOH, m.p. 116-117° (536), 114° (535), 113-114° (504), 111-112° (533)). — For important study of sulfonation of N-benzyl-N-ethylaniline see (537).]

With heterocyclic secondary amines. [\bar{C} with piperidine reacts vigorously giving (538) (541) (542) N-benzylpiperidine [Beil. XX-23, XX₁-(8)], b.p. 248° (539), 245-247° (540), 245° (538) (541), 119° at 13 mm (542); $D_4^{20}=0.96049$ (542), $D_4^{16}=0.9625$ (541), $D_4^{15}=0.96451$ (542); $n_{\pi}^{20}=1.52269$ (542) (\bar{B} HCl, m.p. 178° (543)).]

[Direct reaction of \bar{C} with morpholine appears never to have been reported; the expected product, viz., N-benzylmorpholine [Beil. XXVII-7, XXVII₁-(203)] (544), has, however, been prepd. by many other methods and has following constants: b.p. 260-261° cor. (545), 136-136.5° at 14 mm. (544), 128-129° at 13 mm. (542); $D_4^{20} = 1.03874$, $D_4^{15} = 1.03396$ (542) (\bar{B} .HCl, m.p. 244-245° dec. (545); \bar{B} .PkOH, m.p. 193.5-195° cor. (544), 184-185° (545)).]

With aliphatic tertiary amines. [C with (CH₃)₃N in abs. alc. (546) (561) (563) or abs. MeOH at 0° (572) gives trimethyl-benzyl-ammonium chloride [Beil. XII-1020, XII₁-(448)], m.p. 235° (572) dec. (546); for studies of behavior of this prod. toward cat. hydrogenation see (573) (574)]

 $[\bar{C} \text{ with } (C_2H_5)_3N \text{ directly (563) or at 100° in s.t. (567) cf. (570) gives triethyl-benzyl-ammonium chloride [Beil. XII-1021], but its constants are not reported.]$

With aromatic tertiary amines. [C with N,N-dimethylaniline at ord. temp. (575) (577) in MeOH or EtOH (576) gives dimethyl-phenyl-benzyl-ammonium chloride [Beil. XII-1025, XII₁-(450)], tbls. of monohydrate from aq or alc., m.p. 110° (575), 109.5° (578), m.p. anhydrous form, 116° (577); for studies of rate of forms. of this salt in MeOH at 29° and 38° see (579); for studies of behavior on cat. hydrogenation see (573) (580); for use of this quaternary salt as reagt. for introduction of benzyl radical see (473).]

[\bar{C} with N,N-diethylaniline in dry C_6H_6 refluxed 30 min gives (581) diethyl-phenyl-benzyl-ammonium chloride, m.p. 104° (581).]

With heterocyclic tertiary amines. [C with pyridine directly (582) (583) (584) (585) (586) or on htg. at 150° for 6 hrs. (587) gives N-benzylpyridinium chloride [Beil. XX-218, XX₁-(74)], but this salt is difficult to crystallize (586) and its properties are not well established; for kinetics of the addition see (4) (579). — Note that C with pyridine in pres. of Cu on htg. gives (588) a mixt. of 2-benzylpyridine and 4-benzylpyridine, but this type of nuclear benzylation cannot be discussed here.]

With arylhydrazines. Č (1 mole) with phenylhydrazine (2 moles) mixed with cooling (589) and subsequently htd. at $115-120^\circ$ (590) (591) (592), or refluxed in alc. (593), or Č with phenylhydrazine + Na in C₆H₆ (594) or liq. NH₃ (595), or Č with phenylhydrazine + NaNH₂ in liq. NH₃ (73% yield (595)), gives N-benzyl-N-phenylhydrazine (α -benzyl-phenylhydrazine) (Beil. XV-532, XV₁-(164)], oil, b.p. 216-218° at 38 mm. (591), 207-208° at 10 mm. (593) (B.HCl, m.p. 176-177° (596), 170° (593), 164-169° (595), 167° (594) (595), 166-167° (590); corresp. acetyl deriv., m.p. 121-122° (594) (595); corresp. benzyl deriv., m.p. 139-140° (590)); note that the N-benzyl-N-phenylhydrazine is often accompanied (593) (591) by some benzaldehyde N-benzyl-N-phenylhydrazine, m.p. 111-112° (590), 111° (593) (594). — The isomeric N-benzyl-N'-phenylhydrazine (β or sym.-benzyl-phenylhydrazine) [Beil. XV-533, XV₁-(165)], m.p. 35-36°, is not obtd. by benzylation of phenylhydrazine but only by indirect methods.]

[For analogous use of C in prepn. of asym.-benzyl-o-tolylhydrazine, asym.-benzyl-m-tolylhydrazine, asym.-benzyl-p-tolylhydrazine, etc., see (597).]

With arythydroxylamines. [C with N-phenylhydroxylamine in pyridine as directed

- (598) gives (69% yield) N-benzyl-N-phenylhydroxylamine, yellowish lfts., colorless after steam distn., cryst. from pet. ether or EtOAc, m.p. 86° (598) (598) (corresp. B.HCl, m.p. 104-105° (600); corresp. benzoyl deriv., m.p. 115-117° (600)).]
 - Benzyl acetate (1:3751): b.p. 217°. [See also text above under behavior of C with salts of organic acids.]
 - —— Benzyl benzoate (1:4422): b.p. 323-324° cor., m.p. 21°. [For extensive study of prepn. from C with NaOBz see (462) (629).]
 - Benzyl p-nitrobenzoate: m.p. 85°. [See also under benzyl alc. (1:6480).]
 - Benzyl 3,5-dinitrobenzoate: m.p. 113°. [From C with Ag 3,5-dinitrobenzoate refluxed in alc. (190); see also under benzyl alc. (1:6480).]
 - **D** Phenylacetic acid (1:0665): m.p. 76.5°; b.p. 265.5° cor.; Neut. Eq. 136. [From \bar{C} via conversion to C_6H_6 .CH₂.MgCl (see text above under behavior of \bar{C} with Mg) and subsequent treatment with CO₂; yields 75-76% (310), 62.7% (335), 60% (340), 51% (318), 40% (333).]
 - **D** Phenylacetanilide: m.p. 115-116° u.c. (601), 117° cor. (602). [From \bar{C} via conversion to C_6H_6 .CH₂.MgCl (see text above under behavior of \bar{C} with Mg) and subsequent reaction with phenyl isocyanate (602) (601).]
 - —— Phenylaceto-p-toluidide: m.p. 135°. [Presumably from \tilde{C} via conversion to C_6H_6 .CH₂.MgCl and reaction with p-tolyl isocyanate (cf. preceding paragraph) but never actually so reported.]
 - **D** Phenylaceto- α -naphthalide: m.p. 175° (603), 169° (604), 166° u.c. (605). [From \bar{C} via conversion to C_6H_6 .CH₂.MgCl (see text above under behavior of \bar{C} with Mg) and subsequent reaction with α -naphthyl isocyanate (605).]
 - —— Phenylaceto- β -naphthalide: m.p. 159° (604), 158° (603). [Presumably from \bar{C} via conversion to C_6H_5 .CH₂.MgCl (cf. preceding paragraph) and subsequent reaction with β -naphthyl isocyanate but never actually so reported.]
 - Benzylmercuric chloride: m.p. 104° u.c. (323) (324) (326). [From \bar{C} via conversion to C_6H_5 .CH₂.MgCl (see text above under behavior of \bar{C} with Mg) and subsequent reaction (84% yield (323)) (324) (325) with HgCl₂; note, however, that excess C_6H_5 .-CH₂.MgCl gives (325) (326) (327) dibenzylmercury, m.p. 111° (326).]
 - D S-Benzylisothiourea picrate: m.p. 188° (606). [From C with thiourea in alc. htd. 2 min., then treated with alc. PkOH (606). Note that S-benzylisothiourea hydrochloride (S-benzylthiuronium chloride), prepd. from C + thiourea by refluxing alc. soln. (607) (608), and existing in two forms, m.p. 175-176° (608), 172-174° (607), and m.p. 150-151° (608), 146-148° (607), is an important general reagt. for identification of organic acids (607) (608) (609).]
 - ₱ N-Benzylphthalimide: cryst. from AcOH m.p. 116° cor. (610), 116° (611) (612), 115–116° (613), 115° (614). [From C with phthalimide in pres. of dry K₂CO₃ under reflux (72–79% yield (610) (611) or in pres. of NaOEt (612), or from C with K phthalimide under reflux (613), or from benzylamine with phthalic anhydride (1:0725) refluxed in AcOH (614).]
 - N-Benzyl-3-nitrophthalimide: ndls. from CS₂, m.p. 142-143° (615). [From C with K 3-nitrophthalimide under reflux (615).]

 - N-(Benzyl)saccharin: ndls. from alc., m.p. 118° (617), 110-111° (618). [From Č with sodium saccharin in aq. butylcarbitol (1:6517) contg. KI on 30 min. reflux (618).]
- N-(Benzyl)-N-(p-bromobenzenesulfonyl)-p-anisidide: cryst. from 75% alc., m.p. 167.5° u.c. (619). [From Č with N-(p-bromobenzenesulfonyl)-p-anisidide in alc. KOH after 1 hr. reflux (619).]

- p-(Benzyloxy)benzoic acid: m.p. 188-190° (620) (621). [From C with ethyl p-hydroxybenzoate (1:1534) in abs. alc. NaOEt on refluxing 1 hr. (620).]
- Benzyl phenyl ether: m.p. 39°, b.p. 286°. [See text under behavior of $\bar{\mathbf{C}}$ with phenols.]
- © Benzyl 2,4,6-triiodophenyl ether: cryst. from alc., m.p. 123° (622), 122.5° cor. (623). [From Č with 2,4,6-triiodophenol in alc. NaOEt refluxed 30 min. (623) cf. (622).]
- Benzyl α-naphthyl ether: m.p. 77.0-77.0° cor. (624), 74.5-75° (625), 61° (626). [Prepd. only by indirect means; corresp. picric acid addn. cpd., dec. 85-100° (624).]
- Benzyl β-naphthyl ether: m.p. 101.5-102.0° cor. (624), 99-100° (625), 99° (418), 98.5° (627), 98° (628), 95° (626). [From C with β-naphthol (1:1540) in conc. aq. KOH (418) or NaOH (627) on htg. 2 hrs.; corresp. picric acid addn. cpd., m.p. 123.0° cor. (624), 122° (627).]
- 3:8535 (1) Timmermans, Bull. soc. chim. Belg. 25, 344 (1913); Cent. 1914, I [618. (2) Lecat, Rec. trav. chim. 46, 243 (1927). (3) Perkin, J. Chem. Soc. 69, 1190, 1203, 1206 (1896). (4) Baker, J. Chem. Soc. 1932, 2634-2635. (5) Fairbrother, Proc. Roy. Soc. (London) A-142, 184 (1933). (6) Weissberger, Sängewald, Z. physik. Chem. B-9, 140 (1930). (7) Smith, Andrews, J. Am. Chem. Soc. 53, 3649-3650 (1931). (8) Arnold, Kistiakowsky, J. Am. Chem. Soc. 54, 1716 (1932). (9) Bell, J. Chem. Soc. 1931, 1373. (10) Schiff, Ann. 220, 99 (1883).
- (1936). (13) Lorges, Rev. chim. intervention of the control of the
- (21) Roberts, Hammett, J. Am. Chem. Soc. 59, 1063-1070 (1937). (22) Beste, Hammett, J. Am. Chem. Soc. 62, 2481-2487 (1940). (23) Sutton, Proc. Roy. Soc. (London) A-133, 672 (1931). (24) Timmermans, Hennaut-Roland, J. chim. phys. 32, 517-519 (1935). (25) Wroczynski, Guye, J. chim. phys. 8, 197-203 (1910). (26) von Schneider, Z. physik. Chem. 22, 230, 233 (1897). (27) Haase, Ber. 26, 1053 (1893). (28) Pound, J. Phys. Chem. 30, 793 (1926). (29) Dunstan, Hilditch, Thole, J. Chem. Soc. 103, 140 (1913). (30) Jahn, Möller, Z. physik. Chem. 13, 389 (1894).
- (31) King, Beazley, Proc. Nova Scotian Inst. Sci. 18, 204-212 (1934); Cent. 1934, I 3201; C.A. 28, 2686 (1934). (32) Ginsburg, Rueggeberg, Tharp, Nottorf, Cannon, Carnahan, Cryder, Fleming, Goldberg, Haggard, Herr, Hoover, Lovell, Mraz, Noll, Oakwood, Patterson, Van Strien, Walter, Zook, Wagner, Weisgerber, Wilkins, Whitmore, Ind. Eng. Chem. 38, 478-485 (1946). (33) Cotton, Mouton, Ann. chim. (8) 28, 214 (1913). (34) Gladstone, J. Chem. Soc. 45, 245 (1884). (35) Prins, Rec. trav. chim. 42, 26 (1923). (36) Kireev, Kaplan, Zlobin, J. Applied Chem. (U.S.S.R.) 7, 1333-1338 (1934); Cent. 1936, I 4286; C.A. 29, 5712 (1935). (37) Lecat, "L'Azeotropisme," 1918; (a) p. 112, (b) p. 76. (38) Lecat, Ann. soc. sci. Bruxelles 49-B, 18, 20, 110 (1929). (39) Fuson, McKeever, Org. Reactions 1, 63-90 (1942). (40) Lock, Ber. 74, 1568-1574 (1941).
- (41) Kulka, Can. J. Research 23-B, 106-110 (1945). (42) Blanc, Bull. soc. chim. (4) 33, 313-319 (1923). (43) Stephen, Short, Gladding, J. Chem. Soc. 117, 510-527 (1920). (44) Sivkov, Matveeva, Sintezy Dushistykh Veshchestv, Sbornik Statei 1939, 154-161; C.A. 36, 3793 (1942). (45) Vorozhtzov, Jurygina, J. Gen. Chem. (U.S.S.R.) 1, 49-64 (1931); Cent. 1931, II 1132; not in C.A. (46) Vavon, Bolle, Calin, Bull. soc. chim. (5) 6, 1025-1033 (1939). (47) Sommelet, Compt. rend. 157, 1445 (1913). (48) Tschunkur, Eichler, Ger. 509,149, Oct. 8, 1930; Cent. 1931, I 360; C.A. 25, 711 (1931). (49) Wohl, Ger. 139,552, Feb. 16, 1903; Cent. 1903, I 607. (50) Wohl, Ger. 160,102, July 4, 1905; Cent. 1905, II 367.
- (51) Wohl, Ger. 162,394, July 22, 1905; Cent. 1905, II 727. (52) Cannizzaro, Ann. chim. (3) 45, 468-475 (1855). (53) Beilstein, Geitner, Ann. 139, 331-337 (1866). (54) Asolkar, Guha, J. Indian Chem. Soc. 23, 47, 50 (1946). (55) Mason, Smale, Thompson, Wheeler, J. Chem. Soc. 1931, 3150-3154. (56) Cohen, Dawson, Blockey, Woodmansey, J. Chem. Soc. 97, 1623-1636 (1910). (57) Schramm, Ber. 18, 607-608 (1885). (58) Gibbs, Geiger, U.S. 1,246,739, Nov. 13, 1917; C.A. 12, 280 (1918). (59) Zelinsky, Schering-Kahlbaum, A.G., Ger. 478,084, June 20, 1929; Cent. 1929, II 1216; [C.A. 23, 4228 (1929)]. (60) The Selden Co., Swiss 87,961, Jan. 17, 1921; Cent. 1921, IV 354; not in C.A.
- (61) Imperial Chem. Ind., Ltd., and Wheeler, Brit. 378,866, Sept. 15, 1932; Cent. 1933, II 936; [C.A. 27, 3947 (1933)]. (62) Conklin (to Solvay Process Co.), U.S. 1,828,858 + 1,828,859, Oct.

1931; Cent. 1932, I 1575; [C.A. 26, 632 (1932)]. (63) Kyrides (to National Aniline Co.), U.S. 1,733,268, Oct. 29, 1929; Cent. 1936, I 3831; C.A. 24, 382 (1930). (64) Perrot, Compt. rend. 196, 1424-1425 (1934). (65) Moyer (to Solvay Process Co.), U.S. 2,152,357, March 28, 1939; Cent. 1939, II 1775; [C.A. 33, 5001 (1939)]. (66) Coleman, Noyes, J. Am. Chem. Soc. 43, 2215-2216 (1921). (67) Clark, Chem. News 143, 265-267 (1931); Cent. 1932, I 1359; C.A. 26, 1591 (1932). (68) Cannizzaro, Ann. 88, 130 (1853). (69) Norris, Am. Chem. J. 38, 638-639 (1907). (70) Imperial Chem. Ind., Ltd., and Bennett, Dodd, and Sprent, Brit. 334,260 + 334,261, Sept. 25, 1930; Cent. 1931, I 158; C.A. 25, 973 (1931).

(71) Halford, Reid, J. Am. Chem. Soc. 63, 1873-1878 (1941).
(72) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929).
(73) Carré, Libermann, Compt. rend. 198, 274 (1934).
(74) Huston, J. Am. Chem. Soc. 46, 2778 (1924).
(75) Thiele, Dont, Ann. 302, 257 (1898),
(76) Bergmann, Zervas, Ber. 65, 1195 (1932).
(77) Durrans, J. Chem. Soc. 123, 1424-1425 (1923).
(78) Whitmore, Langlois, J. Am. Chem. Soc. 55, 1519-1520 (1933).
(79) Elliott, Speakman, J. Chem. Soc. 1940, 643-644.
(80) Solonina, J. Russ. Phys.-Chem. Soc. 30, 431-439 (1898); Cent. 1898, II 887.

(81) Solonina, J. Russ. Phys.-Chem. Soc. 30, 822-825 (1898); Cent. 1899, I 254.
(82) Wieland, Schamberg, Ber. 53, 1330, 1334 (1920).
(83) O. Silberrad, C. A. Silberrad, B. Parke, J. Chem. Soc. 127, 1244-92450.
(1925).
(85) Firth, Smith, J. Chem. Soc. 1936, 337-339.
(86) Lubs, Clark, J. Am. Chem. Soc. 40, 1449-1453 (1918).
(87) Tsypin, Chekalina, Org. Chem. Ind. (U.S.S.R.) 6, 504-506 (1939);
(CA. 34, 2288 (1940).
(88) Vandevelde, Bull. acad. roy. Belg. (3) 34, 894-920 (1897); Cent. 1898, I 438.
(89) Löb, Ber. 36, 3060 (1903).
(90) Staudinger, Kupfer, Ber. 44, 2195 (1911).

(91) Meyer, Hofmann, Monatsh. 38, 157 (1917).
(92) Shriner, Berger, J. Org. Chem. 6, 305–317 (1941).
(93) Jacobson, J. Am. Chem. Soc. 54, 1513–1518 (1932).
(94) Dermer, Hooper, J. Am. Chem. Soc. 63, 3525–3526 (1941).
(95) Fisher, Eisner, J. Org. Chem. 6, 169–173 (1941).
(96) Olivier, Wick, Rec. trav. chem. 57, 1117–1124 (1938).
(97) Smythe, J. Chem. Soc. 121, 1270–1279 (1922).
(98) Busch, Stöve, Ber. 49, 1068 (1916).
(99) Kelber, Ber. 50, 308 (1917).
(100) Borsche, Heimburger, Ber. 48, 457 (1915).

(101) C. Ingold, E. Ingold, J. Chem. Soc. 1928, 2259. (102) Tommasi, Ber. 7, 826 (1874). (103) Busch, Weber, J. prakt. Chem. (2) 146, 48-49 (1936). (104) Busch, Weiss, Ber. 33, 2702-2703 (1900). (105) Korczynski, Reinholz, Schmidt, Roczniki Chem. 9, 731-740 (1929); Cent. 1930, I 2075; [C.A. 24, 1858 (1930)]. (106) Muller, Ehrmann, Ber. 69, 2209-2210 (1936). (107). Courtot, Pierron, Compt. rend. 190, 1057 (1930). (108) Kyrides (to Monsanto Chem. Co.), U.S. 1,968,300, July 31, 1934; Cent. 1934, II 3555; [C.A. 28, 5833 (1934)]. (109) Fischer, J. Am. Chem. Soc. 56, 2056-2057 (1934). (110) Etard, Ann. chim. (5) 22, 235-240 (1881).

(111) Lauth, Grimaux, Bull. soc. chm. (2) 7, 106-107 (1867); Ann. 143, 80-82 (1867). (112)
Shorigin, Kizber, Smol'yaninova, J. Applied Chem. (U.S.S.R.) 3, 721-726 (1930); Cent. 1930,
II 3397; C.A. 25, 94 (1931). (113)
Blanc, Ger. 347,583, Jan. 23, 1922; Cent. 1922; II 1138, not in C.A. (114)
Sommelet, Compt. rend. 157, 852 (1913). (115)
Fabriques de Produits de Chimie Organique de Laire, Ger. 268,786, Jan. 2, 1914; Cent. 1914, I 539, not in C.A.; French 452,537,
Mar. 7, 1912; C.A. 7, 3641 (1913). (116)
Shorigin, Kızberg, Troitzkın, Smol'yaninova, J. Chem. Ind. (U.S.S.R.) 6, 258-260 (1929); Cent. 1929, II 730, 2603; C.A. 23, 3680 3681 (1929). (117)
Schorigin, Russian 19,621, Mar. 31, 1931; Cent. 1931, II 2659; not in C.A. (118)
Masson, Hamilton, Ind. Eng. Chem. 20, 814 (1928). (119)
Seyewetz, Trawitz, Compt. rend. 136, 241 (1903). (120)
Olivier, Rec. trav. chrm. 41, 419-421 (1921).

(121) Beilstein, Kuhlberg, Ann. 146, 320-322 (1868). (122) van der Linden, Rec. trav. chim. 57, 1083-1084 (1938). (123) Heble, Nadkarni, Wheeler, J. Chem. Soc. 1938, 1322. (124) Asinger, J. prakt. Chem. (2) 152, 4-5, 7-8 (1939). (125) Pajeau, Compt. rend. 204, 1203 (1937). (126) Srpek, Monatsh. 11, 429,430 (1890). (127) Errera, Gazz. chim. idl. 17, 198-203 (1887). (128) Rohner and Co., Ger. 293,319, July 25, 1916; Cent. 1916, II 359; [C.A. 11, 1884 (1917)]. (129) Soc. Chem. Ind. Basel, Ger. 312,959, June 21, 1919; Cent. 1919, IV 373-374; not in C.A. (130) Conant, Kirner, Hussey, J. Am. Chem. Soc. 47, 498-499 (1925).

(131) Olivier, Rec. trav. chim. 41, 309-311 (1921). (132) Gabriel, Borgmann, Ber. 16, 2066 (1883). (133) Holleman, Vermeulen, Rec. trav. chim. 33, 12-17 (1914). (134) Norrish, Smith, J. Chem. Soc. 1928, 130. (135) Grimaux, Ann. 145, 46-49 (1868). (136) Strakosch, Ber. 6, 1059 (1873). (137) Abelli, Gazz. chim. ital. 13, 97-99 (1883). (138) Noelting, Ber. 17, 385 (1884). (139) Klumpf, Ann. 224, 98-103 (1884). (140) Alway, J. Am. Chem. Soc. 24, 1060-1063 (1902).

(141) Flurscheim, Holmes, J. Chem. Soc. 1928, 1611. (142) Shaw, J. Chem. Soc. 1928, 1278.
(143) van der Linden, Rec. trav. chim. 50, 1105-1110 (1931). (144) Pictet, Khotinsky, Ber. 40, 1165 (1907). (145) Tronov, Bair, J. Russ. Phys.-Chem. Soc. 62, 2337-2345 (1930); Cent. 1931, II 422; C.A. 25, 3973 (1931). (146) Lyman, Reid, J. Am. Chem. Soc. 39, 702 (1917). (147)

Lyons, Reid, J. Am. Chem. Soc. 39, 1730 (1917). (148) Bither, Sturtevant, Thomas, J. Am. Chem. Soc. 67, 1562-1566 (1945). (149) Escales, Ber. 37, 3599 (1904). (150) Friedländer, Cohn. Monatsh. 23, 545-548 (1902).

(151) Niederist, Ann. 196, 353-354 (1879). (152) von Braun, Moldaenke, Ber. 56, 2169 (1923). (153) Harker, J. Chem Soc. 125, 500-511 (1924). (154) Benrath, Ann. 382, 223 (1911). (155) Lloyd, Kennedy, U.S. 1,849,844, Mar. 15, 1932; Cent. 1932, I 2994; [C.A. 26, 2747 (1932)]. (156) Yamasaki, Titani, Bull. Chem. Soc. Japan 9, 503 (1934). (157) Meunier, Bull. soc. chim. (2) 38, 159-160 (1882). (158) Pospiech (to Chem. Fabrik Pott and Co.), Ger. 484,662, Oct. 23. 1929; Cent. 1930, I 1051; C.A. 24, 1125 (1930). (159) Klever, French 462,438, Sept. 10, 1913; C.A. 8, 2781 (1914); Brit. 20,505, Sept. 10, 1913; C.A. 9, 694 (1915). (160) Gomberg, Buchler. J. Am. Chem. Soc. 42, 2059-2072 (1920).

(161) Rosenberg (to National Oil Products Co.), U.S. 2,221,882, Nov. 19, 1940; C.A. 35, 1411 (1941). (162) Gavankar, Heble, Wheeler, J. Univ. Bombay 6, Pt. II, 112-113 (1937); Cent. 1938, I 4610; [C.A. 32, 3757 (1938)]. (163) Olivier, Rec. trav. chim. 53, 891-894 (1934). (164) Olivier, Berger, Rec. trav. chim. 41,637-640 (1921). (165) Olivier, Rec. trav. chim. 41,304 (1921). (166) Olivier, Rec. trav. chrm. 48, 234 (1929). (167) Olivier, Rec. trav. chrm. 49, 697-704 (1930). (168) Moelwyn-Hughes, J. Chem. Soc. 1932, 102. (169) Titani, Kurano, Bull. Chem. Soc. Japan 6, 152-162 (1931). (170) Heble, Wheeler, Proc. Indian Acad. Sci. A-7, 411-415 (1938).

(171) Marcker, Ann. 136, 75-78, 88-89 (1865). (172) Scheibler, Voss, Ber. 53, 382-383 (1920). (173) Hoffman, Reid, J. Am. Chem. Soc. 45, 1833 (1923). (174) Leaper (to National Aniline and Chem. Co.), U.S. 1,842,414, Jan. 26, 1932; Cent. 1932, I 1829; [C.A. 26, 1618 (1932)]. (175) Olin, Deger (to Sharples Chemicals, Inc.), U.S. 2,349,191, May 16, 1944, C.A. 39, 710 (1945). (176) Fallow, Signaigo (to du Pont Co.), U.S. 2,402,613, June 25, 1946; C.A. 40, 5759 (1946). (177) Wertheim, J. Am. Chem. Soc. 51, 3661-3664 (1929). (178) Kilmer, du Vigneaud, J. Buol. Chem. 154, 248, 250 (1944). (179) Shriner, Struck, Jorison, J. Am. Chem. Soc. 52, 2066-2068 (1930). (180) Lewin, J. prakt. Chem. (2) 118, 286 (1928).

(181) Smythe, J. Chem. Soc. 121, 1400-1405 (1922). (182) Knoll, J. prakt. Chem. (2) 113, 45 (1926). (183) Lewin, J. prakt. Chem. (2) 119, 213-214 (1928). (184) Smythe, J. Chem. Soc. 101, 2079-2080 (1912). (185) Bost, Turner, Norton, J. Am. Chem. Soc. 54, 1986-1987 (1932). (186) Blaksma, Rec. trav. chim. 20, 137 (1901). (187) Moran, Crandall (to Socony-Vacuum Oil Co), U.S. 2,113,092 and 2,113,093, Apr. 5, 1938; Cent. 1938, II 414-415, C.A. 32, 4178 (1938). (188) Wojcik (to Hooker Electrochemical Co.), U.S. 2,185,007, Dec. 26, 1939; C.A. 34, 2865 (1940). (189) Bergmann, Hervey, Ber. 62, 914 (1929). (190) Elliott, Speakman, J. Chem. Soc. 1940, 645, 648.

(191) Hofmann, Ber. 20, 15 (1887). (192) Fromm, de Seixas Palma, Ber. 39, 3312-3316 (1906). (193) Hinsberg, Ber. 41, 2839 (1908). (194) Bohler, Ann. 154, 50-55 (1870). (195) Mohr, Ann. 221, 215-216 (1883). (196) Vogt, Henninger, Ann. 165, 375-376 (1873). (197) Davies, Dick, J. Chem. Soc. 1932, 484. (198) Turckiewicz, St. Pilat, Ber. 71, 285 (1938). (199) Johnson, Ambler, J. Am. Chem. Soc. 36, 381 (1914). (200) Dodge, J. Am. Chem. Soc. 58, 437-438 (1936).

(201) Lee, Dougherty, J. Org. Chem. 5, 84 (1940). (202) Otto, Luders, Ber. 13, 1286-1287 (1880). (203) Lampricht, von Pechmann, Ber. 6, 534-535 (1873). (204) Kostsova, J. Gen. Chem. (U S S.R.) 11, 63 66 (1941); C.A. 35, 5462 (1941). (205) C. K. Ingold, E. H. Ingold, F. R. Shaw, J. Chem. Soc. 1927, 819. (206) Purgotti, Gazz. chim ital. 20, 25-27 (1890). (207) Hess, Leaper (to Barrett Co.), U.S. 1,729,615, Oct. 1, 1929; Cent. 1930, I 436; C.A. 23, 5474 (1929). (208) Snyder, Speck, J. Am. Chem. Soc. 61, 670 (1939). (209) Douglass, Johnson, J. Am. Chem. Soc. 60, 1488 (1938). (210) Dougherty, Barth (to Heyden Chemical Corpn.), U.S. 2,293,971, Aug. 25, 1942; C.A. 37, 889 (1943).

(211) Steinkopf, Bessaritsch, J. prakt. Chem. (2) 109, 243, Note 1 (1925). (212) Coleman, Hauser, J. Am. Chem. Soc. 50, 1194-1196 (1928). (213) Whitmore, Thurman, J. Am. Chem. Soc. 51, 1497 (1929). (214) Spath, Monatsh. 34, 1995 (1913). (215) Kumpf, Ann. 224, 126-128 (1884). (216) Fischer, Ber. 48, 101 (1915). (217) Conant, Kirner, Hussey, J. Am. Chem. Soc. 47, 587-589 (1925). (218) van Duin, J. Am. Chem. Soc. 47, 585-587 (1925). (219) Nef, Ann. 309, 171-172 (1899). (220) Baker, Nathan, J. Chem. Soc. 1936, 240.

(221) Nabar, Wheeler, Proc. Indian Acad. Sci. A-2, 265-278 (1935). (222) Nabar, Wheeler, Proc. Indian Acad. Sci. A-4, 91-96 (1936). (223) Holleman, Rec. trav. chim. 13, 403-410 (1894). (224) van Raalte, Rec. trav. chim. 18, 383-387 (1899). (225) Neogi, Adhicary, Z. anorg. Chem. 69, 270-272 (1910). (226) Konowalow, Ber. 28, 1861 (1895). (227) Gabriel, Ber. 18, 1254 (1885). (228) Holleman, Rec. trav. chim. 14, 121 (1895). (229) Sherrill, J. Am. Chem. Soc. 46, 2757 (1924). (230) Wislicenus, Endres, Ber. 35, 1760 (1902).

(231) Baker, Ingold, J. Chem. Soc. 1926, 2467. (232) Black, Babers, Org. Syntheses, Coll. Vol. 2 (1st ed.), 512-515 (1943); 19, 73-76 (1939). (233) von Auwers, Ottens, Ber. 57, 458 (1924). (234) Curtius, Ehrhart, Ber. 55, 1565-1567 (1922). (235) Wohl, Oesterlin, Ber. 33, 2741 (1900). (236) Curtius, Darapsky, J. prakt. Chem. (2) 63, 433 (1901). (237) Philip, J. Chem. Soc. 93. 919 (1908). (238) Perkin, J. Chem. Soc. 69, 1208 (1896). (239) Baillie, Tafel, Ber. 32, 71 (1899). (240) Walden, Z. physik. Chem. 70, 579 (1910).

(241) Ssachanow, Prsheborowski, Z. Elektrochem. 20, 40 (1914); Cent. 1914, I 602. (242) Curtius, Boetzelen, J. prakt. Chem. (2) 64, 322 (1901). (243) Dunstan, Hilditch, Thole, J. Chem. Soc. 163, 141 (1913). (244) Brühl, Z. physik. Chem. 16, 216-218 (1895). (245) Hoogewerff, van Dorp, Rec. trav. chim. 5, 253 (1886). (246) Frankland, J. Chem. Soc. 99, 1779 (1911). (247) Jerusalem, J. Chem. Soc. 95, 1283 (1909). (248) Moureu, Lazennec, Bull. soc. chim. (3) 35, 1183 (1906). (249) Buehler, Currier, Lawrence, Ind. Eng. Chem., Anal. Ed. 5, 277 (1933). (250) Noller, Liang, J. Am. Chem. Soc. 54, 672 (1932).

(251) Neber, Uber, Ann. 467, 61 (1928). (252) Limpricht, Ann. 144, 313-314 (1867). (253) Smirnow, J. Russ. Phys.-Chem. Soc. 43, 12 (1911); Cent. 1911, I 1683. (254) Timmermans, Bull. soc. chim. Belg. 30, 69 (1921). (255) Jaeger, Z. anorg. Chem. 101, 151 (1917). (256) von Braun, Ber. 70, 983 (1937). (257) Mussell, Thole, Dunstan, J. Chem. Soc. 101, 1014 (1912). (258) Curtius, J. prakt. Chem. (2) 62, 99 (1900). (259) Scheibler, Beiser, Cobler, Schmidt, Ber.

67, 1511-1512 (1934). (260) Mailhe, Ann. chim. (9) 13, 189 (1920).

(261) Wegler, Frank, Ber. 69, 2075 (1936). (262) Limpricht, Ann. 144, 307-313 (1867). (263) Spica, Gazz. chim. ital. 10, 515 (1880). (264) Darzens, Compt. rend. 208, 1504 (1939). 265) Barbieri, Heard, U.S. 2,113,640, April 12, 1938; Cent. 1938, II 413; [C.A. 32, 4174 (1938)]. [266] McKee, Bahner, U.S. 2,164,587, July 4, 1939; Cent. 1939, II 3193; [C.A. 33, 8211 (1939)]. (267) Limpricht, Ann. 144, 305-307 (1867). (268) Cannizzaro, Bull. soc. chim. (2) 2, 126 (1864); Ann. 134, 128 (1865); Ann. Suppl. 4, 24-27 (1866). (269) Mason, J. Chem. Soc. 63, 1311-1314 (1893). (270) Dhommée, Compt. rend. 133, 636 (1903).

(271) Seelig, Ber. 23, 2971-2972 (1890). (272) Gabriel, Ber. 20, 2227 (1887). (273) Herzberg, Lange (to I.G.), Ger. 442,774, April 7, 1927; French 610,830, Sept. 14, 1926; Cent. 1927, II 505-506; not in C.A. (274) Herzberg, Lange, Ger. 462,652, July 17, 1928; Cent. 1929, I 2236; not in C.A. (275) Letts, Ber. 5, 90-94 (1872). (276) Strakosch, Ber. 5, 692-699 (1872). (277) Ladenburg, Struve, Ber. 10, 46-47 (1877). (278) Rudolph, Ber. 12, 1297-1298 (1879). (279) Delépine, Compt. rend. 124, 292 (1897); Bull. soc. chim. (3) 17, 293-297 (1897). (280) Matter, Ger. 301,450, Oct. 22, 1917; Cent. 1918, I 53; C.A. 13, 324 (1919).

(281) Schramm, Ber. 16, 2184-2185 (1883). (282) Walder, Ber. 19, 1626-1631 (1886). (283) Behrend, Leuchs, Ann. 257, 216-222 (1890). (284) Haase, Wolffenstein, Ber. 37, 3235 (1904). (285) Gambarjan, Cialtician, Ber. 60, 391 (1927). (286) Jones, Fleck, J. Am. Chem. Soc. 50, 2024 (1928). (287) Neubauer, Ann. 298, 200 (1897). (288) Behrend, Leuchs, Ann. 257, 214, 235 (1890). (289) Beckmann, Ber. 22, 516 (1889). (290) Busch, Weiss, Ber. 33, 2702-2703 (1900).

(291) Pascal, Bull. soc. chim. (4) 15, 456 (1914). (292) Kenner, Wilson, J. Chem. Soc. 1927, (293) Curtius, J. prakt. Chem. (2) 62, 92-93 (1900). (294) Schlubach, Goes, Ber. 55, 2890, 2900 (1922). (295) Cannizzaro, Rossi, Ann. 121, 250-251 (1862). (296) Stelling, Fittig, Ann. 137, 258-260 (1866). (297) Comey, Ber. 23, 1115 (1890). (298) Dains, Brewster, J. Am. Chem. Soc. 42, 1578 (1920). (299) Dean, Berchet, J. Am. Chem. Soc. 52, 2824 (1930). (300) Onufrowicz. Ber. 17, 836-837 (1884).

(301) Ray, Dutt. J. Indian Chem. Soc. 5, 107-108 (1928). (302) Paneth. Lautsch. J. Chem. Soc. 1935, 382. (303) Keiser, McMaster, J. Am. Chem. Soc. 32, 388-391 (1910). (304) Hell, Ber. 37, 453-458 (1904); Ber. 38, 1682 (1905). (305) Klages, Heilmann, Ber. 37, 1449 (1904). (306) Klages, Ber. 38, 2220 (Note 5) (1905). (307) Gilman, McCracken, J. Am. Chem. Soc. 45, 2462-2466 (1923). (308) Gilman, Zoellner, Dickey, J. Am. Chem. Soc. 51, 1585 (1929). (309) Houben, Boedler, Fischer, Ber. 69, 1783 (1936). (310) H. Gilman, E. L. St. John, N. B. St. John, Rec. trav. chim. 48, 593-596 (1929).

(311) Gilman, Vanderwal, Bull. soc. chim. (4) 45, 348, 641-644 (1929). (312) Gilman, Zoellner, J. Am. Chem. Soc. 53, 1581-1583 (1929). (313) Gilman, McCracken, Rec. trav. chim. 46, 463-472 (1937). (314) H. Gilman, E. L. St. John, Bull soc. chim. (4) 45, 1091-1095 (1929). (315) Gilman, Catlin, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 471-473 (1941); (1st ed.), 458-460 (1932); 4, 59-61 (1925). (316) Adkins, Zartman, Org. Syntheses, Coll. Vol. 2 (1st ed.), 606-607 (1943); 17, 89-90 (1937). (317) Oldham, Ubbelohde, J. Chem. Soc. 1938, 202-204. (318) Gilman, Kirby, J. Am. Chem. Soc. 51, 1571-1576 (1929). (319) Mikhailenko, Protasova, J. Russ. Phys.-Chem. Soc. 53, I 347-349 (1921); Cent. 1923, III 1014; C. A. 18, 2338 (1924).. (320) Gasopoulos, Praktika Akad. Athenon 7, 180-183 (1932); Cent. 1933, II 534; C.A. 28, 4726 (1934).

(321) Bouveault, Bull. soc. chim. (3) 29, 1053-1054 (1903). (322) Ivanoff, Bull. soc. chim (4) 39, 53 (1926). (323) Hilpert, Grüttner, Ber. 48, 913-914 (1915). (324) Pope, Gibson. J. Chem. Soc. 101, 735 (1912). (325) Jones, Werner, J. Am. Chem. Soc. 40, 1266 (1918). (326) Wolff, Ber. 46, 64-66 (1913). (327) Garcia-Banus, Anales soc. españ. fis. quím. 20, 667-668 (1922): Cent. 1923, III 1265; C.A. 17, 2109 (1923). (328) Hardtmann (to I.G.), Ger. 466,364, Oct. 5, 1928; Cent. 1929, I 3010; [C.A. 23, 2187 (1929)]. (329) Coleman, Forrester, J. Am. Chem. Soc. 58, 27-28 (1936). (330) Coleman, Soroos, Yager, J. Am. Chem. Soc. 55, 2075-2080 (1933).

(331) Coleman, Buchanan, Paxson, J. Am. Chem. Soc. 55, 3669-3672 (1933). (332) Gilman, Kirby, J. Am. Chem. Soc. 54, 345-355 (1932). (333) Austin, Johnson, J. Am. Chem. Soc. 54, 647-660 (1932). (334) Johnson, J. Am. Chem. Soc. 55, 3029-3032 (1933). (335) Whitmore, Sloat, J. Am. Chem. Soc. 64, 2968-2970 (1942). (336) Medoks, J. Gen. Chem. (U.S.S.R.) 8. 291-293 (1938); Cent. 1939, I 4934; [C.A. 32, 5392 (1938)]. (337) Soshestvenskaya, J. Gen. Chem. (U.S.S.R.) 8, 294-297 (1938); C.A. 32, 5392 (1938). (338) Kharasch, Weinhouse, J. Org. Chem. 1, 209-230 (1937). (339) Fischer, Stoffers, Ann. 500, 266 (1933). (340) Houben, Kesselkaul, Ber. 35, 2523 (1902).

(341) Reichstein, Cohen, Ruth, Meldahl, Helv. Chim. Acta 19, 414-415 (1936). (342) Grignard. Bull. soc. chim. (3) 29, 953-954 (1903). (343) Tiffeanu, Delange, Compt. rend. 137, 573-574 (1903). (344) Gerrard, Kenyon, J. Chem. Soc. 1928, 2564. (345) Schmidlin, Garcia-Banus, Ber. 45. 3193-3205 (1912). (346) Garcia-Banus, Anales soc. españ. fís. quím. 26, 372-398 (1928); Cent. 1929, II 1412-1414; C.A. 23, 2178-2180 (1929). (347) Grignard, Compt. rend. 130, 1324 (1900); Ann. chim. (7) 24, 471-472 (1901). (348) Hell, Wiegandt, Ber. 37, 1429-1431 (1904). (349) Gilman, Fothergill, J. Am. Chem. Soc. 51, 3155, 3157 (1929). (350) Madinaveitia, Bull.

soc. chim. (4) 25, 604 (1919).

(351) Muller, Deut. Parfum. Ztg. 17, 498 (1931); Cent. 1932, I 811-812; C.A. 26, 3785 (1932). (352) F. Bayer and Co., Ger. 154,658, Oct. 17, 1904; Cent. 1904, II 1355. (353) Bottomley. Lapworth, Walton, J. Chem. Soc. 1930, 2215-2216. (354) Ranedo, Anales soc. españ. fis. quim. 16, 351-354 (1918); C.A. 13, 2514-2515 (1919). (355) Houben, Ber. 36, 3088-3089 (1903). (356) Gilman, Fothergill, J. Am. Chem. Soc. 51, 3506 (1929). (357) Hepworth, Clapham. J. Chem. Soc. 119, 1193 (1921). (358) Gilman, Beaber, J. Am. Chem. Soc. 47, 523 (1925). (359) Gilman, Hoyle, J. Am. Chem. Soc. 44, 2625 (1922). (360) Gilman, Robinson, Org. Syntheses, Coll. Vol. 2 (1st ed.), 47-48 (1943); 10, 4-5 (1930).

(361) Gilman, Heck. J. Am. Chem. Soc. 50, 2228 (1928). (362) Rossander, Marvel, J. Am. Chem. Soc. 50, 1491-1496 (1928). (363) Zincke, Ann. 159, 374-376 (1871); Ber. 6, 119-122 (1873). (364) Chakrabarty, Dutt. J. Indian Chem. Scc. 5, 516 (1928). (365) Lal. Dutt. J. Indian Chem. Soc. 12, 392-394 (1935). (366) Hartman, Phillips, Org. Syntheses, Coll. Vol. 2 (1st ed.), 232-234 (1943); 14, 34-35 (1934). (367) Hirst, Cohen, J. Chem. Soc. 67, 826-829 (1895). (368) Radziewanowski, Ber. 28, 1136, 1139 (1895). (369) Friedel, Crafts, Ann. chim.

(6) 1, 477-484 (1884). (370) Friedel, Balsohn, Bull. soc. chim. (2) 33, 337 (1880).

(371) Lavaux, Lombard, Bull. soc. chim. (4) 7, 540-541 (1910); Ann. chim. (8) 20, 477-481 (1910). (372) Olivier, Rec. trav. chrm. 45, 817-818 (1926). (373) Norris, Klemka, J. Am. Chem. Soc. 62, 1434 (1940). (374) Bredereck, Lehmann, Schönfeld, Fritzsche, Ber. 72, 1421-1423 (1939). (375) Stadnikoff, Kaschtanoff, Ber. 61, 1390 (1928). (376) Krishnamurti, J. Madras Univ. 1928, 5 pp. (preprint); Cent. 1929, I 2156; C.A. 23, 2164 (1929). (377) Zonew, J. Russ. Phys.-Chem. Soc. 48, 567-568 (1916); Cent. 1923, I 1498; not in C.A. (378) Kashtanov, J. Gen. Chem. (U.S.S.R.) 2, 515-523 (1932); Cent. 1933, I 600; C.A. 27, 975 (1933). (379) Schroeter, Ann. 418, 198-199 (1919). (380) Lecher, Ger. 281,802, Jan. 27, 1915; Cent. 1915, I 281; [C.A. 9, 2292 (1915)].

(381) Simons, Archer, J. Am. Chem. Soc. 61, 1522 (1939). (382) Zincke, Ann. 161, 93-98 (1872). (383) Plascuda, Zincke, Ber. 6, 906-910 (1873). (384) Weber, Zincke, Ber. 7, 1153-1157 (1874). (385) Steele, J. Chem. Soc. 83, 1486-1489 (1903). (386) Martin, Pizzolato. McWaters, J. Am. Chem. Soc. 57, 2584-2589 (1935). (387) Montagne, Ann. chim. (10) 13, 108-110 (1930). (388) Zincke, Ber. 5, 799 (1872). (389) Zincke, Blatzbecker, Ber. 9, 1761 (1876).

(390) Louise, Ann. chim. (6) 6, 176-180 (1885).

(391) Nenitzescu, Isacescu, Ionescu, Ann. 491, 217-218 (1931). (392) Goldschmiedt. Monatsh. 2, 432-437 (1881). (393) Sharma, Dutt, J. Indian Chem. Soc. 12, 774-778 (1935). (394) Froté, Compt. rend. 76, 639 (1872). (395) Miguel, Bull. soc. chim (2) 26, 2-6 (1876). (396) Roux, Ann. chim. (6) 12, 323-331 (1887). (397) Dziewonski, Dziecielewski, Bull. intern. acad. polon. sci. 1927-A, 273-286; Cent. 1928, I 57; C.A. 22, 2164 (1928). (398) Vincent, Roux, Bull. soc. chim. (2) 40, 163-166 (1883). (399) Dziewonski, St. Wodelski, Roczniki Chem. 12, 366-377 (1932); Bull. intern. acad. polon. sci. 1932-A, 115-127; Cent. 1933, I 774; C.A. 27, 2145 (1933). (400) Price, Ciskowski, J. Am. Chem. Soc. 60, 2502 (1938).

(401) Sintenis, Ann. 161, 334-337 (1872). (402) Bacon, Philippine J. Sci. 3, 65-86 (1907); Cent. 1908, II 947. (403) Sah, Lei, Science Repts. Natl. Tsing Hua Univ. A-1, 193-195 (1932). (404) Kahovec, Reitz, Monatsh. 69, 372 (1936). (405) Ipatieff, Burwell, J. Am. Chem. Soc. 63, 970 (1941). (406) Baril, Megrdichian, J. Am. Chem. Soc. 58, 1415 (1936). (407) Rojahn, Schulten, Ber. 59, 500 (1926). (408) White, Morrison, Anderson, J. Am. Chem. Soc. 46, 964 (1924). (409) Chelintzev, Pavlov, J. Russ. Phys.-Chem. Soc. 45, 295 (1913); Cent. 1913, I 1962;
 [C.A. 7, 2227 (1913)]. (410) Semikhatova, Geskin, Gurevich, Ditkovskaya, Nauch. Zapiski

Dnepropetrovsk. Gosudarst. Univ. 15, 135-143 (1940), C.A. 37, 6527 (1943).

(411) von Halban, Gast, Z. physik. Chem. 91, 597-598 (1916). (412) Franzen, J. prakt. Chem. (2) 97, 82-83 (1918). (413) Monacelli, Hennion, J. Am. Chem. Soc. 63, 1723 (1941). (414) Malkiel, Mason, J. Org. Chem. 8, 199-204 (1943). (415) Love, Ann. 241, 374-376 (1887). (416) Bayer and Co., Ger. 343,930, Nov. 11, 1921, Cent. 1922, II 700; C.A. 17, 1242-1243 (1923). (417) Van Dusee, Adkins, J. Am. Chem. Soc. 57, 149-150 (1935). (418) Staedel, Ann. 217, 43-49 (1883). (419) Claisen, Ann. 442, 237 (1925). (420) van Alphen, Rec. trav. chim. 46, 804 (1927).

(421) Short, Stewart, J. Chem. Soc. 1929, 553-559.
(422) Powell, Adams, J. Am. Chem. Soc. 42, 5056 (1920).
(423) McMaster, Bruner, Ind. Eng. Chem. 28, 505-500 (1936).
(424) Lal, Dutt, J. Indian Chem. Soc. 9, 567-568 (1932).
(425) Huston, J. Am. Chem. Soc. 46, 2778 (1924).
(426) Paterno, Gazz. chim. ital. 2, 2-3 (1872); Ber. 5, 288 (1872).
(427) Paterno, Fileti, Gazz. chim. ital. 3, 121-123 (1873), Ber. 6, 757 (1873).
(428) Rennie, J. Chem. Soc. 41, 34, 220 (Note) (1822).
(429) Zincke, Walter, Ann. 334, 373 (1904).
(430) Bakunin, Gazz. chim. ital. 33, II
454-457 (1903).

(431) Å.G.F.A., Ger. 17,311, July 10, 1881; Friedlander 1, 22 (1888). (432) Liebmann, Ger. 18,977, Sept. 30, 1881; Friedlander 1, 23 (1888). (433) Liebmann, Ber. 15, 152-153 (1882). (434) Andrianov, J. Gen. Chem. (U.S.S. R.) 6, 846-851 (1936); Cent. 1937, I 1930; C.A. 30, 6718-6719 (1936). (435) Andrianov, Russ. 48,217, Aug. 31, 1936, Cent. 1937, II 289; not in C.A. (436) Claisen, Ger. 412,169, April 15, 1925; Cent. 1925, II 94; not in C.A. (437) Claisen, Z. angew. Chem. 36, 478 (1923). (438) Akimoff (to Monsanto Chem. Co.), U.S. 2,016,848, Oct. 8, 1935; Cent. 1936, I 3014, C.A. 29, 8008 (1935). (439) Paterno, Gazz. chim. ital. 1, 589-590 (1871). (440) Goldschmidt, Larsen, Z. physik. Chem. 48, 428-430 (1904).

(441) Spath, Monatsh. 34, 2007 (1913). (442) Klages, Allendorff, Ber. 31, 1002 (1898). (443) Cannizzaro, Ann. 96, 247 (1855). (444) Radzıszewski, Ber. 3, 198 (1870). (445) Mann, Ber. 14, 1645 (1881). (446) Staedel, Ber. 19, 1950 (1886). (447) Rosenmund, Luxat, Tiedemann, Ber. 56, 1956–1957 (1923). (448) Adams, Thal, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 107–109 (1941); (1st ed.), 101–103 (1932); 2, 9–11 (1922). (449) Berthelot, Petit, Ann. chim. (6) 18, 124

(1889). (450) Walden, Z physik. Chem. 70, 575 (1910).

(451) Walden, Z. physik. Chem. 73, 261 (1910).
(452) Walden, Z. physik. Chem. 65, 138 (1999).
(453) Bruhl, Z. physik. Chem. 16, 218-219 (1895).
(454) Turner, Merry, J. Chem. Soc. 97, 2075 (1910).
(455) Walden, Z. physik. Chem. 59, 394 (1907).
(456) Johnson, Org. Syntheses 18, 89 (1936).
(457) Seelig, J. prakt. Chem. (2) 39, 162-164 (1889); Ger. 41,507, Jan. 8, 1887; Friedlander 1, 577 (1888).
(458) Wassmuth (to F. Bayer and Co.), Ger. 387,453, Dec. 28, 1923; Cent. 1924, II 403; not in C A.
(459) Bodroux, Bull. soc. chim. (3) 21, 288-289 (1899).
(460) Conrad, Hodgkinson, Ann. 193, 298-299, 311-312, 317-318 (1878).

(461) Klover, Brit. 20,504, Sept. 10, 1913; C.A. 9, 694 (1915). (462) Rueggeberg, Ginsburg, Frantz, Ind. Eng. Chem. 38, 207-211 (1946). (463) Dolique, Ann. chim. (10) 15, 445 (1931).
(464) Leuchs, Ber. 44, 1509 (1911). (465) Marvel, Org. Syntheses 21, 99 100 (1941). (466) Conrad, Ann. 204, 174-175 (1880). (467) Wislicenus, Munzesheimer, Ber. 31, 555 (1898).
(468) Vogel. J. Chem. Soc. 1928, 1019. (469) Brewin, Turner, J. Chem. Soc. 1930, 503. (470)

Fittig, Röders, Ann. 256, 91-92 (1890).

(471) Ramart-Lucas, Papadakis, Ann. chim. (10) 18, 53-54 (1932). (472) Wojick, Adkins, J. Am. Chem. Soc. 56, 2425 (1934). (473) Snyder, Smith, Stewart, J. Am. Chem. Soc. 66, 200-204 (1944). (474) Gardner, Rydon, J. Chem. Soc. 1938, 43. (475) Wallingford, Homeyer, Jones, J. Am. Chem. Soc. 63, 2058 (1941). (476) Wallingford, Homeyer (to Mallinckrodt Chem. Works), U.S. 2,367,632, Jan. 16, 1945, C.A. 39, 4333 (1945). (477) Vavon, Ducasse, Bull. soc. chim. (5) 10, 325-329 (1943); C.A. 38, 4504 (1944). (478) Billmann, Madson, Ann. 402, 337 (1914). (479) Fichter, Schiess, Ber. 34, 1998 (1901). (480) Norris, Tucker, J. Am. Chem. Soc. 55, 4700 (1933).

(481) Jakubowicz, Z. anorg. allgem. Chem. 121, 117-119 (1922). (482) Lellmann, Schleich, Ber. 20, 439 (1887). (483) Maxim, Bull. soc. chm. (4) 39, 1024-1029 (1926). (484) Lund, Hansen, Voigt, Kgl. Danske Videnskab. Selskab. Math.-Fys. Mcdd. 12, No. 9, 23 pp. (1933); Cent. 1934, I 1961-1963; C.A. 28, 2333 (1934). (485) Leuchs, Radulescu, Ber. 45, 194 (1912). (486) Thomas, Rec. trav. chim. 6, 87-88 (1887). (487) Krollpfeiffer, Rosenberg, Ber. 69, 470 (1936). (488) Dolique, Ann. chim. (1) 15, 464-465 (1931). (489) Ehrlich, Ann. 187, 11-15, 24-26 (1877). (490) Conrad, Bischoff, Ann. 204, 179-180 (1880).

(491) Fichter, Alber, J. prakt. Chem. (2) 74, 334 (1906). (492) Breslow, Hauser, J. Am. Chem. Soc. 62, 2388 (1940). (493) Fittig, Christ, Ann. 268, 122-124 (1892). (494) Tafel, Jürgens, Ber. 42, 2556 (1909). (495) Heilbron, Heslop, Irving, Wilson, J. Chem. Soc. 1931, 1338. (496)

Meerwein, Ann. 398, 249 (1913). (497) Leuchs, Heller, Hoffmann, Ber. 62, 875 (1929). (498) von Auwers, Dersch, Ann. 462, 121 (1928). (499) Schlenk, Bergmann, Ann. 463, 48-49 (1928). (500) Hill, J. Chem. Soc. 1926, 956.

(501) Mills, Akers, J. Chem. Soc. 127, 2476-2477 (1925). (502) Fleischer, Ann. 138, 225-230 (1866). (503) Nolan, Clapham, J. Soc. Chem. Ind. 44, 220-221 T (1925); Cent. 1925, II 394: C.A. 19. 2194 (1925). (504) Desai, J. Indian Inst. Sci. 7, 235-251 (1924); Cent. 1925, I 1297; C.A. 19, 2645 (1925). (505) Rivier, Schalch, Helv. Chim. Acta 6, 608-609 (1923). (506) Willson, Wheeler. Org. Syntheses, Coll. Vol. 1 (2nd ed.), 102-104 (1941); (1st ed.), 97-98 (1932); 8, 38-40 (1928). (507) Britton, Slagh (to Dow Chem. Co), U.S. 1,887,228, Nov. 8, 1932; Cent. 1933, I 1515-1516; [C.A. 27, 1360 (1933)] (508) Courtot, Petitcolas, Bull. soc chim. (4) 39, 452-457, 461 (1926). (509) Brand, Ber. 42, 3461-3462 (1909). (510) Tafel, Pfeffermann, Ber. 35, 1513-1514 (1902).

(511) Block, Z. physik. Chem. 82, 412 (1913). (512) Pascal, Normand, Bull. soc. chim. (4) 13, 209-216 (1913). (513) Buehler, Calfee, Ind. Eng. Chem., Anal. Ed. 6, 351-352 (1934). (514) Ritter (to I.G.), Ger. 523,603, April 25, 1931; Cent. 1931, II 3545; [C.A. 25, 3665 (1931)]: French 687,826, Aug. 13, 1930; Cent. 1931, II 3545; [C A. 25, 711 (1931)]. (515) Peacock, J. Chem. Soc. 127, 2177-2180 (1925). (516) Peacock, J. Chem. Soc. 125, 1975-1980 (1924). (517) Hickinbottom, J. Chem Soc. 1937, 1124-1125. (518) Matzudaira, Ber. 20, 1611-1612 (1887). (519) Matter, Ger. 301,832, Oct. 30, 1917; Cent. 1918, I 149, C.A 13, 324-325 (1919). (520) Hinman, Hollmann (to F. Post Co.), U.S. 2,150,832, March 14, 1939, Cent. 1939, I 4681; [C.A. **33.** 4599 (1939)].

(521) Wedekind, Ber. 32, 519-522 (1899). (522) Bischoff, Ber. 31, 2674 (1898). (523) Sudborough, J. Chem. Sec. 109, 1346 (1916). (524) Drumm, O'Connor, Reilly, J. Am Chem. Soc. 62. 1241-1243 (1940). (525) Meisenheimer, Greeske, Willmersdorf, Ber. 55, 520 (1922). (526) Martin, McQueen (to Dow Chem. Co.), U.S. 1,887,772, Nov. 15, 1932; Cent. 1934, II 512-513; [C.A. 27, 1361 (1933)]. (527) Noelting, Jahresber. 1883, 702. (528) Courtot, Dondelinger, Bull. soc. chim. (4) 37, 116 (1925). (529) Meisenheimer, Glawe, Ann. 449, 202 (1926) (530) Singh, J. Chem. Soc. 109, 790 (1916).

(531) Thomson, Stevens, J. Chem. Soc. 1932, 1938. (532) McMeeking, Stevens, J. Chem. Soc. 1933, 349. (533) Komatsu, Mem. Coll. Sci. Eng. Kyoto Imp. Univ 3, 371-426 (1912). Cent. 1913. I 799; [C.A. 7, 1020-1021 (1913)]. (534) Friedlander, Ber 22, 588 (1889). (535) Livingston (to National Andrea and Chem Co.), U.S 1,854,553, April 19, 1932, Cent. 1932, II 442-443; [C.A. 26, 3262 (1932)]. (535) Schultz, Bosch, Ber 35, 1292-1293 (1902). (536) Schultz, Rohde, Bosch, Ann. 334, 236-237 (1904). (537) Blangey, Fierz-David, Stamm, Helv. Chim. Acta 25, 1162-1179 (1942). (538) Schotten, Ber. 15, 423 (1882). (539) Wallach, Huttner, Altonburg, Ann. 343, 73-74 (1905). (540) Baillie, Tafel, Ber. 32, 72, 74 (1899).

(541) Clarke, J. Chem. Soc. 99, 1935 (1911). (542) Clarke, J. Chem. Soc. 101, 1807-1808 (1912). (543) Haase, Wolffenstein, Ber. 37, 3232 (1904). (544) Mason, Zief, J. Am. Chem. Soc. (545) Gabriel, Stelzner, Ber 29, 2386 (1896) (546) Emde, Arch. Pharm. **62**, 1450–1452 (1940). (547) Cromwell, Babson, Harns, J Am. Chem. Soc. 65, 313 (1943). **247.** 358–368 (1909). (548) Zaunschirm, Ann. 245, 280, 282 (1888). (549) Meisenheimer, Ann. 438, 258 (1924). (550)

Young, Robinson, J. Chem. Soc. 1933, 277-278.

(551) Prevost, Cerf de Mauny, Compt. rend. 216, 771-772 (1943). (552) Dobrosserdow. J. Russ. Phys.-Chem. Soc. 43, 124 (1911), Cent. 1911, I 955 (553) Meisenheimer, Denner, Ber. 65, 1801 (1932). (554) Holmes, Ingold, J. Chem. Soc. 127, 1812 1813 (1925). (555) Wegler, Frank, Ber. 69, 2074-2075 (1936). (556) Blicke, Zienty, J. Am. Chem. Soc. 61, 775 (1939). (557) Hughes, Ingold, J. Chem. Soc. 1933, 75. (558) Krafft, Ber. 23, 2781-2782 (1890). (559) Graymore, J. Chem. Soc. 1941, 41. (560) Jackson, Wing, Am. Chem. J. 9, 79-81 (1887).

(561) Emde, Ber. 42, 2590-2593 (1909). (562) Tiffeneau, Fuhrei, Bull. soc. chim. (4) 15, 168 (1914). (563) Collie, Schryver, J. Chem. Soc. 57, 778, 781 (1890). (564) Coleman, J. Am. Chem. Soc. 55, 3004 (1933) (565) King, McMillan, J. Am Chem. Soc. 68, 1469 (1946). (566) Skita, Keil, Ber. 63, 41 (1930). (567) Meyer, Ber. 10, 310-312 (1877). (568) Noelting, Kregczy, Bull. soc. chim. (4) 19, 336 (1916). (569) Emde, Schellbach, Arch. Pharm. 249, 122 (1911).

(570) Ladenburg, Struve, Ber. 10, 40-48 (1877).

(571) Rascanu, Ann. sci. univ. Jassy, Pt. I, 25, 395 424 (1939); Cent. 1939, II 3068; C.A. 34, 394 (1940). (572) Achmatowicz, Perkin, Robinson, J. Chem. Soc. 1932, 500. Kull, Arch. Pharm. 274, 179-180 (1936). (574) Achmatowicz, Lindenfeld, Roczniki Chem. 18, 75-87 (1938); Cent. 1939, II 626; [C.A. 32, 9047 (1938)]. (575) Michler, Gradmann, Ber. 10, 2078-2081 (1877). (576) Izmailskii, Danchev, Russian 33,149, Nov. 30, 1933; Cent. 1934, II 2451; C.A. 29, 2179 (1935). (577) Emde, Arch. Pharm. 249, 106-111 (1911). (578) Straus, Thiel, Ann. 525, 182 (1936). (579) Hol'tsshmidt, Vorob'ev, J. Phys. Chem. (U.S.S.R.) 13, 473-482 (1939); C.A. 34, 1234 (1940). (580) Birkofer, Ber. 75, 436 (1942).

(581) Marvel, Scott, Amstutz, J. Am. Chem. Soc. 51, 3638-3641 (1929). (582) Hofmann, Ber. 14, 1504 (1881). (583) Ferns, Lapworth, J. Chem. Soc. 101, 283 (1912). (584) Magidson, Menschikoff, Ber. 59, 1210 (1926). (585) Hamilton, Adams, J. Am. Chem. Soc. 50, 2262 (1928). (586) Suichev, J. Russ. Phys.-Chem. Soc. 60, 325-330 (1928); Cent. 1930, I 2564; C.A. 23, 1329-1330 (1929). (587) Hamer, Kelly, J. Chem. Soc. 1931, 780. (588) Crook, McElvain, J. Am. Chem. Soc. 52, 4007-4008 (1930). (589) Ruff, Ollendorf, Ber. 32, 3235, Note 2 (1899). (590) Minunni, Gazz. chim. ital. 22, II 217-224 (1892).

(591) Ofner, Monatsh. 25, 593-602 (1904). (592) Milrath, Monatsh. 29, 910, Note 2 (1908). (593) Ponzio, Valente, Gazz. chim. ital. 38, I 520-521 (1908). (594) Michaelis, Philips, Ann. 252, 286-290 (1889). (595) Audrieth, Weisiger, Carter, J. Org. Chem. 6, 418-419 (1941). (596) von Auwers, Wegener, J. prakt. Chem. (2) 106, 244 (1923). (597) Busch, Lang, J. prakt. Chem. (2) 144, 299-301 (1936). (598) Utzinger, Ann. 556, 60-61 (1944). (599) Vavon, Crajcinovic, Compt. rend. 187, 420-422 (1928). (600) Emerson, Shunk, J. Am. Chem. Soc. 63, 2485-2486

(1941).

(601) Underwood, Gale, J. Am. Chem. Soc. 56, 2118-2119 (1934). (602) Schwartz, Johnson, J. Am. Chem. Soc. 53, 1063-1068 (1931). (603) Aggarwal, Das, Ray, J. Indian Chem. Soc. 6, 718 (1929). (604) Crippa, Caracci, Gazz. chim. ital. 69, 136 (1939). (605) Gilman, Furry, J. Am. Chem. Soc. 50, 1214-1216 (1928). (606) Brown, Campbell, J. Chem. Soc. 1937, 1700. (607) Donleavy, J. Am. Chem. Soc. 58, 1004-1005 (1936). (608) Veibel, Lillelund, Bull. soc. chim. (5) 5, 1153-1158 (1938). (609) Chambers, Scherer, Ind. Eng. Chem. 16, 1272-1273 (1924). (610) Manske, Org. Syntheses, Coll. Vol. 2 (1st ed.), 83-84 (1943); 12, 10-11 (1932).

(611) Ing, Manske, J. Chem. Soc. 1926, 2349. (612) Weisz, Lanyi, Magyar Chem. Folyóirat 39, 153-155 (1933); C.A. 28, 5815 (1934). (613) Gabriel, Ber. 20, 2227 (1887). (614) Vanags, Acta Univ. Latviensis, Kim. Fakultat, Ser. 4, No. 8, 405-421 (1939); Cent. 1939, II 3815-3816; C.A. 34, 1982-1983 (1940). (615) Sah, Ma, Ber. 65, 1630-1633 (1932). (616) Allen, Nicholls, J. Am. Chem. Soc. 56, 1409-1410 (1934). (617) Eckenroth, Koerppen, Ber. 29, 1048 (1896). (618) Merritt, Levey, Cutter, J. Am. Chem. Soc. 61, 15-16 (1939). (619) Gillespie, J. Am. Chem. Soc. 56, 2740-2741 (1934). (620) Lauer, Sanders, Leekley, Ungnade, J. Am. Chem. Soc. 61, 3050 (1939).

(621) Cohen, Dudley, J. Chem. Soc. 97, 1737 (1910). (622) Brenans, Bull. soc. chim. (3) 25, 819 (1901). (623) Drew, Sturtevant, J. Am. Chem. Soc. 61, 2666 (1939). (624) V. H. Dermer, O. C. Dermer, J. Org. Chem. 3, 289-293 (1938). (625) Baw, J. Indian Chem. Soc. 3, 102-103 (1926). (626) von Braun, Reich, Ann. 445, 233 (1925). (627) Wang, J. Chinese Chem. Soc. 1, 59-63 (1933). (628) Thiele, Ann. 376, 255 (1910). (629) Tharp, Nottorf, Herr, Hoover, Wagner, Weisgerber, Wilkins, Whitmore, Ind. Eng. Chem. 39, 1300-1302 (1947).

3:8538 ETHYL
$$\beta$$
-CHLOROCROTONATE $C_6H_9O_2Cl$ Beil. II - 416 CH_3 —C—Cl II₁-(189) II₂-(396) B.P. [184° cor. (1)] $D_4^{20} = 1.106$ (3) (4) $n_D^{20} = 1.4587$ (3) 179–180° (2) 1.101 (7) 77° at 15 mm. (3) $D_4^{19.2} = 1.1018$ (7) $n_D^{10.6} = 1.4588$ (4) 76–77° at 14 mm. (4) (5) 75.3–76.0° at 14 mm. (6) $D_4^{17.9} = 1.1526$ (6) $n_D^{17.9} = 1.4509$ (6) 66° at 10 mm. (7)

[See also ethyl β -chloroisocrotonate (3:8325).]

[For prepn. of \bar{C} from β -chlorocrotonic acid (3:2625) in EtOH with HCl gas (100% yield (2)) (4) or with conc. H₂SO₄ (7) see indic. refs.]

[For form. of \bar{C} from ethyl acetoacetate (1:1710) with PCl₅ as a by-product of prepn. of ethyl β -chloroisocrotonate (3:8325) see (8) (9), but this is definitely not a good means of prepn. of \bar{C} .]

[\tilde{C} with Al/Hg in alc. on warming is both dehalogenated and hydrolyzed yielding (10) crotonic acid (1:0425); note that with \tilde{C} this reactn. goes more readily than with the isomeric ethyl β -chloro-isocrotonate (3:8325).]

[$\ddot{\mathbf{C}}$ (2 moles) with $\mathbf{K}_2\mathbf{S}$ (1½ moles) in 5 vols. abs. EtOH refluxed 16 hrs. (11) or $\ddot{\mathbf{C}}$ with Na enolate of ethyl thioacetoacetate (14) gives (53% yield (11)) diethyl β,β' -thiodicrotonate

S(—C(CH₃)=CH.COOC₂H₅)₂, b.p. 150-153° at 4 mm. {11}, accompanied by some ethyl β -mercaptocrotonate (see below).]

[\bar{C} with alc. NaSH (12) or alc. KSH (11) (13) gives (30% yield (13)) ethyl β -mercaptocrotonate; note that this prod. is apparently a mixt. of the two geom. stereoisomers of ethyl β -mercaptocrotonate with the corresp. keto form, viz., ethyl thioacetoacetate, CH₃-CS.CH₂.COOC₂H₅; for details see indic. refs. — Note also that, since the same prod. results by similar treatment of the isomeric ethyl β -chloroisocrotonate (3:8325), a mixture of the stereoisomers can be used as the starting material.]

[\bar{C} with alkali derivs. of alcohols, phenols, mercaptans, etc., splits out alkali halide yielding corresp. ethyl β-substituted crotonates: e.g., \bar{C} with Na allylate gives (9) ethyl β-allyloxycrotonate; \bar{C} with Na cinnamylate gives (9) ethyl β-cinnamyloxycrotonate; \bar{C} with Na phenolate gives (15) cf. (16) ethyl β-phenoxycrotonate, b.p. 147–148° at 14 mm. (15); \bar{C} with Na salt of ethyl mercaptan gives (17) ethyl β-ethylmercaptoisocrotonate, b.p. 139–141° at 16 mm. (17); \bar{C} with Na salt of benzyl mercaptan gives (90% yield (17)) ethyl β-benzylmercaptocrotonate, cryst. from lgr., m.p. 64.5° (17). Note that in the first three of the five preceding examples either \bar{C} or the isomeric ethyl β-chloroisocrotonate (3:8325) or their mixture gives the same result; for the last two, however, such is not the case.

[\bar{C} with diethyl sodiomalonate gives (5) cf. (18) trans diethyl α -carbethoxy- β -methyl gluconate, ($C_2H_5OOC)_2CH.C(CH_3)$ — $CH.COOC_2H_5$ [Beil. II-853], b.p. 169-170° at 13 mm., $D_4^{20} = 1.0937$, $n_D^{20} = 1.4595$ (5); cf. behavior of stereoisomeric ethyl β -chloroisocrotonate (3:8325).]

Č with phenylhydrazine gives the same (2) products as obtd. from the stereoisomeric ethyl β-chloroisocrotonate (3:8325): e.g., Č (1 mole) with phenylhydrazine (1 mole) at 100° for 6-8 hrs. gives by ring closure mainly (2) 3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-20, XXIV₁-(190)], pr. from aq., m.p. 127°, accompanied by small amts. of 4-benzene-azo-3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-328, XXIV₁-(319)], m.p. 155-156°, and 3,3′-dimethyl-1,1′-diphenyl-bis-pyrazolone-5,5′ [Beil. XXVI-484], dec. at high temp. without melting. — Note that with excess phenylhydrazine (2-4 moles) only traces of the 3-methyl-1-phenylpyrazolone-5 are formed while the amt. of the other two (less desirable) products is greatly increased (2).

3:8538 (1) Geuther, Zeil. für Chemie 1871, 240. (2) Autenrieth, Ber. 29, 1653-1664 (1896). (3) von Auwers, Wissenbach, Ber. 56, 724 (1923). (4) von Auwers, Ber. 45, 2807 (1912). (5) Gidvani, Kon, Wright, J. Chem. Soc. 1932, 1034-1035. (6) Errera, Lepingle, Bull. sci. acad. roy. Belg. (5) 11, 150-153 (1925); Cenl. 1925, II 897; C.A. 19, 3057 (1925). (7) von Auwers, Ann. 432, 61 (1923). (8) Thomas-Mamert, Bull. soc. chim. (3) 13, 70-71 (1895). (9) Lauer, Kilburn, J. Am. Chem. Soc. 59, 2587-2588 (1937). (10) Wislicenus, J. prakt. Chem. (2) 54, 59-60 (1896). (11) Scheibler, Ber. 48, 1450-1451 (1915). (12) Scheibler, Topouzada, Schulze, J. prakt. Chem. (2) 124, 7-10 (1930). (13) Mitra, J. Indian Chem. Soc. 8, 471-474 (1931). (14) Mitra, J. Indian. Chem. Soc. 15, 36 (1938). (15) Ruhemann, Wragg, J. Chem. Soc. 79, 1189-1190 (1901). (16) Ruhemann, Ber. 53, 285-286 (1920). (17) Scheibler, Voss, Ber. 53, 385-388 (1920). (18) Fichter, Schwab, Ann. 348, 251-256 (1906).

3: 8540
$$d$$
, l -2,5-DICHLORO-2-METHYLPENTANE $C_0H_{12}Cl_2$ Beil. I - 148 Cl Cl $I_1 I_{2-}(111)$ $CH_2.CH_2.CH_2 CH_3$

B.P. 179-180° (1)

[For prepn. of \bar{C} from 5-chloro-2-methylpentanol-2 [Beil. I-410, I₂-(440)] with fumg. HCl or AcCl see (1); for formn. (together with other prods.) from dimethyl-cyclopropyl-carbinol [Beil. VI-10] by treatment with excess fumg. HCl see (2).]

3:8546 (1) Henry, Compt. rend. 143, 1224 (1906). (2) Bruylants, Dewael, Bull. sci. acad. roy. Bela. (5) 14, 148 (1928); Cent. 1928, I 2709; C.A. 22, 3883 (1928).

3:8545 n-PROPYL
$$\beta$$
-CHLOROPROPIONATE $C_6H_{11}O_2Cl$ Beil. II - 250 n - $C_3H_7O.CO.CH_2.CH_2Cl$ II _____ II ____

B.P. 179-181° (1)
$$D_4^{20} = 1.0656$$
 (2) $n_D^{20} = 1.4290$ (2)

3:8545 (1) Moureu, Ann. chim. (7) 2, 172 (1894). (2) Schjanberg, Z. physik. Chem. A-172, 231 (1935).

B.P. 180° (1)

[For form. of \bar{C} from ethylbenzene (1:7410) by chlorination (other products are also formed) see (1); for form. from chlorobenzene (3:7903) with ethylene + AlCl₃ at 80° under pressure (3,5-diethyl-1-chlorobenzene is also formed) see (2).]

C on oxidn. with alk. KMnO4 yields (1) o-chlorobenzoic acid (3:4150).

 $[\bar{\mathbf{C}}$ on htg. with 15% NaOH + Cu powder for 2 hrs. at 315-320° in steel autoclave is thought (1) to undergo partial rearrangement, thus yielding some *m*-ethylphenol (1:1744).]

[\bar{C} on passing through an Fe or Ni-Cr tube at 675–700° is alleged (3) to lose HCl with production of phenylethylene (styrene) (1:7435).]

 $[\bar{C} \text{ on htg. with conc. NH}_3 + \text{CuO for 20 hrs. at 225}^\circ \text{ yields (2) } o\text{-aminocthylbenzene.}]$

3:8550 (1) Meharg, Allen, J. Am. Chem. Soc. **54**, 2920–2922 (1932). (2) Dreisbach (to Dow Chem. Co.), U.S. 2,159,370, May 23, 1939, Cent. **1939**, II 1775, C.A. **33**, 6875 (1939). (3) Smith (to Naugatuck Chem. Co.), U.S. 1,687,903, Oct 16, 1928, Cent. **1929**, I 2922; C.A. **23**, 156 (1929).

3: 8570 p-CHLORO-ETHYLBENZENE
$$C_8H_9Cl$$
 Beil. V - 354 V_1 -(176) V_2 —

B.P. 180–182° (1) $D_{20}^{20} = 1.0463$ (4) $I_{20}^{20} = 1.0463$ (4) $I_{20}^{20} = 1.0575$ (3) $I_{20}^{20} = 1.5223$ (3) $I_{20}^{20} = 1.5223$ (3) $I_{20}^{20} = 1.5235$ (4) $I_{20}^{20} = 1.5235$ (4)

[For prepn. of \bar{C} from ethylbenzene (1:7410) with Cl_2 in the dark and in pres. of I_2 (2) or with $SO_2Cl_2 + AlCl_3$ (1) see indic. refs.; for prepn. of \bar{C} from chlorobenzene (3:7903) with EtBr + $AlCl_3$ (3) or EtOH + $AlCl_3$ (4) see indic. refs.; for prepn. of \bar{C} from p-chloroacetophenone (3:6735) by reduction with Zn/Hg + HCl (27% yield) see (5).]

 \bar{C} on oxidn. with CrO₃ in AcOH (3) or with HNO₃(2) yields p-chlorobenzoic acid (3:4940), m.p. 234° (3).

[C on attempted nitration gives only (3) a liquid mixt. of isomers.]

[C with Br₂ in AcOH + trace of I₂ yields (2) 3-bromo-4-chloro-ethylbenzene, b.p. 143-144° at 10 mm. (2); C with Br₂ in CHCl₃ exposed in silica flask to sunlight yields (2) p-chloro-α-bromo-ethylbenzene, b.p. 120-121° at 8 mm. (2).]

64-66°

[\tilde{C} on htg. with 15% NaOH + Cu powder for 2 hrs. at 315-320° in a steel autoclave is thought (6) to undergo partial rearr., thus yielding *m*-ethylphenol (1:1744).]

[Č on passing through an Fe or Ni-Cr tube at 675-700° is alleged (7) to lose HCl with production of styrene (1:7435).]

3:8570 (1) Töhl, Eberhard, Ber. 26, 2944 (1893). (2) Varma, Sahay, Subrammonium, J. Indian Chem. Soc. 14, 157-159 (1937). (3) Schreiner, J. prakt. Chem. (2) 81, 557-558 (1910). (4) Tsukervanik, J. Gen. Chem. (U.S.S.R.) 8, 1512-1515 (1938); Cent. 1939, I 4929; C.A. 33, 4587 (1939). (5) Lock, Bayer, Ber. 72, 1068 (1939). (6) Meharg, Allen, J. Am. Chem. Soc. 54, 2920-2922 (1932). (7) Smith (to Naugatuck Chem. Co.), U.S. 1,687,903, Oct. 16, 1928; Cent. 1929, I 2922; C.A. 23, 156 (1929).

```
3:8575 1.5-DICHLOROPENTANE
                                                                         C<sub>5</sub>H<sub>10</sub>Cl<sub>2</sub>
                                                                                           Beil. I - 131
             (Pentamethylene dichloride)
                                                   Cl.CH<sub>2</sub>.CH<sub>2</sub>.CH<sub>2</sub>.CH<sub>2</sub>.CH<sub>2</sub>.Cl
                                                                                                  I_{1}-(43)
                                                                                                  I<sub>2</sub>-( 95)
  B.P.
                                       F.P.
                                       -72.8^{\circ} (1) D_4^{25} = 1.0940 (3) (7)
   182.3° cor. at 760 mm. (1)
                                                                 1.0918 (1)
   179.5-180.5°
                                 \langle 2 \rangle
  178-180°
                                 (3)
   176-178° sl. dec.
                                 (4)
                                                        D_4^{20} = 1.1028 (8)
                                                                                       n_{\rm D}^{20} = 1.4563 (8)
                 at 60 mm. (8)
                                                                 1.0697 (1)
   102.4°
   79-80°
                 at 21 mm. (4)
   76-78°
                 at 21 mm. (5)
  68°
                 at 14 mm. (4)
```

Colorless liq. with characteristic odor; sol. org. solv., insol. aq.

[For prepn. (yield 77-78% (1); 75-80% (4)) from N-benzoylpiperidine [Beil. XX-46] + PCl_5 see (4) (1) (2); note that by-product benzonitrile may be removed by acid hydrolysis (4) (9) (2) or stdg. with aq. (10); for prepn. from pentanediol-1,5 (1:6519) + PCl_5 in CCl_4 see (5); for prepn. from N_1N -dibenzoylpentamethylenediamine + $SOCl_2$ see (11) (12); for formn. (19%) in direct chlorination of 1-chloropentane see (8).]

Č htd. in s.t. 5 hrs. at 130° with NaCN in MeOH yields (5) 1,5-dicyanopentane (pimelonitrile) which after hydrolysis with conc. HCl at 110° for 5 hrs. (5) gives pimelic acid (1:0456), m.p. 104° (5).

[For reaction with NaI in acetone see (8).]

at 10 mm. (6)

- ₱ 1,5-bis-(Phthalimido)pentane [Beil. XXI-493]: from C + K phthalimide in 60-70% yield (13) by htg. at 190-200°, pale yel. ndls. from CHCl₃ + alc., m.p. 186° (13). [The half reaction prod., viz., 1-chloro-5-phthalimidopentane N-(ε-chloro-n-amyl)-phthalimide (14), has m.p. 30-31° (14).]
- —— Pentamethylene- ω , ω' -bis-(isothiourea hydrochloride): monohydrate, m.p. 206° (15), anhydrous epd., m.p. 210° (15). [From \tilde{C} with thiourea (2 moles) in *n*-BuOH refluxed 1 hr. (15).]
- —— 1,5-Diphenoxypentane (pentamethylene glycol diphenyl ether) [Beil. VI-147]: m.p. 48-49° (16); b.p. 340° sl. dec., 215-217° at 12 mm. (16). [From Č in 75% yield on protracted boilg. (30 hrs.) with large excess (3 moles) sodium phenolate in alc. (16).]
- 3:8575 (1) Serwy, Bull. soc. chim Belg. 42, 486, 488 (1933). (2) Clarke, J. Chem. Soc. 101, 1805 (1912). (3) Hilditch, Dunstan, Z. Elektrochem. 18, 883 (1912). (4) von Braun, Ber. 37, 2918–2920 (1904). (5) Pummerer, Schönsamgruber, Ber. 72, 1842 (1939). (6) Bost, Conn. Oil Gas J. 32, No. 3, 17 (1933). (7) Dunstan, Hilditch, Thole, J. Chem. Soc. 103, 137 (1913). (8) Hass, Huffman, J. Am. Chem. Soc. 63, 1233–1235 (1941). (9) von Braun, Sobecki, Ber. 44, 1469 (1911). (10) Zappi, Bull. soc. chim. (4) 19, 249 (1916).

(11) von Braun, Ber. 38, 2343-2344 (1905). (12) von Braun, Pinkernelle, Ber. 67, 1220 (1934). (13) von Braun, Ber. 37, 3584-3586 (1904). (14) Gabriel, Ber. 42, 4051-4052 (1909). (15) Kawai, Hosono, Shikinami, Yonechi, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 16, Nos. 306-309, 9-16 (1931); Cent. 1931, II 1694; C.A. 25, 5665 (1931). (16) von Braun, Steindorff, Ber. 38, 959-960 (1905).

3: 8580 HEXAHYDROBENZOYL CHLORIDE
$$C_7H_{11}OCl$$
 Beil. IX-9 (Cyclohexanecarboxylic acid $CH_2.CH_2$ H IX₁— chloride) H_2C $CH_2.CH_2$ CH_3 CH_4 CH_5 CH_5 CH_6 CH_6 CH_7 CH_8 CH_8 CH_8 CH_8 CH_8 CH_8 CH_8 CH_8 CH_8 CH_9 CH

[For prepn. of \overline{C} from hexahydrobenzoic acid (1:0575) with PCl₅ (1) (3) (8) or with SOCl₂ (yield: 100% (9), 92% (7)) see indic. refs.; for prepn. of \overline{C} from cyclohexane (1:8405) with oxalyl (di)chloride (3:5060) (85% yield (4)) or with phosgene (3:5000) see (4).

[Č with Na hexahydrobenzoate htd. at 100° yields (1) hexahydrobenzoic anhydride, b.p. 280-283°, m.p. 25° (1).]

[\bar{C} with SO₂Cl₂ in pres. of dibenzoyl peroxide gives (34% yield (5)) α -chloro-hexahydrobenzoyl chloride, b.p. 95–96° at 18 mm., $D_4^{20}=1.2280, n_D^{20}=1.4866$ (amide, m.p. 117–118° (5)); \bar{C} with Br₂ yields (9) α -bromohexahydrobenzoyl chloride, b.p. 115–118° at 12 mm. (corresp. acid, m.p. 103°; amide, m.p. 136°; monoureide, m.p. 159–160° (9)).]

[\bar{C} with C_6H_6 + AlCl₃ gives (3) cyclohexyl phenyl ketone (hexahydrobenzophenone) [Beil. VII-378, VII₁-(200)], m.p. 54° (3); \bar{C} with Na phenolate yields (10) phenyl hexahydrobenzoate, b.p. 160-163° at 15 mm. (10); \bar{C} with Na perbenzoate gives (53% yield (7)) benzoyl-hexahydrobenzoyl peroxide, m.p. 56° dec. (7).]

Č on hydrolysis yields hexahydrobenzoic acid (1:0575), m.p. 30-31° (for the amide, m.p. 185-186° (4), 184° (1), and anilide corresp. to Č see 1:0575).

S:8580 (1) Lumsden, J. Chem. Soc. 87, 92 (1897).
 Hopff (to I.G.), Ger. 520,154, March 7, 1931; Cent. 1931, I 3060.
 Meyer, Scharwin, Ber. 30, 1941-1942 (1897).
 Kharasch, Brown, J. Am. Chem. Soc. 62, 454 (1940).
 Price, Schwarcz, J. Am. Chem. Soc. 62, 2895 (1940).
 Chem. Fabrik, Sandoz, Brit. 230,432, April 29, 1925; French 592,541, Aug. 4, 1925; Swiss 109,582, April 1, 1925; Cent. 1926, II 1585.
 Wieland, Schapiro, Metzger, Ann. 513, 103 (1934).
 Godchot, Bull. soc. chim. (4) 9, 262 (1911).
 Fourneau, Montagne, Payal, Anales soc. españ. fis. quím. (2) 19, 192-198 (1921); Cent. 1921, III 828; C.A. 16, 240 (1922).
 Blicke, J. Am. Chem. Soc. 47, 237 (1925).

185-187°

3:8585-3:8590

3: 8585 1-CHLORO-OCTANE (n-Octyl chloride) CH₃(CH₂)₆CH₂Cl C₈H₁₇Cl Beil. I - 159 I₁-(60) I₂-(124) B.P. 183.6-184.6° cor. (1)
$$D_{25}^{25} = 0.87192$$
 (3) 183.0-183.5° cor. (2) 182.5-183.5° cor. (3) $D_{4}^{20} = 0.8748$ (13) $n_{D}^{20} = 1.43424$ (4) 181.5° at 765 mm. (13) 1.43058 (13) 179.5-180.5° (7) $D_{20}^{20} = 0.8745$ (4) 179-180° (4) $D_{15}^{15} = 0.87857$ (3) 78° at 15 mm. (5) 68.8-70.0° at 12 mm. (6)

Colorless liq. with characteristic fatty odor. - Insol. aq., spar. sol. abs. alc., eas. sol.

[For prepn. of C from octanol-1 (1:6255) with HCl + ZnCl₂, PCl₃ + ZnCl₂ (60% yield), PCl₅ + ZnCl₂ (69% yield), or SOCl₂ (yield: 80% (13), 70% (4)) see indic. refs.; by saturating with HCl and htg. in s.t. at 120° see (5) (7).]

[For study of reaction with NaI (8) or KI (2) see these; for reactn. with Mg see (9) (note that \bar{C} with Mg in dry ether + trace I₂ gives (96.3% yield in 8 hrs. (12)) RMgCl); for reactn. with liq. NH₃ and with amines see (10).

① n-Octyl mercuric chloride: m.p. 115.0-115.5° (11). [From RMgCl + HgCl₂ (11).]

3:8585 (1) Perkin, J. Chem. Soc. 69, 1173 (1896). (2) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925). (3) Perkin, J. prakt. Chem. (2) 31, 495 (1885). (4) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-79 (1929). (5) Bouveault, Blanc, Bull. soc. chim. (3) 31, 673 (1904). (6) Kohlrausch, Köppl, Monatsh. 63, 268 (1933). (7) Zincke, Ann. 152, 4-5 (1869). (8) Apolit, Ann. chim. (10) 2, 83 (1924). (9) Schorigin, Issaguljanz, Gussewa, Ber. 66, 1430 (1933). (10) Westphal, Jerchel, Ber. 73, 1004-1010 (1940).

(11) Whitmore, Bernstein, J. Am. Chem. Soc. 60, 2627 (1938). (12) Houben, Boedler, Fischer, Ber. 69, 1768, 1778 (1936). (13) Vogel, J. Chem. Soc. 1943, 638, 640.

[For prepn. of C from 2-amino-1,3-dimethylbenzene (vic.-m-xylidine) [Beil. XII-1107, XII₁-(482)] via diazotization and Cu₂Cl₂ reactn. see (1); for prepn. of C from m-xylene (1:7420) via sulfonation to 2,4-dimethylbenzenesulfonic acid, chlorination, conversion to sodium salt of 3-chloro-2,4-dimethylbenzenesulfonic acid, and hydrolysis of the latter with superheated steam in H₂SO₄ at 160-170° see (2).]

3:8590 (1) Kohlrausch, Pongratz, Monatsh. 64, 369 (1934). (2) Kalischer, Frister (to I.G.), Ger. 491,220, March 13, 1927; C.A. 24, 2307 (1930); I.G., Brit. 313,207, July 4, 1929; Cent. 1939, II 1591; I.G., French 650,732, Jan. 12, 1929; Cent. 1929, II 653.

3: 8595 n-BUTYL
$$d_1l$$
- α -CHLOROPROPIONATE H $C_7H_{18}O_2Cl$ Beil. S.N. 162 n - $C_4H_9O.CO.C.CH_3$

B.P.
$$183.5-185.0^{\circ}$$
 at 760 mm. (1) $D_4^{20} = 1.0253$ (2) $n_D^{20} = 1.4263$ (2) $71.6-72.6^{\circ}$ at 10 mm. (1)

3:8595 (1) Burkhard, Kahovec, Monatsh. 71, 340 (1938). (2) Schjanberg, Z. physik. Chem. A-172, 230 (1935).

3:8596 ETHYL
$$d$$
, l - α -CHLORO- n -VALERATE $C_7H_{13}O_2Cl$ Beil. II - 302 CH_3 . CH₂. CH₂. CH₂. CH. COOC₂H₅ II_1 — II_2 —

B.P. 185° at 752 mm. (1)
$$D_{-}^{11.8} = 1.040$$
 (1) $n_{-}^{11} = 1.43071$ (1)

Liq. with peppermint-like odor; insol. aq.; sol. alc., ether.

[For prepn. of \bar{C} from α -chloro-n-valeronitrile with abs. EtOH + HCl see (1).]

3:8596 (1) Servais, Rec. trav. chim. 20, 47-48 (1901).

3: 8597 ETHYL
$$\gamma$$
-CHLORO- n -BUTYRATE $C_6H_{11}O_2Cl$ Beil. II - 278 CH_2 -CH $_2$ -COOC $_2H_6$ II $_1$ -(124) II_2 -(254) B.P. 186° at 760 mm. (1) $D_4^{20} = 1.0754$ (4) $n_D^{20} = 1.43107$ (4) 183–184° (2) 77° at 16 mm. (3) 76° at 16 mm. (4) 72° at 16 mm. (12) 70–71° at 10 mm. (5) 64–66° at 10 mm. (6)

[For prepn. of \bar{C} from γ -chloro-n-butyric acid (3:0020) with EtOH + H₂SO₄ (80% yield (3)) see (3); from γ -chloro-n-butyric with EtOH + HCl see (2); from γ -ethoxy-n-butyric acid by htg. with SOCl₂ (77% yield) see (5); from ethyl n-butyrate (1:3127) with SO₂Cl₂ + dibenzoyl peroxide in CCl₄ (40% \bar{C} + 10% α - and 40% β -isomers) see (7); from γ -ethoxy-n-butyryl chloride (12) in almost 100% yield merely by htg. at 100° for 10 hrs. see (12).]

Č added dropwise to solid KOH at 180° loses HCl and by ring closure yields (8) ethyl cyclopropanecarboxylate [Beil. IX-4, IX₁-(3)], b.p. 134°.

[Č heated with NaI in acetone yields (5) (6) (9) ethyl γ -iodo-n-butyrate, b.p. 69-71° at 3 mm. (5), 84-85° at 4 mm. (9); Č with excess MeMgI yields (10) 5-chloro-2-methylpentanol-2; Č with NaN₃ in aq. alc. yields (11) ethyl γ -azido-n-butyrate; Č with diethylamine in s.t. at 100° yields (3) ethyl γ -diethylamino-n-butyrate, b.p. 73-75° at 4 mm. (5).]

 $\bar{\mathbf{C}}$ on htg. with conc. HCl yields (5) γ -chloro-n-butyric acid (3:0020).

For the amide, anilide, p-toluidide, and other derivs. corresp. to \bar{C} see γ -chloro-n-butyric acid (3:0020).

◆ 1-Phenylpyrrolidone-2 [Beil. XXI-237]: cryst. from aq., m.p. 69° (12). [From Č with aniline at 110° for 1 hr. (12).]

3:8597 (1) Henry, Bull. acad. roy. Belg. (3) 35, 507-520 (1898); Cent. 1898, II 273. (2) Henry, Bull. soc. chim. (2) 45, 341 (1886). (3) Wohlgemuth, Ann. chim. (9) 2, 307, 316 (1914). (4) Karvonen, Ann. Acad. Sci. Fennicae A-10, No. 4, p. 21; Cent. 1919, III 808. (5) Blicke, Wright, Zienty, J. Am. Chem. Soc. 63, 2489-2490 (1941). (6) Conant, Kirner, J. Am. Chem. Soc. 46, 249 (1924). (7) Price, Schwarcz, J. Am. Chem. Soc. 62, 2894-2895 (1940). (8) Rambaud, Bull. soc. chim. (5) 5, 1564 (1938). (9) Fuson, Arnold, Cooke, J. Am. Chem. Soc. 69, 2272 (1938). (10) Henry, Compt. rend. 143, 1223 (1906).

(11) Curtius, Giulini, Ber. 45, 1046 (1912). (12) Prelog, Heimbach-Juhasz, Ber. 74, 1703-1704 (1941).

[For prepn. of \bar{C} from p-xylene (1:7415) with Cl_2 in pres. of Fe (82–86% yield (4)) (5) or I_2 (2), by refluxing with PbCl₄.2NH₄Cl (6), with $SO_2Cl_2 + AlCl_3$ (7), or with Cl_2 aq. (1) see indic. refs.; for prepn. of \bar{C} from p-xylidine [Beil. XII-1135, XII₁-(488)] via diazotization and use of Cu_2Cl_2 reaction see (3).]

 \tilde{C} on nitration with a mixt. of HNO₃ + H₂SO₄ acids as directed (4) (8) gives 5-nitro-2-chloro-1,4-dimethylbenzene, cryst from ether, m.p. 77-78° (4), 78° (8) (accompanied by other products). [This mononitro- \tilde{C} on further nitration yields 5,6-dinitro-2-chloro-1,4-dimethylbenzene, cryst. from alc., m.p. 101° (4).]

C on monosulfonation with fumg. H₂SO₄ (2), 100% H₂SO₄ (4), or chlorosulfonic acid (9) yields 2-chloro-1,4-dimethylbenzenesulfonic acid-5 [Beil. XI-127] (corresp. sulfonyl chloride, m.p. 50° (4) (9); sulfonamide, m.p. 185° (4); sulfonanilide, m.p. 155° (4)).

[C on further chlorination yields mainly 2,5-dichloro-1,4-dimethylbenzene [Beil. V-384], m.p. 71° (2) (4), b.p. 221° cor. (2), 224° at 770 mm. (4) (together with small amts. of other prods.).] [For side-chain chlorination of C and conversion of resultant prods. by hydrolysis to 2-chlorobenzenedicarboxylic acid-1,4 (chloroterephthalic acid) (3:4995) see (10).]

 \tilde{C} with $Br_2 + Fe$ (5) or with $Br_2 + HNO_3 + H_2SO_4$ (11) as directed yields 5-bromo-2-chloro-1,4-dimethylbenzene [Beil. V-385], lfts. from hot alc., m.p. 66° (5) (11). [Some dibromo- \tilde{C} , m.p. 93°, and tribromo- \tilde{C} , m.p. 234°, are also formed (5).]

3:8600 (1) Datta, Fernandes, J. Am. Chem. Soc. 38, 1811 (1916). (2) Kluge, Ber. 18, 2099 (1885). (3) Kohlrausch, Pongratz, Monatsh. 64, 369 (1934). (4) Wahl, Ann. chim. (11) 5, 5-82 (1936). (5) Willgerodt, Wolfien, J. prakt. Chem. (2) 39, 402-405 (1889). (6) Seyewets, Biot, Compt. rend. 135, 1121 (1902). (7) Töhl, Eberhard, Ber. 26, 2942 (1893). (8) Varma, Raman, J. Indian Chem. Soc. 12, 540-541 (1935). (9) I.G., Brit. 281,290, Jan. 25, 1928; French 644,319, Oct. 5, 1928; Cent. 1929, II 352. (10) I.G., French 663,791, Aug. 26, 1929; Cent. 1929, II 2731.

(11) Varma, Raman, J. Indian Chem. Soc. 12, 248 (1935).

3:8605
$$\beta_1\beta'$$
-DICHLORO-DI-ISOPROPYL ETHER C_0H_{12} OCl₂ Beil. S.N. 24 (bis-(β -Chloro-isopropyl) ether) CH₃ CH₃ CH₃ ClCH₂.CH—O—CH.CH₂Cl B.P. 187–188° at 761 mm. (1) $D_4^{20} = 1.103$ (1) $n_D^{20} = 1.45046$ (1) 187.4° (3) $D_{20}^{20} = 1.1127$ (2) 1.1135 (3)

Colorless liq. with agreeable odor (1).

[For prepn. from 1-chloropropanol-2 $(3:7747) + H_2SO_4$ see (2).]

 \bar{C} on htg. with KOAc + AcOH yields corresp. diacetate, b.p. 248° at 761 mm., $D_4^{20}=1.050, n_D^{20}=1.42654$ (1).

3:8605 (1) Dewael, Bull. soc. chim. Belg. **39**, 396 (1930). (2) Wickert (to Union Carbide and Carbon Corp.), U.S. 2,052,264, Aug. 25, 1936; Cent. **1936**, II 3846; C.A. **30**, 7127 (1936). (3) McClure, Chem. Eng. News **32**, 421 (1944).

3: 8610
$$\beta,\beta'$$
-DICHLORO-DI- n -PROPYL ETHER C_6H_{12} OCl₂ Beil. S.N. 24 (bis -(β -Chloro- n -propyl) ether) Cl Cl CH₃-CH.CH₂—O—CH₂.CH.CH₃

B.P. 188° at 762 mm. (1) $D_2^{20} = 1.109$ (1) $n_D^{20} = 1.44675$ (1)

Colorless liq. with agreeable odor.

4 mm. (1)

45-50°

[For prepn. from 2-chloropropanol-1 (3:7917) by htg. with SO_2Cl_2 see (1); for prepn. from propylene + HOCl see (2).]

3:8610 (1) Dewael, Bull. soc. chim. Belg. **34**, 345-346 (1925). (2) Nutting, Britton, Croope (to Dow Chem. Co.), U.S. 2,095,612, Oct. 12, 1937; Cent. **1938**, I 2059; C.A. **31**, 8545 (1937).

[For prepn. from K 6-chloro-2-methylphenol-4-sulfonate by htg. with dil. H_2SO_4 at 130° see (2).]

Č on treatment with nitrous acid yields 6-chloro-2-methyl-4-nitrosophenol, brownish ndls., m.p. 112° (3).

3:8615 (1) Huston, Neely, J. Am. Chem. Soc. 57, 2177 (1935). (2), Fahlberg, List and Co., Ger. 256,345, Feb. 10, 1913; Cent. 1913, I 866. (3) von Auwers, Wittig, Ber. 57, 1271, Note 3 (1924).

3: 8629 ETHYL
$$d,l$$
- β -CHLORO- n -VALERATE $C_7H_{13}O_2Cl$ Beil. S.N. 162 CH₃.CH₂.CH.CH₂.COOC₂H₅ Cl

B.P. 189° (1) $D_4^{20} = 1.0330$ (1) $n_D^{20} = 1.42777$ (1)

[For prepn. of \tilde{C} from β -chloro-n-valeric acid (3:0270) with EtOH + H₂SO₄ see (1).] [The levorotatory isomer of \tilde{C} , b.p. 66.5–67° at 10 mm., has been obtd. from levorotatory β -chloro-n-valeronitrile with alc. HCl (2) or from levorotatory ethyl β -hydroxy-n-valerate with PCl₅ or SOCl₂ in CHCl₃ (2).]

3:8629 (1) Schjanberg, Ber. 70, 2385-2391 (1937). (2) Levene, Mori, J. Biol. Chem. 78, 9-10 (1928).

[For prepn. of \tilde{C} from nonanol-2 (*n*-heptyl-methyl-carbinol) (1:6259) with HCl gas see (1).]

3:8635 (1) van Gysegen, Bull. acad. roy. Belg. 1906, 692-706; Cent. 1907, I 530; C.A. 1, 1969 (1907).

[For prepn. of \bar{C} from 5-amino-1,3-dimethylbenzene (sym.-m-xylidine) [Beil. XII-1131, XII₁-(487)] via diazotization and use of Sandmeyer reactn. with Cu₂Cl₂ see (1) (3); from 5-chloro-1,3-dimethylcyclohexadiene-3,5 [Beil. V-119, V₁-(64)] by addn. of Br₂ and subsequent elimination of 2HBr by boilg, with quinoline see (2).

C on shaking with 10 pts. fumg. H_2SO_4 (15% SO_3) at 30-40° yields (2) (1) 5-chloro-1,3-dimethylbenzenesulfonic acid-2, non-hygroscopic cryst., m.p. 52° (1) (corresp. sulfonyl chloride, m.p. 56-58° (1); sulfonamide, m.p. 191-192° (1)).

3:8640 (1) Klages, Ber. 29, 310-311 (1896). (2) Klages, Knoevenagel, Ber. 27. 3024-3025 (1894). (3) Kohlrausch, Pongratz, Monatsh. 64, 370 (1934).

[For prepn. of \tilde{C} from 3-amino-1,2-dimethylbenzene (vic.-o-xylidine) [Beil. XII-1101, XII₁-(478)] via diazotization and use of Cu_2Cl_2 reactn. see (1); for formn. of \tilde{C} from o-xylene (1:7430) with Cl_2 in pres. of I_2 (2) or Fe (3) (the isomeric 4-chloro-1,2-dimethylbenzene (3:8675) is also formed) see (2) (3).]

Č on oxidn. with dil. HNO₃ in a s.t. yields (2) (3) 3-chloro-2-methylbenzoic acid (3:4435). [The behavior of Č on nitration has not as yet been reported, all three possible mononitro derivatives have, however, been independently prepared; viz., 4-nitro-Č, m.p. 46° (4); 5-nitro-Č, m.p. 101° (5); 6-nitro-Č, m.p. 62° (6).]

Č on sulfonation yields exclusively 3-chloro-1,2-dimethylbenzenesulfonic acid-6 [Beil. XI-121] (corresp. sulfonyl chloride as yet unreported; corresp. sulfonamide, m.p. 199° (2)).

[\overline{C} with Cl_2 in pres. of Fe yields (1) 3,4-dichloro-1,2-dimethylbenzene, b.p. 234°, m.p. 8-9° (2).]

3:8645 (1) Hinkel, Ayling, Walters, J. Chem. Soc. 1934, 1947-1948. (2) Krüger, Ber. 18, 1755-1758 (1885). (3) Claus, Bayer, Ann. 274, 305-311 (1893). (4) Hinkel, Ayling, Walters, J. Chem. Soc. 1934, 287. (5) Hinkel, J. Chem. Soc. 125, 1852-1853 (1924). (6) Hinkel, Collins, Ayling, J. Chem. Soc. 123, 2972 (1923).

B.P. 191° cor. (1)
$$D_4^{20} = 1.011$$
 (3) $n_D^{20} = 1.4440$ (3) $82-84^\circ$ at 30 mm. (2) 82° at 20 mm. (3)

[For prepn. of \bar{C} from n-heptaldehyde (1:0183) with PCl₅ at 150° (1) (2) (16% yield (6)), in the cold (61% yield (4)) (11), or in C₆H₆ at 20° (3) (50% yield (5)), see indic. refs. (much loss is incurred by polymerization of the initial aldehyde by the HCl resulting in the reactn.).]

 \bar{C} with alc. KOH gives (1) (2) 1-chloroheptene-1 (3:8219) and on protracted actn. (1) (2) heptyne-1 (1:8085), b.p. 100°. — \bar{C} passed over soda-lime at 420° (3) (5) or htd. with powdered KOH + mineral oil at 250° (5) or dropped onto NaNH.C₆H₅ (7) or treated with NaNH₂ in xylene or mineral oil (60% yield (8) (10)) (9) gives n-amylacetylene (heptyne-1) (1:8085).

[For conversion of \bar{C} to 1,1-diffuoroheptane by use of HgO + HF see (6).]

3:8650 (1) Limpricht, Ann. 103, 81-82 (1857). (2) Welt, Ber. 30, 1496 (1897). (3) Bachmann, Hill, J. Am. Chem. Soc. 56, 2730-2732 (1934). (4) Loevenich, Losen, Dierichs, Ber. 60, 951 (1927). (5) Hill, Tyson, J. Am. Chem. Soc. 50, 172-176 (1928). (6) Henne, Renoll, Leicester, J. Am. Chem. Soc. 61, 938-940 (1939). (7) Bodroux, Compt. rend. 208, 1023 (1939). (8) Bourgeul, Ann. chim. (10) 3, 223-224 (1925). (9) Meunier, Desparmet, Bull. soc. chim. (4) 35, 481-482 (1924). (10) Guest, J. Am. Chem. Soc. 47, 862 (1925).

(11) Kuz'min, Soobschemie o Nauch.-Isslodovatel Rabote Kiev Ind. Inst. 2, 18 (1940); C.A. 37, 3047 (1943).

3:8655 ISOBUTYL β -CHLOROPROPIONATE $C_7H_{13}O_2Cl$ Beil. II-250 (CH₃)₂CH.CH₂.O.CO.CH₂.CH₂Cl II₁— II₂—

B.P. 191-193° (1)
$$D_4^{20} = 1.0323$$
 (2) $n_D^{20} = 1.4295$ (2)

3:8655 (1) Moureu, Ann. chim. (7) 2, 172-173 (1894). (2) Schjanberg, Z. physik. Chem. A-172, 231 (1935).

```
3:8657 ETHYL y-CHLOROCROTONATE
                                                       C6H9O2Cl
                                                                       Beil. II - 418
                                     CH2.CH=CH.COOC2H5
                                                                            П1---
                                                                            II<sub>2</sub>-(397)
                                            D_{-}^{15} = 1.130 (2)
                                                                    n_{-}^{15} = 1.4625 (2)
  B.P. 191-193° at 760 mm. (1)
       84-85°
                    15 mm. (2)
       80°
                  at 10 mm. (3)
       77-82°
                    12 mm. (4)
       66-68°
                      2 mm. (3)
```

[See also γ -chlorocrotonic acid (3:2170).]

Although \bar{C} is capable of existing in two geometrically isomeric forms, only this one is known; collateral evidence (but not actual proof) indicates that \bar{C} is the *trans* stereoisomer. [For prepn. of \bar{C} from ethyl vinylacetate [Beil. II-407] (5) with Cl₂ in CCl₄ (forming ethyl β , γ -dichloro-n-butyrate) followed by treatment with alc. NaOEt at 0° (splitting out HCl) and giving 65% yield see (5); from ethyl γ -chloro- β -hydroxy-n-butyrate [Beil. III-310, III₁-(116)] by dehydration with P₂O₅ (yields: 65% (4), 62.5% (3), 60% (2)) (6) (accompanied by some γ -chlorocorotonic acid (3:2170) (3) (2) and also by ethyl γ -chlorovinylacetate (3)) see indic. refs.l

 \tilde{C} on hydrolysis with Ba(OH)₂ below 0° or even (but less advantageously) with KOH gives (60% yield (3) (5)) (7) (2) γ -chlorocrotonic acid (3:2170), m.p. 83°; note, however, that hydrolysis with hot cone. alk. gives also two other products, viz., O(CH₂—CH—CH.-COOH)₂, m.p. 195° (2), and γ -hydroxycrotonic acid, m.p. 108° (2).

[$\bar{\rm C}$ in EtOH/NaOEt undergoes addition of EtOH to unsatd. linkage followed to small extent by elimination of HCl with consequent ring closure to a cyclopropane deriv.; e.g., $\bar{\rm C}$ (0.134 mole) in 2½ pts. EtOH treated dropwise in cold with soln. of Na (0.087 mole) in the same vol. of EtOH as above gives (yields: 42% (8), 25% (9)) ethyl γ -chloro- β -ethoxy-n-butyrate, b.p. 108.0–108.5° at 20 mm., $D_{-}^{17.5} = 1.078$, $n_{-}^{17.5} = 1.4295$ (8), accompanied by a little (3% yield (8)) ethyl 2-ethoxycyclopropane-1-carboxylate (1-carbethoxy-2-ethoxycyclopropane), b.p. 77.50–77.75° at 13 mm., $D_{-}^{18} = 0.995$, $n_{-}^{18} = 1.453$ (8); the latter is also obtd. (22% yield (8)) by distn. of the ethyl γ -chloro- β -ethoxy-n-butyrate with dry powdered KOH at 180° and 45 mm. press.]

[\bar{C} on dropwise addition to dry powdered KOH at 180° gives ethyl cyclopropane-1-carboxylate [Beil. IX-4, IX₁-(3)], b.p. 130° at 728 mm., $D=0.970, n_{-}^{15}=1.416$.]

[\bar{C} with excess dry powdered CaBr₂ heated several days under reflux gives (2) (10) ethyl γ -bromocrotonate. — \bar{C} (1 mole) with NaI (1 mole) in acetone reacts readily at ord. temp. pptg. NaCl (80% theory) and yielding (3) ethyl γ -iodocrotonate, b.p. 92–93° at 2 mm.]

[\bar{C} with NaOAc in AcOH heated at 100° cf. (11) yields (8) ethyl γ -acetoxycrotonate, b.p. 115–116° at 15 mm., $D_{-}^{23} = 1.075$, $n_{-}^{23} = 1.4445$ (11).]

[\bar{C} with conc. aq. NH₄OH not only has its halogen replaced by $-NH_2$ but also is hydrolyzed with consequent formn. of γ -aminocrotonic acid; this was not isolatable as such but only as its picrate, the m.p. of which, however, is not reported (2).]

[\bar{C} with Me₃N (excess) in alc. contg. a trace of NaI in s.t. at 100° followed by evapn. with HCl gives (4) γ -dimethylaminocrotonic acid chloromethylate (γ -dimethylaminocrotonbetain chloride), m.p. 203-205° dec. (4).]

3:8657 (1) Lespieau, Bull. soc. chim. (3) 33, 466-467 (1905). (2) Rambaud, Bull. soc. chim. (5) 3, 139-141 (1936). (3) Braun, J. Am. Chem. Soc. 52, 3167-3176 (1930). (4) Linneweh, Z. physiol. Chem. 176, 217-221 (1928). (5) Glattfeld, Rietz, J. Am. Chem. Soc. 62, 976 (1940). (6) Lespieau, Compt. rend. 130, 1410 (1900). (7) Bacher, Benninga, Rec. trav. chim. 55, 610 (1936).

(8) Rambaud, Bull. soc. chim. (5) 5, 1552-1565 (1938).
(9) Rambaud, Compt. rend. 200, 2089-2091 (1935).
(10) Rambaud, Bull. soc. chim. (5) 1, 1347 (1934).
(11) Rambaud, Bull. soc. chim. (5) 1, 1328 (1934).

3:8660 p-XYLYL CHLORIDE (p-Methylbenzyl chloride;
$$\omega$$
-chloro-p-xylene) CH₃CH₂Cl C_8H_9Cl Beil. V - 384 V₁-(186) V₂-(299) B.P. 192° at 760 mm. (1) $D_4^{20} = 1.0512$ (2) $n_{\overline{D}}^{\overline{D}} = 1.5380$ (2) 98-101° at 27 mm. (2) 92-94° at 20 mm. (1) 90° at 20 mm. (3) 81.5° at 15 mm. (4)

[For prepn. of \tilde{C} from p-tolylcarbinol (1:5954) by distn. with HCl see (3) (4A) (8); by treatment with PCl₃ (87% yield) see (6); for prepn. from toluene (1:7405) with paraformaldehyde + HCl (75% yield (2)) see also (5); with sym-dichlorodimethyl ether (3:5245) + ZnCl₂ see (1) (5).]

 \bar{C} stood with N/10 alc. NaOEt at 30° yields ethyl p-xylyl ether [Beil. VI-498], b.p. 203°, to extent of 15% yield in 6 hrs., 40.5% in 24 hrs. (7) cf. (8) (9). [For data on rate of hydrolysis with acid or alk. in acetone soln. at 30° see (10).]

 \bar{C} with Mg in ether yields RMgCl; on carbonation at 0° (11) this yields $p\text{-CH}_3.C_6H_4$.-CH₂.COOMgCl; this upon acidification presumably (no record) would yield p-tolylacetic ac. [Beil. IX-530], m.p. 92°; on treatment (12) with C_2H_5MgBr , however, it gives a mixt. contg. 64.2% p-tolylmalonic ac., sepd. with C_6H_6 , cryst. from aq., m.p. 143.5–144.5° with evoln. of CO₂ (12). [Use of isopropyl MgCl instead of C_2H_5MgBr gave 93% p-tolylmalonic ac. (12).]

 \bar{C} boiled for 6 hrs. with 10 pts. 7% NaHCO₃ soln. gave (66% yield (2)) p-tolylearbinol (1:5954).

N-(p-Xylyl)phthalimide [Beil. XXI-468]: from \(\tilde{C}\) by htg. at 180° with K phthalimide
 (3); ndls. (from dil. alc.), m.p. 116-117° (3), 120° (13).

3:8660 (1) Stephen, Short, Gladding, J. Chem. Soc. 117, 520 (1920). (2) Shorygin, Bogdanowa, J. Applied Chem. (U.S.S.R.) 11, 1217-1221 (1938); Cent. 1939, II 1277; C.A. 33, 4216 (1939). (3) Curtius, Sprenger, J. prakt. Chem. (2) 62, 111 (1900). (4) Bennett, Jönes, J. Chem. Soc. 1935, 1818. (4A) Halford, Reid, J. Am. Chem. Soc. 63, 1875 (1941). (5) Hill, Short, J. Chem. Soc. 1935, 1126. (6) Ingold, Rothstein, J. Chem. Soc. 1928, 1279. (7) Franzen, J. prakt. Chem. (2) 97, 84 (1913). (8) Olivier, Rec. trav. chim. 41, 305-306 (1921). (9) von Braun, Engel, Ann. 436, 319-320 (1924). (10) Olivier, Weber, Rec. trav. chim. 53, 885 (1934).

(11) Ivanoff, Spassoff, Bull. soc. chim. (4) 9, 20 (1931). (12) Ivanoff, Pchenitchny, Bull. soc. chim. (5) 1, 228 (1934). (13) Curtius, Schmidt, Ber. 55, 1577-1578 (1922).

C₈H₉Cl

Beil. V - 373

 V_{1} -(183)

CH₃

3:8665 4-CHLORO-1,3-DIMETHYLBENZENE

(unsym.-Chloro-m-xylene)

$$V_{2}$$
-(291)

B.P. 192.2-193.9° (1) (?)
 $D_{20}^{20} = 1.0598$ (3) $n_{D}^{25} = 1.5230$ (5)
187-188° at 755 mm. (2)
186.5° cor. at 767 mm. (3)
183-184° (6)
73-75° at 16 mm. (4)

[For prepn. of \tilde{C} from 1,2-dimethylbenzene (m-xylene) (1:7420) with Cl_2 in pres. of I_2 see (6) (3), with SO_2Cl_2 in the dark see (7), as by-product in prepn. of m-xylyl (di)chloride (3:8700) see (5); for prepn. of \tilde{C} from 4-amino-1,2-dimethylbenzene (unsym.-m-xylidine) [Beil. XII-1111, XII₁-(483)] via diazotization and use of Cu_2Cl_2 reaction see (2) (1); for formn. of \tilde{C} from 1,3-dimethylbenzenesulfonic acid-4 [Beil. XI-123, XI₁-(34)] by htg. with $SOCl_2$ in a s.t. at 160° for 3-4 hrs. see (8); for formn. of \tilde{C} from 4-bromo-1,3-dimethylbenzene via conversion to RMgBr and reactn. with Cl.CN see (4); for prepn. of \tilde{C} from p-chlorotoluene (3:8287) by chloromethylation with Cl_2O + HCl to 4-chloro-3-(chloromethyl)-toluene and subsequent reduction with Zn + NaOH see (20).]

[For reactn. of \bar{C} with 4,4'-tetramethyldiaminobenzophenone (Michler's ketone) + Na in toluene yielding bis-(4-dimethylaminophenyl)-4-m-xylylcarbinol, odorless ndls. from m.p. 145°, see (9); for use of this prod. in prepn. of homologs of malachite green alc., (10) (11) and other dyestuffs (12) see indic. refs.]

 \tilde{C} on oxidn. with $K_2Cr_2O_7 + H_2SO_4$ (6) (3) (7) yields 4-chloro-3-methylbenzoic acid (3:4915), cryst. from aq., m.p. 209-210° (3) (7). — \tilde{C} on oxidn. with aq. KMnO₄ gives (13) (14) 4-chlorobenzenedicarboxylic acid-1,3 (4-chloroisophthalic acid) (3:4980), ndls. from hot aq., m.p. 294.5° (14), 295° (13).

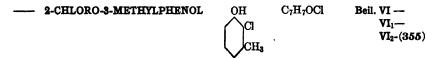
 \bar{C} in Ac₂O treated with mixt. of HNO₃ + H₂SO₄ as specified (15) yields 6-nitro-4-chloro-1,3-dimethylbenzene [Beil. V-379, V₁-(184)], m.p. 42° (15). [The other mononitro derivs. of \bar{C} have been prepd. indirectly, viz., 5-nitro- \bar{C} [Beil. V-379] (16), m.p. 51°; 3-nitro- \bar{C} , m.p. 72-73° (17).]

 \tilde{C} on sulfonation with a mixt. of equal pts. fumg. H_2SO_4 + conc. H_2SO_4 yields (18) 4-chloro-1,3-dimethylbenzenesulfonic acid-6 [Beil. XI-123] (corresp. sulfonamide, m.p. 195° (3)).

Č on bromination with Br₂ + HNO₃/H₂SO₄ mixt. (19) yields 6-bromo-4-chloro-1,3-dimethylbenzene [Beil. V-374], m.p. 66° (19).

3:8665 (1) Kohlrausch, Pongratz, Monatsh. 64, 370 (1934). (2) Klages, Ber. 29, 310 (1896). (3) Jacobsen, Ber. 18, 1761 (1885). (4) Grignard, Bellet, Courtot, Ann. chim. (9) 4, 45 (1915). (5) King, Merriam, Proc. Nova Scotian Inst. Sci. 18, 276-281 (1933/1934); Cent. 1935, II 2359; C.A. 29, 6214 (1935). (6) Vollrath, Ann. 144, 266-267 (1867). (7) Töhl, Eberhard, Ber. 26, 2942 (1893). (8) Meyer, Ann. 433, 336 (1923). (9) Rodd, Linch, J. Chem. Soc. 1927, 2177. (10) Lawrie, Linch, Rodd, British Dyestuffs Corp., Brit. 297,897, Nov. 25, 1928; Cent. 1929, I 1274.

(11) British Dyestuffs Corp., Linch, Rodd, Brit. 301,193, Dec. 20, 1928; Cent. 1929, I 1747. (12) Imperial Chem. Ind., Rodd, Linch, Brit. 314,825, Aug. 1, 1929; Cent. 1929, II 2610. (13) Davies, Wood, J. Chem. Soc. 1928, 1126. (14) Ullmann, Uzbachian, Ber. 36, 1799 (1903). (15) Varma, Raman, J. Indian. Chem. Soc. 12, 540 (1935). (16) Karrer, Fritzsche, Helv. Chim. Acta 19, 482 (1936). (17) Dadswell, Kenner, J. Chem. Soc. 1927, 1106. (18) Gundelach, Bull. soc. chim. (2) 28, 343 (1877). (19) Varma, Raman, J. Indian Chem. Soc. 12, 248 (1935). (20) Tschunkur, Eichler (to I.G.), Ger. 509,149, Oct. 8, 1930; Cent. 1931, I 360; [C.A. 25, 711 (1931)].



B.P. abt. 194°

M.P. 55-56°

See 3: 1055. Division A: Solids.

3:8667
$$d_{r}l_{-\alpha}$$
-CHLOROETHYLBENZENE H $C_{8}H_{9}Cl$ Beil. V - 354 (Methyl-phenyl-carbinyl chloride) V_{1} -(177) V_{2} -(277)

B.P. 195° dec. (1) $D_{4}^{20} = 1.0620$ (9) $n_{D}^{20} = 1.5276$ (9) 194° dec. (2) 90-91° at 33 mm. (3) $D_{4}^{20} = 1.0598$ (6) $n_{D}^{13} = 1.5337$ (6) 82-83° at 18 mm. (4) 81-82° at 17 mm. (5) 91-92° at 15 mm. (6) 69-70° at 13 mm. (7) 67.5° at 12 mm. (8) 68° at 9 mm. (9)

 \bar{C} even on stdg. tends to lose HCl with formn, of styrene and styrene polymers (9); such decompn, is facilitated by pres. of any HCl and \bar{C} could not be dried with P_2O_5 (10).

[Both opt. act. stereoisomerides of C are known but cannot be discussed here.]

[For prepn. of $\bar{\mathbb{C}}$ from methyl-phenyl-carbinol (1:6475) with 6 N HCl (75% yield (3)) (7), with aq. HCl in pres. of $\mathrm{CaCl_2}$ (2) (8), with HCl + $\mathrm{ZnCl_2}$ (71% yield (11)), with SOCl₂ (82-88% yield (11)) (4) (5) (10), or with acetyl chloride (3:7065) (12) see indic. refs.; from ethylbenzene (1:7410) with $\mathrm{Cl_2}$ in light (1) (13) (14) (15) or in pres. of 1% PCl₅ (90% yield (16)) see indic. refs.; from styrene (1:7435) by addn. of HCl (9) (17) (18) under press. in solvent (100% yield (19)) or at -80° (68% yield (29)) see indic. refs.; for formn. of $\bar{\mathbb{C}}$ from methyl-phenyl-carbinyl MgBr during reaction with cyanogen chloride (47% $\bar{\mathbb{C}}$ + 10% methyl-phenyl-carbinyl cyanide + 5% 2,3-diphenylbutane) see (6); for formn. of $\bar{\mathbb{C}}$ from methyl phenyl ketone (acetophenone) (1:5515) during reduction with $\mathrm{Zn/Hg}$ + HCl see (20).]

[C passed at elevated temp. over dehydrohalogenating cat. (21), or htd. with pyridine in s.t. 6 hrs. at 130° (77% yield (22)), or boiled with a small excess quinoline for ½ hr. (75–80% yield (16)) (23), or its quat. salt with pyridine htd. in vac. (24), or htd. with acids less volatile than HCl (25), or htd. with salts of org. bases (26) (23) yields styrene (1:7435), b.p. 145°.]

[\bar{C} with H₂ and Pd in pres. of MgO as specified (8) gives rapidly and quant ethylbenzene (1:7410); note that \bar{C} reduces much more readily than the isomeric β -chloroethylbenzene (3:8712) (8).]

 \bar{C} on hydrolysis, e.g., by boilg. with 25% excess of 10-15% aq. Na₂CO₃ soln., gives (90% yield (16)) (27) methyl-phenyl-carbinol (1:6475) q.v.; \bar{C} with aq. alc. or with aq. alc. NaOH gives at 50° only (5) methyl-phenyl-carbinol; at 100° both styrene (1:7435) and α,α -diphenyl-diethyl ether are also formed (5); under certain circumstances α -diphenyl-diethyl ether may also appear (5) (1). [For study of hydrolysis of \bar{C} in acetone contg. HgCl₂ see (4).]

[\overline{C} with aq. Na₂SO₃ on boilg. for 9 hrs. (14) (7) gives (43-45% yield (14)) sodium α -phenylethanesulfonate (corresp. sulfonyl chloride, ndls. from alc., m.p. 79° (14) cf. (7), corresp. sulfonamide and anilide are unreported).]

C on oxidn. with Cu(NO₃)₂ (13) or on boilg. with aq. or dil. alc. soln. of hexamethylenetetramine (28) gives (60% yield (13)) methyl phenyl ketone (acetophenone) (1:5515).

3:8667 (1) Schramm, Monatsh. 8, 101–105 (1887). (2) Engler, Bethge, Ber. 7, 1127 (1874). (3) Norris, Watt, Thomas, J. Am. Chem. Soc. 38, 1078 (1916). (4) Read, Taylor, J. Chem. Soc. 1949, 681. (5) Ward, J. Chem. Soc. 1927, 445–458. (6) Grignard, Ono, Bull. soc. chim. (4)

1593 (1926).
 Kharasch, May, Mayo, J. Org. Chem. 3, 188-189 (1939).
 Paal, Müller-Lobeck, Ber. 64, 2148-2149 (1931).
 Breitenbach, Maschin, Z. physik. Chem. A-187, 181 (1940).
 Hughes, Ingold, Scott, J. Chem. Soc. 1937, 1275.

(11) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929). (12) Radziszewski, Ber. 7, 142 (1874). (13) Fischer, Schmitz, Ber. 39, 2210 (1906). (14) Evans, Mabbott, Turner, J. Chem. Soc. 1927, 1159-1160, 1162-1163. (15) Darapsky, J. prakt. Chem. (2) 146, 287 (1936). (16) Zal'kind, Berkovich, Amusin, Plasticheskie Massy 1934, No. 1, 14-20; Cent. 1934, II 3435; C.A. 28, 5810 (1934). (17) I.G., French 745,533, May 12, 1933; Cent. 1933, II 2327. (18) I.G. French 724,105, April 22, 1932; Cent. 1933, I 505. (19) I.G., Ger. 646,479, June 15, 1937; Brit. 464,054, April 12, 1937; Cent. 1937, II 1662; C.A. 31, 6252 (1937). (20) Steinkopf, Wolfram, Ann. 430, 157 (1923).

(21) Smith (to Naugatuck Chem. Co.), U.S. 1,687,903, Oct. 16, 1928; Brit. 298,152, Oct. 4, 1927; Cent. 1929, I 2922; C.A. 23, 156 (1929). (22) Klages, Keil, Ber. 36, 1632 (1903). (23) I.G., French 729,730, July 30, 1932; Cent. 1932, II 3015. (24) Dorough (to du Pont Co.), U.S. 1,892,386, Dec. 27, 1932; Cent. 1933, I 2872; C.A. 27, 1897 (1933). (25) I.G., French 729,687, July 29, 1932; Cent. 1932, II 3015. (26) Naugatuck Chem. Co., French 721,843, March 8, 1932; Cent. 1932, II 2109. (27) Zal'kind, Berkovich, Amusin, Russ. 34,547, Feb. 28, 1934; Cent. 1935, I 3347. (28) Fabr. de Laire, Ger. 268,786, Jan. 2, 1914; Cent. 1914, I 589. (29) Kharasch, Kleiman, J. Am. Chem. Soc. 65, 13-44 (1943).

3:8670 2,2-DICHLORO-OCTANE Cl
$$C_3H_{16}Cl_2$$
 Beil. I - 160 I_1 — $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2$ — CH_3 — CH_3

B.P. 190-200° (1)

[For prepn. of \bar{C} from octanone-2 (*n*-hexyl methyl ketone) (1:5490) with PCl_5 see (1).] 3:8670 (1) Dachauer, *Ann.* 106, 271 (1858).

B.P.
$$195^{\circ}$$
 u.c. (1) F.P. -6.25° (2) $D_{15}^{15} = 1.0692$ (4) 194° at 755 mm. (2) $192.2-194.0^{\circ}$ (3) 191.5° cor. (4) $75.6-75.8^{\circ}$ at 15 mm. (3)

[For prepn. of $\bar{\mathbb{C}}$ from 4-amino-1,2-dimethylbenzene (unsym.-o-xylidine) [Beil. XII-1103, XII₁-(480)] via diazotization and use of $\mathrm{Cu_2Cl_2}$ reaction see (2) (3); for prepn. of $\bar{\mathbb{C}}$ from o-xylene (1:7430) with $\mathrm{Cl_2}$ in pres. of I₂ (4) (1) or Fe (5) (1) (the isomeric 3-chloro-1,2-dimethylbenzene (3:8645) and other products are also formed) see indic. refs.]

 \bar{C} on oxidn. with hot dil. HNO₃ (D=1.2) or by htg. with HNO₃ (D=1.1) in a s.t. at 160° yields (4) (5) a mixt. of 5-chloro-2-methylbenzoic acid (3:4670), m.p. 130°, and 4-chloro-2-methylbenzoic acid (3:4700), eas. volatile with steam, ndls. from aq. or dil. AcOH (6), m.p. 170° (5) (6).

 \bar{C} added to 3-4 vols. HNO₃ (D=1.5) in the cold, then htd. ½ hr. at 100°, then poured into aq. yields (2) 4-chloro-5-nitro-1,2-dimethylbenzene, m.p. 63° (2) (7). [Note (a) that small amt. of a dinitro cpd., m.p. 111° (2), is also formed; (b) that the prod. of m.p. 73° so obtd. by earlier work (1) was certainly impure; and (c) that the isomeric 3-nitro-4-chloro-1,2-dimethylbenzene has m.p. 75° (7).]

Č on sulfonation (4) (5) yields exclusively 4-chloro-1,2-dimethylbenzenesulfonic acid-5 [Beil. XI-121] (corresp. sulfonyl chloride, as yet unreported; sulfonamide, ndls. from alc., m.p. 207° (4)).

 \tilde{C} with Cl_2 in pres. of Fe yields (2) 4,5-dichloro-1,2-dimethylbenzene, m.p. 76°, b.p. 240° (2).

Claus, Groneweg, J. prakt. Chem. (2) 43, 257 (1891). (2) Hinkel, Ayling, Walters, J. Chem. Soc. 1934, 1947–1948. (3) Kohlrausch, Pongratz, Monatsh. 64, 371 (1934). (4) Krüger, Ber. 18, 1756–1758 (1885). (5) Claus, Bayer, Ann. 274, 305–309 (1893). (6) Huntress, Seikel, J. Am. Chem. Soc. 61, 820 (1939). (7) Hinkel, Ayling, Walters, J. Chem. Soc. 1934, 286–287.

3:8680 n-OCTANOYL CHLORIDE
$$CH_3$$
.(CH₂) $_6$.C=O C_8H_{16} OCl Beil. II - 348 (n-Capryloyl chloride) H_1 .— H_2 -(303)

B.P. F.P. 195.55° at 760 mm. (1)
$$-61.1$$
° (1) cf. (19) $D_4^2 = 0.94483$ (1) 194-195° at 756 mm. (2) -63 ° to -62.5 ° cor. (19) 188-192° (3) $D_4^{20} = 0.94866$ (1) 91° at 22 mm. (4) 83° at 15 mm. (5) (19) $D_4^{15} = 0.95349$ (1) 74-77° at 11 mm. (6) [104-105° at 9 mm. (18)] $n_{\text{He}\alpha}^{15} = 1.43408$ (1)

Care must be taken not to confuse \bar{C} , the acid chloride of *n*-caprylic acid, with the corresponding relatives of *n*-caproic acid (C_6) and of *n*-capric acid (C_{10}); for this reason the name *n*-octanoyl chloride is preferred.

[For prepn. of \bar{C} from *n*-octanoic acid (*n*-caprylic acid) (1:1145) with PCl₅ (yield: 82% (19), 64% (7), with PCl₃ (2) (8), with PCl₃ + ZnCl₂ (90% yield (7)), with SOCl₂ (3) (96% yield (6)), or with oxalyl (di)chloride (3:5060) (18) see indic. refs.]

[For use of \bar{C} in prepn. of corresp. cellulose esters see (9) (10); for use in syntheses of glycerides see (11) (12); for use with AlCl₃ in Friedel-Crafts synthesis of various ketones see (13) (14) (19); for use in prepn. of derivatives of vanillylamine see (4) (16); for cathydrogenation to octanaldehyde (1:0192) see (15).]

[\bar{C} with AlCl₃ + phenol yields (17) 45% o-(n-octanoyl)phenol, m.p. 22.3°, b.p. 169-170° at 11 mm., D_{-}^{24} = 0.9989, n_{D}^{25} = 1.5169 (17) (semicarbazone, m.p. 157-158° (17)), and 38% p-(n-octanoyl)phenol, m.p. 62°, b.p. 224-225° at 10 mm. (17) (benzoate, m.p. 107-108° (17)).]

 \tilde{C} on hydrolysis yields n-octanoic acid (n-caprylic acid) (1:1145) q.v. (for the amide, anilide, p-toluidide, and other derivs. corresponding to \tilde{C} see 1:1145).

3:8680 (1) Deffet, Bull. soc. chim. Belg. 40, 389-394 (1931). (2) Henry, Bull. acad. roy. Belg. (3) 37, 63-72 (1899); Cent. 1899, I 968; Rec. trav. chim. 18, 252-253 (1899). (3) Bardan, Bull. soc. chim. (5) 1, 143 (1934). (4) Ford-Moore, Phillips, Rec. trav. chim. 53, 855 (1934). (5) Krafft, Koenigs, Ber. 23, 2384 (1890). (6) Fierz-David, Kuster, Helv. Chim. Acta 22, 86-89 (1939). (7) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (8) Aschan, Ber. 31, 2348 (1898). (9) Brit. 201,510, Sept. 19, 1923; Cent. 1923, IV 961. (10) Brit. 313,616, Aug. 8, 1929; Cent. 1929, II 2743.

(11) Heiduschka, Schuster, J. prakt. Chem. (2) 120, 155-156 (1928). (12) Robinson, Roche, King, J. Am. Chem. Soc. 54, 705-710 (1932). (13) Hartung, Munch, Deckert, Crossley, J. Am. Chem. Soc. 52, 3320 (1930). (14) Ralston, Bauer, J. Org. Chem. 5, 165-170 (1940). (15) Escourrou, Bull. soc. chim. (5) 6, 1181 (1939). (16) Nelson, J. Am. Chem. Soc. 41, 2124 (1919). (17) Sandulesco, Girard, Bull. soc. chim. (4) 47, 1309-1310 (1930). (18) Averill, Roche, King, J. Am. Chem. Soc. 51, 868 (1929). (19) Paquette, Lingafelter, Tartar, J. Am. Chem. Soc. 65, 686 (1943).

3:8700 m-XYLYL CHLORIDE (m-Methylbenzyl chloride, ω-chlorom-xylene)

$$\begin{array}{cccc} CH_2Cl & C_8H_9Cl & Beil. \ V - 373 & & V_{1^-}(183) \\ CH_3 & & V_{2^-}(291) & & & \end{array}$$

 $D_{20}^{20} = 1.064 (2) \quad n_{\rm D}^{25} = 1.5327 (1)$

[For special study of prepn. (76% yield) by chlorination of m-xylene (1:7420) in light see (1).]

 \bar{C} stood with N/10 alc. NaOEt at 30° yields ethyl m-xylyl ether [Beil. VI-494], b.p. 202°, to extent of 10.9% in 6 hrs., 32.4% in 24 hrs. (3) cf. (4). [For data on rate of hydrolysis with acid or alkali in acetone soln. at 30° see (5).]

Č with Mg in ether yields R.MgCl; on carbonation at 0° (7) this yields m-CH₃.C₆H₄.CH₂.-COOMgCl; this upon acidification presumably (no record) would yield m-tolylacetic acid [Beil. IX-528], m.p. 61°; upon treatment (8) with C₂H₅MgBr, however, it gives a mixt. contg. 57.6% m-tolylmalonic acid, colorless pdr. from CHCl₃, m.p. 130-131° with loss of CO₂ (8). [Use of isopropyl MgCl in place of C₂H₅MgBr gave 88% of m-tolylmalonic ac. (8).]

 \overline{C} on boiling with Pb(NO₃)₂ soln. (2), or Cu(NO₃)₂ soln. (30% yield (6)), or alk. Na₂CrO₄ (90% yield (6)) gives *m*-tolualdehyde (1:0208).

N-(o-Xylyl)phthalimide [Beil. XXI-467]: ndls. from alc., m.p. 117-118°. [Reported
 (9) from m-xylyl bromide and therefore presumably obtainable under appropriate
 conditions from C.]

3:8700 (1) King, Merriam, Proc. Nova Scotian Inst. Sci. 18, 276-281 (1933/34); C.A. 29, 6214 (1935); Cent. 1935, II 2359. (2) Gundelach, Bull. soc. chim. (2) 26, 43 (1876). (3) Franzen, J. prakt. Chem. (2) 97, 83-84 (1918). (4) Olivier, Rec. trav. chim. 41, 306-307 (1921). (5) Olivier, Weber, Rec. trav. chim. 53, 885 (1934). (6) Posner, Schreiber, Ber. 57, 1131, 1137 (1924). (7) Ivanoff, Spassoff, Bull. soc. chim. (4) 9, 20 (1931). (8) Ivanoff, Pchenitchny, Bull. soc. chim. (5) 1, 227 (1934). (9) Brömme, Ber. 21, 2700 (1888).

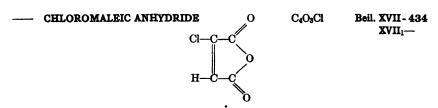
3: 8703 ETHYL
$$d,l-\gamma$$
-CHLORO- n -VALERATE $C_7H_{13}O_2Cl$ Beil. II - 302 CH_3 -CH.CH₂.CH₂.COOC₂H₅ II_1 -(131) II_2 —

B.P. 196° (1) $D_4^{20} = 1.0393$ (1) $n_D^{20} = 1.4310$ (1) 70.5° at 9 mm. (2)

Oil with odor like amyl acetate.

[For prepn. of \bar{C} from γ -chloro-n-valeric acid (3:9270) + EtOH + H₂SO₄ see (1); from γ -n-valerolactone (1:5080) with HCl in EtOH see (3).] [For the opt. active isomers of \bar{C} see Beil. II₂-(268) and subsequent literature.]

3:8763 (1) Schjanberg, Ber. 76, 2385-2391 (1937). (2) Wohlgemuth, Compt. rend. 158, 1578 (1914); Ann. chim. (9) 2, 300-301 (1914). (3) Noyes, Cox, J. Am. Chem. Soc. 25, 1094 (1903).



B.P. 196° cor.

M.P. 33-34°

 $D_4^{15} = 1.5427$

See 3:0280. Division A: Solids.

--- 6-CHLORO-3-METHYLPHENOL OH
$$C_7H_7OCl$$
 Beil. VI -- $VI_{1^-}(187)$ VI $_{2^-}(355)$ B.P. 196° M.P. 46° $D_{-5}^{15}=1.215$

See 3:0700. Division A: Solids.

3:8705 4-CHLORO-ISOPROPYLBENZENE
$$C_9H_{11}Cl$$
 Beil. V - 395 $V_1-V_2-(307)$

B.P. 195-197° at 750 mm. (1)
$$D_{20}^{20} = 1.0257$$
 (2) $n_{\rm D}^{25} = 1.514$ (1) 81° at 15 mm. (2) 1.0022 (1) 66-72° at 11 mm. (7) 1.0190 (7) $n_{\rm D}^{20} = 1.5120$ (2) 1.5109 (7)

The first reference given in Beil. V-395 is erroneous.

[For prepn. of \bar{C} from β -(p-chlorophenyl)propene (2) by cat. hydrogenation see (2); from chlorobenzene (3:7903) with isopropyl alc. (1:6135) + H₂SO₄ (72% yield) see (3) or with isopropyl alc. (1:6135) + BF₃ + P₂O₅ (63% yield) see (7); for formn. of \bar{C} from isopropylbenzene (cumene) (1:7440) with Cl₂ (together with other prods.) (4) (5) or with SO₂Cl₂ + AlCl₃ (6) see indic. refs.]

 \overline{C} on oxidn. with HNO₃ (D=1.2) yields (3) (4) p-chlorobenzoic acid (3:4940).

Č with chlorosulfonic acid yields a sulfonyl chloride which with NH₃ yields a sulfonamide, probably 2-chloro-5-isopropylbenzenesulfonamide, m.p. 91° (2).

3:8705 (1) Tsukervanik, J. Gen. Chem. (U.S.S.R.) 8, 1512-1515 (1938); Cent. 1939, I 4929; C.A. 33, 4587 (1939). (2) Ellingboe, Fuson, J. Am. Chem Soc. 55, 2965 (1933). (3) Meyer, Bernhauer, Monatsh. 53/54, 741 (1929). (4) Qvist, Acta Acad. Aboensus, Math. et Phys. 8, No. 4, 30 pp. (1934); Cent. 1934, II 595; 1936, I 540; C.A. 29, 6885 (1935). (5) Varma, Srinivasan, J. Indian Chem. Soc. 13, 191 (1936). (6) Töhl, Eberhard, Ber. 26, 2944 (1893). (7) Hennion, Pieronek, J. Am. Chem. Soc. 64, 2751-2752 (1942).

3:8710 o-XYLYL CHLORIDE (o-Methylbenzyl chloride,
$$\omega$$
-chloro-o-xylene) CH₃ C₈H₉Cl Beil. V - 364 V₁-(180) CH₂Cl V₂-(283)

B.P. 197-199° (1) 92-94° at 20 mm. (2) 76-80° at 14 mm. (3) Lachrymatory oil.

[For prepn. (88% yield) from o-tolylcarbinol (1:5922) by action of thionyl chloride and pyridine see (2), by action of $H_2SO_4 + HCl$ (85-92% yield) see (3); the prepn. from o-xylene (1:7430) by action of trioxymethylene + HCl gives a mixture of \bar{C} and p-xylyl chloride (3:8660) (4) (5) (6).]

 \bar{C} stood with N/10 alc. NaOEt at 30° yields ethyl o-xylyl ether [Beil. VI-484], oil, b.p. 208-210°, to extent of 21% in 6 hrs., 52% in 24 hrs. (7) cf. (8). [For data on rate of hydrolysis with acid or alkali in acetone soln. at 30° see (9).]

Č with Mg in ether yields R.MgCl; on carbonation at 0° (10) this yields o-CH₃.C₆H₄.CH₂.-COOMgCl; this upon acidification presumably (no record) would yield o-tolylacetic acid [Beil. IX-527], m.p. 88−89°; upon treatment (11) with C₂H₅MgBr, however, it gives 83.3% yield of o-tolymalonic ac., ndls. from aq., m.p. 139−140°, with loss of CO₂ (11), + 16% yield of o-tolylacetic ac.

Č refluxed 5 hrs. with dil. alc. KCN gives 74% yield (2) o-tolylacetonitrile [Beil. IX-527], b.p. 244°, which on boiling 1 hr. with dil. H₂SO₄ (2) gives 73% yield (2) of o-tolylacetic ac. [Beil. IX-527], ndls. from aq., m.p. 88-89°.

Č on warming at 100° with 1.3 moles pyridine gives ppt. of o-xylylpyridinium chloride, cryst. from CH₃OH + dry ether, m.p. 183° (12).

N-(o-Xylyl)phthalimide [Beil. XXI-467]: cryst. from alc., m.p. 148-149°. [Reported (13) from o-xylyl bromide and therefore presumably obtainable under appropriate conditions from C.]

3:8710 (1) Reyman, Bull. soc. chim. (2) 26, 534 (1876). (2) Hill, Short, J. Chem. Soc. 1935, 1125. (3) Reichstein, Cohen, Ruth, Meldahl, Helv. Chim. Acta 19, 415 (1936). (4) Darzens, Compt. rend. 208, 818-820 (1839). (5) Shorygin, Skoblinskaya, J. Gen. Chem. (U.S.S.R.) 6, 1578-1582 (1936); Cent. 1937, I 1678; C.A. 31, 2196 (1937). (6) Hoch, Compt. rend. 192, 1465 (1931). (7) Franzen, J. prakt Chem. (2) 97, 83 (1918). (8) Olivier, Rec. trav. chim. 41, 306 (1921). (9) Olivier, Weber, Rec. trav. chim. 53, 885 (1934). (10) Ivanoff, Spassoff, Bull. soc. chim. (4) 9, 20 (1931).

(11) Ivanoff, Pchenitchny, Bull. soc. chim. (5) 1, 226 (1934). (12) von Braun, Nelles, Ber. 70, 1762 (1937). (13) Strassmann, Ber. 21, 576 (1888).

3:8712 β-CHLOROETHYLBENZENE C₈H₉Cl Beil. V-(354) (ω-Chloroethylbenzene, β-phenylethyl chloride, benzylcarbinyl chloride) CH₂.CH₂Cl V₁-(177) V₂-(277)

	•				
B.P.	I	B.P. (conta			
197-198°	(1) 8	88°	at 16 mm.	(9) D	$_{4}^{25} = 1.069 (14)$
192-198° dec. at 760 mm.	(2) 8	82-84°	at 16 mm.	(2)	
190-200° sl. dec.	(3)	83-84°	at 14 mm.	(10)	$n_{\rm D_s}^{20} = 1.5294 (11)$
96° at 23 mm.	(4) 8	81-84°	at 14 mm.	(11)	
91-92° at 20 mm.	(3) (5) 8	85-86°	at 12 mm.	(5)	
80° at 20 mm.	(6)	79°	at 12 mm.	(12)	
94-96° at 18 mm.	(7) <i>E</i>	68.5-69°	at 4 mm.	(13)	
89-92° at 16 mm.	(8)				

Colorless oily liquid.

[For prepn. of \tilde{C} from β -phenylethyl alc. (1:6505) with fumg. HCl in s.t. 4 hrs. at 140° (57% yield (13)) (15), with conc. HCl + ZnCl₂ (82% yield (8)), with 6 N HCl (small yield (16)), with PCl₅ in CHCl₃ (yield 70% (3)) (10) (12) (prod. conts. P compounds (10) removed with NaHCO₃ (12)) or in CCl₄ (80% yield (5)), with SOCl₂ at room temp. (yields:

87% (10) (11), 74% (6)) or warming in dimethylaniline (91% yield (1)) (17) (for intermediate forms, of β -phenylethyl chlorosulfite see (18)) see indic. refs.]

[For formn. of Č from β -chloroethyl p-toluenesulfonate with C_6H_5MgBr (36% yield (19)) (20) see indic. refs.; from di-(β -chloroethyl) sulfate with C_6H_5MgBr (25% yield) see (21); from C_6H_5HgCl with ICl in CCl₄ (35% yield) see (11); from methyl β -phenylethyl ether (22) or N-(β -phenylethyl)benzamide (7) (15) or N,N-bis-(β -phenylethyl)benzamide (60% yield (23)) with PCl₅ see indic. refs.; from β -phenylethylamine hydrochloride with HNO₂ see (24); from bis-(β -phenylethyl) ether with AcCl + ZnCl₂ see (9); from bislg. ethylbenzene (1:7410) with Cl₂ (as by-product of the α -isomer) see (25) (26) (27) (35).]

 \ddot{C} on oxidn. with CrO_5/H_2SO_4 is much more resistant than benzyl chloride (3:8535) (28) but ultimately yields benzoic acid (1:0715), m.p. 121°. — [\ddot{C} passed with steam and air at 450° over pumice impregnated with V_2O_5 gives (29) benzoic acid (52%), benzaldehyde (35%), phenylacetaldehyde (6%), and styrene (3%).]

[\bar{C} on reduction with $H_2 + Pd/CaCO_3$ in pres. of MgO ultimately gives ethylbenzene (1:7410) but rate is very much slower than with α -chloroethylbenzene (3:8667) (12).]

[For study of rate of reactn. of \bar{C} with aq. alc. NaOH (much slower than with α -chloroethylbenzene (3:8667) see (10); for rate with NaOEt see (30); for rate with NaOPr see (47); \bar{C} with KOC₆H₅ in alc. gives (45–50% yield (31)) phenyl β -phenylethyl ether [Beil. VI-479], b.p. 180° at 23 mm., $D_4^{20} = 1.0501$ (31); \bar{C} with NaOAc + AcOH yields (32) mainly β -phenylethyl acetate (1:3922), but 15% of the isomeric methyl-phenyl-carbinyl acetate [Beil. VI-476, VI₁-(236)], b.p. 222° (32), is also formed.]

[C with NaI in acetone boiled 4 hrs. gives (33) β-phenylethyl iodide, b.p. 125-128° at 18-20 mm. (33) (for rate of reactn. of C with KI in acetone see (13) (34)): C with alc. KCN yields (25) (26) (27) β-phenylethyl cyanide [Beil. IX-512, IX₁-(199)] which on hydrolysis gives hydrocinnamic acid (1:0615), m.p. 48-49°; C on boilg, for 20 hrs. with conc. aq. Na₂SO₃ gives (65% yield (35)) sodium β-phenylethanesulfonate (corresp. sulfonyl chloride, m.p. 34° (35); corresp. sulfonamide, m.p. 119° (35), 124° (20); corresp. sulfonamide m.p. 77° (35)) accompanied by a little β-phenylethyl alcohol (1:6505) but without any evolution of SO₂ (contrary to previous report (36)).]

Č with Mg in dry ether yields (2) (11) (19) (5) (37) (38) C₆H₅.CH₂.CH₂.MgCl: this RMgCl epd. with dry CO₂ yields (19) hydrocinnamic acid (1:0615), m.p. 48-49°; with phenylisocyanate it yields (2) hydrocinnamanilide, m.p. 96°; with HgCl₂ it gives (85% yield (11)) β-phenylethyl HgCl, m.p. 163-166° (11). [For reactn. of this RMgCl epd. with cyclopentanone (38), cyclohexanone (37), α-tetralone (37), and other ketones see indic. refs.]

[\bar{C} with AlCl₃ in CS₂ or lgr. gives (12) (1) a resin; \bar{C} with AlCl₃ + C₆H₆ gives (85% yield (39)) (40) dibenzyl (1:7149) together with other products (26) (27).]—[\bar{C} with Na in C₆H₆ or ether (41) gives ethylbenzene (1:7410) and 1,4-diphenylbutane [Beil. V-616, V₁-(290)], m.p. 52°.] [For behavior of \bar{C} with benzhydryl sodium (42), triphenylmethyl sodium, etc. (6), see indic. refs.]

[Č on mononitration, e.g., with HNO₃ (D=1.52) at -15° (3) (24) (4) (45) or even at -70° (45) gives (70% yield (44)) β -(4-nitrophenyl)ethyl chloride, m.p. 49° (3) (44), 48–49° (4), 48° (45) (43), 46–47° (24), accompanied by (30% yield (44)) β -(2-nitrophenyl)ethyl chloride, an oil, b.p. 156.5–158° at 15 mm., $D_{-}^{20}=1.5620$, $n_{D}^{20}=1.562$ (46); some β -(2,4-dinitrophenyl)ethyl chloride, m.p. 136° (4), is sometimes formed (4).]

3:8712 (1) Sisido, Kato, J. Soc. Chem. Ind. Japan 43, Suppl. bind., 450-451 (1940); C.A. 35, 3246 (1941). (2) Underwood, Gale, J. Am. Chem. Soc. 56, 2119 (1934). (3) Barger, J. Chem. Soc. 95, 2194-2195, 2197 (1909). (4) Ferber, Ber. 62, 187 (1929). (5) Bergs, Ber. 67, 242-244 (1934). (6) Schlenk, Bergmann, Ann. 479, 83-84 (1930). (7) von Brau, Ber. 44, 2870 (1911). (8) Norris, Taylor, J. Am. Chem. Soc. 46, 756 (1924). (9) Gans, Holton, U.S. 2,013,752, Sept. 10, 1935; Cent. 1936, I 2207; C.A. 29, 6902 (1933). (10) Ward, J. Chem. Soc. 1937, 453, 458.

Beil. V - 476

 V_{1} -(230)

(11) Whitmore, Thorpe, J. Am. Chem. Soc. 55, 785 (1933). (12) Paal, Müller-Lobeck, Ber. 64, 2148-2150 (1931). (13) Conant, Kirner, J. Am. Chem. Soc. 46, 241, 249 (1924). (14) Dunstan, Hilditch, Thole, J. Chem. Soc. 163, 140 (1913). (15) von Braun, Deutsch, Ber. 45, 1268-1269 (1912). (16) Norris, Watt, Thomas, J. Am. Chem. Soc. 38, 1078 (1916). (17) Darzens, Compt. rend. 152, 1316 (1911). (18) Carré, Libermann, Compt. rend. 198, 274-276 (1934). (19) Gilman. Beaber, J. Am. Chem. Soc. 45, 842 (1923). (20) Ashworth, Burkhardt, J. Chem. Soc. 1928, 1798-1799.

(21) Suter, Evans, J. Am. Chem. Soc. **60**, 537 (1938). (22) Madinaveitia, Bull. soc. chim. (4) **25**, 604 (1919). (23) von Braun, Cahn, Ann. **436**, 266 (1924). (24) Shoesmith, Connor, J. Chem. Soc. **1927**, 2232. (25) Fittig, Kiesow, Ann. **156**, 246-247 (1870). (26) Schramm, Monatsh. 8, 104-105 (1887); Ber. **26**, 1706-1707 (1893). (27) Fischer, Schmitz, Ber. **39**, 2209-2210 (1906). (28) Courtot, Pierron, Compt. rend. **190**, 1057 (1930). (29) Shoruigin, Losev, J. Gen. Chem. (U.S.S.R.) **3**, 821-824 (1933); Cent. **1934**, II 2206; C.A. **28**, 6103 (1934). (30) Kindler, Ann. **452**, 119-120 (1927).

(31) Shoruigin, Ber. 58, 2035 (1925). (32) von Braun, Bartsch, Ber. 46, 3055 (1913). (33) Coleman, Hauser, J. Am. Chem. Soc. 50, 1196 (1928). (34) Baddeley, Bennett, J. Chem. Soc. 1935, 1820. (35) Evans, Mabbott, Turner, J. Chem. Soc. 1927, 1159-1163. (36) Clutterbuck, Cohen, J. Chem. Soc. 123, 2509 (1923). (37) Bergs, Ber. 67, 1621 (1934). (38) Denissenko, Ber. 69, 2184-2185 (1936). (39) Nenitzescu, Isacescu, Ionescu, Ann. 491, 219-220 (1931). (40) Anschutz, Ann. 235, 329-330 (1886).

(41) von Braun, Deutsch, Ber. 45, 2181 (1912). (42) Bergmann, J. Chem. Soc. 1936, 412-413. (43) Sobotka, Ber. 62, 2192 (1929). (44) Holleman, Hoeflake, Rec. trav. chim. 34, 261-264 (1915). (45) von Braun, Ber. 45, 1277-1278 (1912). (46) Kursanov, Kichkina, J. Gen. Chem. (U.S.S.R.) 5, 1342-1347 (1935); Cent. 1936, II 1534; C.A. 30, 2188 (1936). (47) Malkiel, Mason, J. Org. Chem. 8, 199-200 (1943).

3:8715 α-CHLOROVINYLBENZENE

 $(\alpha$ -Chlorostyrene)

B.P. F.P. 199° (1)
$$-24^{\circ}$$
 to -23° (5) $D_4^{24.6} = 1.0983$ (2) 83.5-84° at 23 mm. (2) $n_D^{24.6} = 1.55898$ (2) 85.0-85.5° at 22.5 mm. (3) $D_4^{20} = 1.101$ (2) 80-83° at 21 mm. (13) 1.0975 (3) 73° at 16 mm. (4) 1.0916 (3) 73-74° at 15 mm. (3) $n_D^{20.5} = 1.5584$ (5) 64° at 9 mm. (5) $n_A^{20.5} = 1.5684$ (5) $n_A^{20.5} = 1.5600$ (13) $n_D^{18} = 1.5645$ (4)

$$D_4^{17} = 1.1030$$
 (2)
 $D_4^{16.6} = 1.1024$ (2)
 $n_D^{16.5} = 1.56226$ (2)

 $n_{\rm D}^{17} = 1.56199$

Colorless liq. with arom. odor soon changing to that of formaldehyde and benzoyl chloride from air oxidation (5). — Č could not be polymerized even in u.v. light, by peroxides or SnCl4 (12).

[For prepn. of \tilde{C} from methyl phenyl ketone (acetophenone) (1:5515) with PCl₅ see (2) (1) (5) (6); from α,α -dichloroethylbenzene ("acetophenone dichloride") on htg. see (7); from β -bromo- α -chloroethylbenzene (styrene chloro-bromide) with alc. KOH in the cold (70% yield) see (4); from α,β -dichloroethyl benzene (styrene dichloride) (3:6685) with aq. alc. NaOH at 50-60° (89% yield) see (13).]

 \tilde{C} on boilg. with conc. HCl (4) (1), or \tilde{C} with 80% H₂SO₄ at 60° for 4 hrs. (13) cf. (14), gives (81% yield (13)) cf. (14) acetophenone (1:5515).

Č is resistant to actn. of alc. KOH (5); Č on refluxing for 13 hrs. with very conc. alc. NaOEt gives (8) some phenylacetylene (1:7425) together with other prods. (8).

[\tilde{C} with NOCl yields (9) α,β,β -trichlorostyrene, b.p. 148–150° at 20 mm. (9); \tilde{C} htd. with alc. KCN in s.t. at 200–220° yields (10) phenylsuccinonitrile which on saponification gives phenylsuccinic acid (1:0790); \tilde{C} with Na in liq. NH₃ gives (15% yield (10)) ethylbenzene (1:7410); \tilde{C} with NaNH₂ in liq. NH₃ gives (57% yield (11)) phenylacetylene (1:7425); \tilde{C} in alc. contg. BF₃/EtOAc (12) or in pres. of HCl (1) condenses with itself by loss of 3 HCl yielding 1,3,5-triphenylbenzene (1:7270).]

 \tilde{C} (10 g.) in C_6H_6 (10 ml.) stood 3 days with PCl_5 (30 g.) in C_6H_6 (50 ml.), then poured into aq. worked up as directed (13), yields 1-phenyl-1-chloroethylenephosphinic acid-2, C_6H_6 —C(Cl)—CH— $P(=0)(OH)_2$, ndls. from dil. HCl, m.p. 162° (13) (together with a little benzoic acid (1:0715), m.p. 121°).

3:8715 (1) Béhal, Bull. soc. chim. (2) 50, 632-638 (1888). (2) von Auwers, Ber. 45, 2799-2801 (1912). (3) Ley, Rinke, Ber. 56, 776 (1923). (4) Urion, Namias, Bull. soc. chim. (5) 3, 2335-2336 (1936). (5) Dufraisse, Viel, Bull. soc. chim. (4) 37, 878-879 (1925). (6) Taylor, J. Chem. Soc. 1987, 504-308. (7) Friedel, Ann. chim. (4) 16, 360 (1869). (8) Nef, Ann. 308, 269-270 (1898). (9) Perrot, Compt. rend. 202, 495 (1936). (10) Vaughn, J. Am. Chem. Soc. 56, 2064 (1934).

(11) Vaughn, Vogt, Nieuwland, J. Am. Chem. Soc. 56, 2121 (1934). (12) Marvel, Moon, J. Am. Chem. Soc. 62, 48 (1940). (13) Emerson, Agnew, J. Am. Chem. Soc. 67, 518-520 (1945). (14) Emerson (to Monsanto Chem. Co.), U.S. 2,372,562, March 27, 1945; C.A. 39, 3555 (1945).

3:8717
$$\beta$$
-CHLOROVINYLBENZENE C_8H_7Cl Beil. V - 476 $(\beta$ -Chlorostyrene, ω -chlorostyrene, styryl CH =CHCl V_2 -(367) chloride)

B.P.				B.P. (con	td.)		
199-199.2°			(1)	92-93°	at 22 mm.	(5)	$D_4^{25} = 1.1040 (1)$
199°	at 76	6 mm.	(2)	88-100°	at 18 mm.(2	20)	$n_{\rm D}^{25} = 1.5736 (1)$
197-199°			(3)	83°	at 18 mm.	(6)	1.5719 (20)
195.5-196.5°	at 71	5 mm.	(4)	89°	at 17 mm.	(7) (1)	1.5700 (20)
113°	at 4	4 mm.	(1)	82-87°	at 16 mm.(2	20) 2	$D_4^{20} = 1.109 (9)$
112°	at 4	0 mm.	(2)	83-84°	at 11 mm.		1.108 (9)
				79.5°	at 11 mm. ((9) 1	$D_4^{15} = 1.1122 (1)$
				78.5°	at 9 mm.	(9)	$n_{\rm D}^{15}=1.5808 (1)$

Liquid with odor of hyacinth; used in perfume industry. Although C should exist in two geom. stereoisomeric forms only this one has as yet been recognized. — Volatile with steam.

[For prepn. of \bar{C} from cinnamic acid (1:0735) with Cl₂/aq. or HOCl (1) (3) (10) (8) (12), with Cl₂ in EtOH (11), with NaOCl (13) (20), or Ca(OCl)₂ (14) see indic. refs.; from α,β -dichlorohydrocinnamic acid (cinnamic acid dichloride) [Beil. IX-514, IX₁-(200)] with Na₂CO₃ at 100° (yield: 97% (15) (1)) (9) (6) or with NaOAc (60% yield (5)) see indic. refs.; from α -chloro- β -hydroxyhydrocinnamic acid [Beil. X-250, X₁-(110)] by htg. with aq. in s.t. at 200–220° see (2) cf. (3): for formn. of \bar{C} from ω,ω -dichloroethylbenzene [Beil. V-354] with alc. KOH in s.t. at 120° see (4); from phenyl-trichloromethyl-carbinol [Beil. VI-476, VI₁-(237)] with Zn dust in alc. see (16); from α,β -dichloroethylbenzene (styrene dichloride) (3:6885) by htg. with pyridine (17) or by passing over Al₂O₃ at 360–400° and 85–105 mm. (92% yield (20)) see indic. refs.; from C₆H₅MgBr with acetylene tetrachloride (3:5750) see (18): from styrene chlorohydrin (3:9570) by dehydration over HPO₃ on silica gel at 370–400° and 95–115 mm. (63% yield) see (20).

[$\bar{\mathbf{C}}$ with Cl₂ in CHCl₃ yields (1) α,β,β -trichloroethylbenzene [Beil. V-355], b.p. 254.5–255.5° sl. dec. at 770 mm., b.p. 137° at 21 mm., $D_4^{15}=1.3619, n_D^{15}=1.5652$ (1); $\bar{\mathbf{C}}$ with

Br₂ in CHCl₃ yields (1) (13) (19) β -chloro- α,β -dibromoethylbenzene [Beil. V-356], ndls. from alc., m.p. 32° (1) (13), b.p. 165° sl. dec. at 26 mm. (1).

 \ddot{C} with alc. KOH in s.t. at 200-250° is partly resinified (2); \ddot{C} with very conc. alc. KOH gives on very strong htg. a chlorine-free oil which on distn. with aq. gives phenylacetaldehyde (1:0200) (4). [For rate of loss of halogen with alc. KOH see (5).] — \ddot{C} with EtOH/NaOEt in s.t. at 175-182° for $5\frac{1}{2}$ hrs. gives (66% yield (20)) β -ethoxystyrene [Beil. VI-564, VI₁-(279)] for conversion of which to phenylacetaldehyde see (20).]

 \bar{C} on oxidn. with $K_2Cr_2O_7 + H_2SO_4$ or with HNO₃ (D=1.2) gives (2) benzoic acid (1:0715).

3:8717 (1) Biltz, Ann. 296, 266-268, 272-273 (1897). (2) Glaser, Ann. 154, 164-167 (1870). (3) Forster, Saville, J. Chem. Soc. 121, 2595-2600 (1922). (4) Forster, Ber. 17, 982-983 (1884). (5) Dann, Howard, Davies, J. Chem. Soc. 1928, 609-610. (6) Durrans, J. Chem. Soc. 123, 1427 (1923). (7) Bergmann, J. Chem. Soc. 1936, 404. (8) Farmer, Hose, J. Chem. Soc. 133, 964. (9) von Auwers, Ber. 45, 2796-2797 (1912). (10) Erlenmeyer, Lipp, Ann. 219, 185-186 (1883). (11) Jackson, Pasiut, J. Am. Chem. Soc. 49, 2074 (1927). (12) Böeseken, Rec. trav. chim. 41, 204 (1921). (13) Ssuknewitsch, Tschilingarjan, Ber. 68, 1214 (1935). (14) Stenhouse, Ann. 55, 3-4 (1845). (15) Erlenmeyer, Ber. 14, 1868 (1881). (16) Jositsch, Favorski, J. Russ. Phys. Chem. Soc. 30, 920-924 (1898), Cent. 1899, I 607. (17) I.G., French 729,730, July 30, 1932; Cent. 1932, II 3015. (18) Swarts, Bull. soc. chim. (4) 25, 168-169 (1919). (19) Reich, van Wijck, Waelle, Helv. Chim. Acta 4, 248 (1921). (20) Emerson, Agnew, J. Am. Chem. Soc. 67, 518-520 (1945).

3: 8718
$$d$$
, l - α -CHLORO- α -METHYL- n -BUTYRIC ACID $C_5H_9O_2Cl$ Beil. II - 306 CH₃ II₁— II₂— CH₃.CH₂.C—COOH

B.P. 200-205° at 754 mm., sl. dec. (1)
$$D_{-}^{10} = 1.101$$
 (1) $n_{-}^{11} = 1.45077$ (1) 123-124° at 36 mm. (1)

Oily liq.; insol. aq.; sol. alc., ether.

[For prepn. of $\bar{\mathbf{C}}$ from α -chloro- α -methyl-n-butyronitrile by hydrolysis with conc. HCl see (1).]

- Methyl α -chloro- α -methyl-n-butyrate: unreported.
- Ethyl α -chloro- α -methyl-n-butyrate (see 3:8518).
- α -Chloro- α -methyl-n-butyramide: unreported.
- α -Chloro- α -methyl-n-butyranilide: unreported.
- —— α -Chloro- α -methyl-n-butyro-p-toluidide: unreported.

3:8718 (1) Servais, Rec. trav. chim. 20, 58-59 (1901).

3:8719 1-CHLORONONANE (
$$n$$
-Nonyl chloride) CH₃. (n -CH₂Cl C₉H₁₉Cl Beil. I — I₁— I₂-(128) B.P. 202° at 760 mm. (4) $D_{20}^{25} = 0.8931$ (3) $D_{20}^{25} = 1.4400$ (3) 98–100° at 22 mm. (1) $D_{20}^{20} = 0.8679$ (1) $D_{20}^{20} = 1.43692$ (1) 92.6–93.0° at 16 mm. (2) $D_{20}^{20} = 0.8704$ (4) 1.43400 (4) 76–79° at 4 mm. (3)

[For prepn. of \tilde{C} from nonanol-1 (1:6265) + PCl₈ + ZnCl₂ (53% yield) or PCl₅ + ZnCl₂ in C₆H₆ (58% yield) or excess SOCl₂ (76% yield (4)) in C₆H₆ (62% yield) see (1);

for prepn. of \tilde{C} (52% yield (3)) from *n*-hexyl MgBr + γ -chloro-*n*-propyl *p*-toluenesulfonate see (3).

3:8719 (1) Clark, Streight, Trans. Roy. Soc. Can. (3) 23, III 77-89 (1929). (2) Kohlrausch, Köppl, Monatsh. 63, 269 (1933). (3) Rossander, Marvel, J. Am. Chem. Soc. 50, 1495 (1928). (4) Vogel, J. Chem. Soc. 1943, 638, 640.

B.P. 203-205° (1) 94° at 22 mm. (2)

[For prepn. of \bar{C} from N,N'-bis-benzoylhexamethylenediamine [Beil. IX-263] via reactn. with PCl₅ and distn. of the resultant bis-(imide chloride) (64% yield (2)), or similarly from N-(benzoyl)hexamethyleneimine [Beil. XX₁-(27)] (3), see (2) (3); for formn. from hexamethylenediamine [Beil. IV-269] with NOCl (1) or from hexamediol-1,6 diphenyl ether [Beil. VI-148] by htg. with HCl in s.t. at 165-175° see (1).]

① Hexanediol-1,6 diphenyl ether (1,6-diphenoxyhexane) [Beil. VI-148]: cryst. from alc., m.p. 83° (2), 83.0-83.5° cor. (3). [From C on refluxing 12½ hrs. with large excess sodium phenolate in alc. (2) (41% yield (3))]. [The half reactn. prod., ω-chloro-n-hexyl phenyl ether [Beil. VI-144], is an oil, b.p. 164-165° at 11 mm. (4).]

3:8720 (1) Solonina, J. Russ. Phys.-Chem. Soc. 30, 606-632 (1898); Cent. 1899, I 25. (2) von Braun, Ber. 38, 2344-2345 (1905). (3) Muller, Sauerwald, Monatsh. 48, 732 (1927). (4) von Braun, Müller, Ber. 39, 4112-4113 (1906).

B.P. 204°

90-91°

M.P. 42°

at 20 mm. (3)

See 3:0460. Division A: Solids.

3:8725 2-CHLORO-1,3,5-TRIMETHYLBENZENE
$$C_9H_{11}Cl$$
 Beil. V - 408 (eso-Chloromesitylene) CH_3 V_1 — V_2 -(315) CH_3 CH_3 CH_3 CH_3 CH_3 B.P. 204-206° (1) $D_-^{20} = 1.0337$ (2) $n_D^{20} = 1.52119$ (2) 103.6-103.7° at 25 mm. (2)

 \bar{C} remains liquid down to -20° . \bar{C} is insol. aq., eas. sol. alc. or ether; volatile with steam but less so than dichloromesitylene.

[For prepn. of \bar{C} from 1,3,5-trimethylbenzene (mesitylene) (1:7455) with Cl₂ either directly (1) or in CHCl₃ at 0° (75% yield (3)) accompanied by 2,4-dichloro-1,3,5-trimethylbenzene (1) and/or 2,4,6-trichloro-1,3,5-trimethylbenzene, m.p. 209° (3), 204-205° (1)), or from 2,4,6-trimethylphenol (mesitol) (1:1467) with PCl₅ in C₅H₅ (2) see indic. refs.]

C with fumg. H₂SO₄ (20% SO₃) shaken for 15 min. gives 2-chloromesitylenesulfonic acid

(corresp. sulfonyl chloride, oil (3), sulfonamide, m.p. 165.5-166° (3)) but gives no evidence of any Jacobsen rearrangement (3).

Č with fumg. HNO₃ yields (1) (4) mainly 4,6-dinitro-2-chloromesitylene, colorless ndls. from alc., m.p. 178-179° (1), 176.5° (4) [the mononitration prod., 4-nitro-2-chloromesitylene, has m.p. 56-57° (1)].

 \bar{C} on oxidn. with boilg. dil. HNO₃ (1 conc. HNO₃: 2 aq.) for 30 hrs. yields (1) 4-chloro-3,5-dimethylbenzoic acid ("chloromesitylenic acid") [Beil. IX-536], browns at 220° but does not melt (unsuitable as derivative). [Note that a little 4-nitro-2-chloromesitylene m.p. 56-57° (1), may be formed in this process; furthermore that attempts to oxidize \bar{C} with $K_2Cr_2O_7$ + dil. H_2SO_4 yield only acetic acid (1).]

C on oxidn. with aq. KMnO₄ gives (63.5% yield (5)) 2-chlorobenzenetricarboxylic acid-1,3,5 (chlorotrimesic acid) (3:4975), readily sol. cold aq., excessively sol. hot aq., m.p. anhydrous acid 285° (5), monohydrate 278° (6).

S:8725 (1) Fittig, Hoogewerff, Ann. 150, 323-329 (1869). (2) Brown, de Bruyne, Gross, J. Am. Chem. Soc. 56, 1291 (1934). (3) Smith, Moyle, J. Am. Chem. Soc. 58, 1, 4, 7 (1936). (4) Anschutz, Boedeker, Ann. 454, 108 (1927). (5) Davies, Wood, J. Chem. Soc. 1928, 1126-1127. (6) Ost, J. prakt. Chem. (2) 15, 310 (1877).

3: 8727 ETHYL &-CHLORO-
$$n$$
-VALERATE $C_7H_{13}O_2Cl$ Beil. II - 302 $CH_2.CH_2.CH_2.CH_2.COOC_2H_5$ II_1 — II_2 -(268)

B.P. 205-206° (1)
120-125° at 40 mm. (2)
93° at 16 mm. (5)
83.5-85° at 8 mm. (4)
83° at 8 mm. (3)

[For prepn. of \tilde{C} from δ -chloro-n-valeric acid (3:0075) with EtOH + dry HCl see (1) (2) (3) (4); from δ -ethoxy-n-valeryl chloride (5) on htg. with 0.7% conc. H₂SO₄ at 100° for 5 hrs. see (5).]

[For reactn. of \bar{C} with diethyl sodio-ethylmalonate see (2); for rate of reactn. of \bar{C} with KI in acctone at 50° see (3).]

Neither \bar{C} nor its halogen is rapidly hydrolyzed by cold aq. 10% NaOH (3) (use in sepn. of \bar{C} from phenol (3)).

3:8727 (1) Funk, Ber. 26, 2574-2575 (1893). (2) Mellor, J. Chem. Soc. 79, 132 (1901). (3) Conant, Kirner, J. Am. Chem. Soc. 46, 244-245, 249 (1924). (4) Cheney, Piening, J. Am. Chem. Soc. 67, 733 (1945). (5) Prelog, Heimbach-Juhasz, Ber. 74, 1704 (1941).

```
3: 8730 ISOAMYL \beta-CHLOROPROPIONATE C_8H_{16}O_2Cl Beil. II — iso-C_5H_{11}O.CO.CH_2.CH_2Cl II<sub>1</sub>-(111) II<sub>2</sub>-(227)

B.P. 207-208° at 740 mm. (1) D_4^{20} = 1.0171 (3) n_D^{20} = 1.4343 (3) 121° at 30 mm. (4) 87° at 12 mm. (2) D_4^{15} = 1.0419 (4) n_D^{11} = 1.4380 (4)
```

87° at 12 mm. (2) $D_4^{15} = 1.0419$ (4) $n_D^{11} = 1.4380$ (4) [For prepn. (97% yield (2), 90% yield (1)) from isoamyl alc. (1:6200) + β -chloro-

propionic ac. (3:0460) see (1) (2).] \ddot{C} on htg. at 220° with diethylaniline gives (poor yield (4)) isoamyl acrylate, b.p. 157–159° at 756 mm., $n_D^{12}=1.4287$ (4).

D Isoamyl β-(phthalimido) propionate: from \tilde{C} in 70% yield on htg. with potassium phthalimide in s.t. at 130° for 1 hr.; prod. repeatedly extracted with dry ether and solvent evapd.; cryst. from alc., m.p. 61° (1). [This product on shaking with 12 pts. HBr (48%) at 40° yields β-phthalimidopropionic acid (40% yield), cryst. from aq., m.p. 150-151° (4).]

3:8730 (1) Hale, Britton, J. Am. Chem. Soc. 41, 844-845 (1919). (2) Fichter, Schnider, Helv. Chim. Acta 14, 857 (1931). (3) Schjanberg, Z. physik. Chem. A-172, 231 (1935). (4) Moureu, Murat, Tampier, Ann. chim. (9) 15, 247, 251 (1921).

3: 8735 o-CHLOROPHENETOLE (o-Chlorophenyl ethyl ether) C_8H_9OCl Beil. VI - 184 VI—

B.P. 210.3° (1)
$$D_4^{25} = 1.1288$$
 (5) $n_D^{25} = 1.5284$ (5) 208° (2) $D_{242}^{242} = 1.12993$ (1) $n_{H\alpha_1}^{242} = 1.52333$ (1) $n_{H\alpha_1}^{242} = 1.54014$ (1)

Colorless oil, volatile with steam.

[For prepn. from 3-chloro-4-ethoxyaniline [Beil. XIII-511, XIII₁-(181)] by replacement of -NH₂ group with H via diazo reaction see (3).]

 \tilde{C} added dropwise to 2 pts. HNO₃ (D=1.38) with cooling, then poured into aq., yields (3) 2-chloro-4-nitrophenetole [Beil. VI-240], yel. ndls. from alc. + lgr., m.p. 82° (3).

3-Chloro-4-ethoxybenzenesulfonamide: cryst. from dil. alc., m.p. 132-133° u.c. (4). [From \(\bar{C}\) by treatment with chlorosulfonic ac. followed by conversion of the intermediate sulfonyl chloride to the sulfonamide by treatment with (NH₄)₂CO₃ (73% yield (4)).] [Note that this prod. depresses the m.p. of the corresponding deriv. (m.p. 134-134.5°) from p-chlorophenetole (3:0090) (4).]

3:8735 (1) Swarts, J. chim. phys. 20, 75-76 (1923). (2) Beilstein, Kurbatow, Ann. 176, 39 (1875). (3) Reverdin, During, Ber. 32, 155-156 (1899). (4) Huntress, Carten, J. Am. Chem. Soc. 62, 603-604 (1940). (5) Anzilotti, Curran, J. Am. Chem. Soc. 65, 609 (1943).

--- d,l- α -CHLORO-ISOVALERIC ACID $C_6H_9O_2Cl$ Beil. II - 316 II_1 -- II_2 -- II_2 --

B.P. 210-212° at 756 mm. M.P. 16° $D_{-}^{13.2} = 1.135$ $n_{-}^{11} = 1.44496$

See 3:0050. Division A: Solids.

— p-CHLOROPHENETOLE Cl OC₂H₅ C₈H₉OCl Beil. VI - 187 VI₁-(101) VI₂-(176)

B.P. 211.6° cor. M.P. 20-21° $D_{20.2}^{20.2} = 1.12310$ $n_{\rm D}^{19} = 1.5227$

See 3:0090. Division A: Solids.

--- α-CHLOROCROTONIC ACID
$$CH_3$$
--C--H $C_4H_5O_2Cl$ Beil. II - 414 Π_1 -(189) Π_2 -(395)

B.P. 212°

M.P. 99-100°

See 3:2760. Division A: Solids.

3:8737 1-CHLORO-3-PHENYLPROPENE-1
$$C_9H_9Cl$$
 Beil. V — V_1 — V_2 —chloroallylbenzene; V_1 — V_2 —CH=CH V_2 —CH=CH V_2 —CH=CH V_3 — V_4 —

Liquid with penetrating odor suggesting benzene.

[For prepn. of \bar{C} from 1,3-dichloropropene-1 (3:5280) with C_6H_6 + AlCl₃ (3), or with C_6H_5MgBr in toluene (1) (4) or ether (2) (alm. quant. yield (1)), see indic. refs.]

 \bar{C} with PCl₅ gives on warming (by addition to \bar{C} of 2 atoms chlorine) alm. quant. yield (5) of 3-phenyl-1,1,2-trichloropropane, b.p. 135–136° at 13 mm., $D_4^{23}=1.293, n_D^{23}=1.553$ (5).

 \bar{C} with Br₂ adds similarly giving (1) (4) 1-chloro-1,2-dibromo-3-phenylpropane, b.p. 160° at 12 mm., $D_4^{10} = 1.727$, $n_D^{10} = 1.611$ (4) (for use of this prod. in prepn. of hydrocinnamaldehyde (1:0225) see (6)).

[\bar{C} resists hydrolysis and is unchanged even after several hours with aq. + PbO in s.t. at 200° (1) (4); however, \bar{C} with KOH (3 moles) in abs. alc. on refluxing at 130–135° is readily converted (by reactn. of the ω -chlorine atom and rearr. or vice versa) into cinnamyl ethyl ether (γ -ethoxyallylbenzene) [Beil. VI-571, VI₁-(281)], b.p. 127–128° at 22 mm., $D_4^{15} = 0.970$, $n_5^{15} = 1.547$ (1) (4), which by cleavage with HCl under press. gives (7) cinnamyl chloride (3:0010) q.v.]

[C with Na (4 moles) in boilg. tolucne gives (8) propenylbenzene (β-methylstyrene) [Beil. V-481, V₁-(371)], b.p. 176°, neither methyl phenylacetylene nor benzylacetylene being formed.]

 $[\bar{C} \text{ with NaNH}_2 \text{ in high-boilg. pet. at } 105-110^\circ \text{ gives } (75\% \text{ yield (9)) (10) (11) benzylacetylene [Beil. V₂-(408)], b.p. abt. 166° at 760 mm. (with resinification).]$

3:8737 (1) Bert, Bull. soc. chim. (4) 37, 879-881 (1925). (2) von Braun, Kuhn, Ber. 58, 2171 (1925). (3) Bert, Compt. rend. 213, 619-620 (1941); Cent. 1942, II 30-31; C.A. 37, 4373 (1943). (4) Bert, Compt. rend. 180, 1504-1506 (1925). (5) Bert, Annequin, Compt. rend. 192, 1107-1108 (1931). (6) Bert, Compt. rend. 215, 356-357 (1942); C.A. 38, 3633 (1944). (7) Bert, Dorier, Compt. rend. 191, 332-333 (1930); Cent. 1930, II 2376; C.A. 24, 5739 (1930). (8) Bert, Raynaud, Compt. rend. 191, 454-455 (1930); Cent. 1930, II 3544; C.A. 25, 89 (1931). (9) Bert, Dorier, Bull. soc. chim. (4) 39, 1611-1612 (1926). (10) Bourgeul, Bull. soc. chim. (4) 41, 192-193 (1927). (11) Bert, Dorier, Bull. soc. chim. (4) 41, 1171-1173 (1927).

[For prepn. of \tilde{C} from o-toluic acid (1:0690) with PCl₅ (10) (yield:100% (3), 75% (13)), with PCl₅ in CHCl₃ (7), with PCl₃ at 110° (14), with POCl₃ (6) or POCl₃+ alk. chloride (15), with SOCl₂ (11) (yield:100% (9), 95% (2), 92% (26), 89% (4)) see indic. refs.; for prepn. of \tilde{C} from o-toluic anhydride (see below) with PCl₅ in POCl₃ see (7).]

 \tilde{C} with pyridine + excess $K_2S_2O_5$ yields (16) o-toluic anhydride, m.p. 39° (16) (7), 36–37° (17).

[For Friedel-Crafts reactn. of \tilde{C} + AlCl₃ + various hydrocarbons to yield corresp. ketones, e.g., with C_6H_6 (5) (6) (18), with toluene (19), with naphthalene (9), with phenanthrene (20), with acenaphthene (4), etc., see indic. refs.; \tilde{C} with MeZnI gives (75% yield (21)) methyl o-tolyl ketone.]

[For studies of rate of reactn. of \bar{C} with MeOH (22) (23), with EtOH (12) see indic. refs.] [For actn. of Br₂ on \bar{C} see (2); for reactn. of \bar{C} with diethyl sodiomalonate see (24); for sulfonation of \bar{C} see (25); for behavior of \bar{C} with C_6H_5MgBr in ether $+ C_0Br_2$ see (26).]

 $\tilde{\mathbf{C}}$ on hydrolysis yields o-toluic acid (1:0690), m.p. 104° (for the amide, anilide, p-toluidide, and other derivatives corresp. to $\tilde{\mathbf{C}}$ see 1:0690).

3:8740 (1) Kohlrausch, Pongratz, Stockmair, Monatsh. 67, 107 (1936). (2) Davies, Perkin, J. Chem. Soc. 121, 2207 (1922). (3) van Scherpenzeel, Rec. trav. chim. 20, 169 (1901). (4) Guyer, Zuffanti, J. Am. Chem. Soc. 57, 1787-1788 (1935). (5) Ador, Filliet, Ber. 12, 2301 (1879). (6) Reddelien, Ber. 48, 1468 (1915). (7) Klages, Lickroth, Ber. 62, 1561 (1889). (8) Hayashi, J. prakt. Chem. (2) 123, 300 (1929). (9) Mayer, Fleckenstein, Gunther, Ber. 63, 1470 (1930). (10) Cohen, Dudley, J. Chem. Soc. 97, 1749 (1910).

(11) Thompson, Norris, J. Am. Chem. Soc. 58, 1955 (1936). (12) Norris, Young, J. Am. Chem. Soc. 57, 1420-1424 (1935). (13) Tanner, Lasselle, J. Am. Chem. Soc. 48, 2164 (1926). (14) Frankland, Wharton, J. Chem. Soc. 69, 1311 (1896). (15) Kissling (to I.G.), Ger. 642,519, March 10, 1937; Cent. 1937, I 3874; C.A. 31, 5816 (1937). (16) Gasopoulos, Praktika Acad. Athenon 6, 347-353 (1931). (17) Adams, Wirth, French, J. Am. Chem. Soc. 49, 426 (1918). (18) Diesbach, Strebel, Helv. Chem. Acta 8, 561 (1925). (19) Mauthner, J. prakt. Chem. (2) 163, 393 (1921). (20) Clar, Ber. 62, 358 (1929).

(21) Ruzicka, Ehmann, Helv. Chim. Acta 15, 150 (1932). (22) Norris, Fasce, Staud, J. Am. Chem. Soc. 57, 1415-1420 (1935). (23) Ott, Ber. 55, 2123 (1922). (24) Mercer, Robertson, J. Chem. Soc. 1936, 292. (25) Meiser (to General Aniline and Film Corp.), U.S. 2,273,974, Feb. 24, 1942; C.A. 36, 3809 (1942). (26) Kharasch, Nudenberg, Archer, J. Am. Chem. Soc. 65, 497 (1943).

210-215° (2) 102-106° at 14 mm. (2) [For prepn. of $\bar{\mathbf{C}}$ from α,β -dichloroisopropylbenzene (α -methylstyrene dichloride) [Beil. V-395] with alc. KOH see (2); from β -chloro- α -hydroxyisopropylbenzene [Beil. VI-507] on distn. at ord. press. (3) or by htg. with oxalic acid (2) see indic. refs.; from the lower-melting stereoisomer of β -methylcinnamic acid [Beil. IX-614, IX₁-(254)] with HOCl see (2).]

3:8742 (1) Tiffeneau, Compt. rend. 138, 986 (1904). (2) Tiffeneau, Ann. chim. (8) 16, 163, 173, 180 (1907). (3) Tiffeneau, Compt. rend. 134, 775 (1902).

3: 8745
$$\gamma_{\gamma\gamma'}$$
-DICHLORO-DI- n -PROPYL ETHER C_0H_{12} OCl₂ Beil. S.N. 24 (bis- $(\gamma$ -Chloro- n -propyl)ether) ClCH₂.CH₂.CH₂ ClCH₂.CH₂

ClCH₂.CH₂.CH₂

B.P. 215° at 745 mm. (1) $D_{20}^{20} = 1.140$ (1) 93-95° at 18 mm. (2)

[For prepn. (10-15% yield (1)) from trimethylene chlorohydrin (3:8285) by refluxing with dil. H_2SO_4 see (1).]

3:8745 (1) Kamm, Newcomb, J. Am. Chem. Soc. 43, 2228-2229 (1921). (2) Eastman Org. Chem. List No. 33 (1942).

```
B.P. F.P. 215.35° at 760 mm. (1) -60.5° (1) D_4^{25} = 0.93780 (1) 220° at 749 mm. (2) D_4^{20} = 0.94206 (1) D_4^{15} = 0.94633 (1) n_{\text{Hex}}^{15} = 1.43802 (1) 93° at 11 mm. (4) 89° at 6 mm. (5)
```

[For prepn. of \tilde{C} from pelargonic acid (n-nonanoic acid) (1:0560) with PCl₅ (3) (65% yield (6)), with PCl₅ (2) (72% yield (1)), with PCl₅ + ZnCl₂ (93% yield (6)), or with SOCl₂ (yield 93.5% (4), 85% (6)) see indic. refs.]

[For reactn. of \tilde{C} with toluene + AlCl₃ to give corresp. ketone see (7), with AlCl₃ + anisole to give corresp. ketone see (8), with ethyl sodio-acetoacetate and hydrolysis to methyl *n*-octyl ketone (decanone-2) see (9), with K carbazole to yield *N*-(*n*-nonyl)carbazole, m.p. 72-73°, see (10), with vanillylamine see (5).]

[Č with AlCl₃ + phenol yields (11) 55% o-(n-nonanoyl)phenol, b.p. 180° at 10 mm., m.p. 18.4°, $D_D^{24} = 0.9887$, $n_D^{255} = 1.5139$ (11) (semicarbazone, m.p. 164° (11), and 35% p-(n-nonanoyl)phenol, m.p. 54.5°, b.p. 232° at 10 mm. (benzoate, m.p. 99.8° (11)).]

 $\bar{\mathbf{C}}$ on hydrolysis yields pelargonic acid (1:0560) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresp. to $\bar{\mathbf{C}}$ see 1:0560).

3:8765 (1) Deffet, Bull. soc. chim. Belg. 40, 389-396 (1931). (2) Henry, Bull. acad. roy. Belg. (3) 37, 63-72 (1899); Cent. 1899, I 968; Rec. trav. chim. 18, 253-254 (1899). (3) Krafft, Koenig, Ber. 23, 2384 (1890). (4) Fierz-David, Kuster, Helv. Chim. Acta 22, 86-89 (1939). (5) Ford-Moore, Phillips, Rec. trav. chim. 53, 855 (1934). (6) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (7) Hasan, Stedman, J. Chem. Soc. 1931, 2117. (8) Skraup, Nieten, Ber. 57, 1302-1303 (1924). (9) Asahina, Nakayama, J. Pharm. Soc. Japan 1925, No. 526, 3-5; Cent. 1926, I 2670. (10) Copisarow, J. Chem. Soc. 113, 818 (1918).

(11) Sandulesco, Girard, Bull. soc. chim. (4) 47, 1310 (1930).

M.P. 48-49°

See 3:0765. Division A: Solids.

3:8770 3-CHLORO-4-ISOPROPYL-1-METHYLBENZENE C10H13Cl Beil. V - 423 (3-Chloro-p-cymene) **V**1--- V_{2} -(326)

B.P. 217.1° at 760 mm. (1)
$$D_4^{18} = 1.01799$$
 (5) $213-214^\circ$ cor. at 735.6 mm. (2) $n_D^{18} = 1.51796$ (5) 214° at 760 mm. (3) $120-122^\circ$ at 20 mm. (4) (5)

[For prepn. of C from thymol (3-hydroxy-p-cymene) (1:1430) with PCl₅ see (1) (4) (5) (6); for prepn. of C from 2-bromo-p-cymene [Beil. V-423, V₁-(205)] by chlorination to 5-chloro-2-bromo-p-cymene [Beil. V-424] followed by replacement of Br by H with Zn/Cu at 200° (7) or in alc. alk. (8) see (7) (8); for prepn. of C from 3-chloromenthadiene dibromide by elimination of 2 HBr with quinoline see (3).

 $[\bar{C} \text{ on oxidn. with 15 pts. boilg. dil. HNO}_3 (D = 1.24) gives (2) a mixt. of 3-chloro-4$ isopropylbenzoic acid (3-chlorocuminic acid) [Beil. IX-549], m.p. 122-123°, 2-chloro-4methylbenzoic acid (2-chloro-p-toluic acid) (3:4355), m.p. 155°, and 2-chloroterephthalic acid (3:4995), m.p. about 320°.]

 $[\bar{C}]$ on mononitration with 6 pts. conc. HNO₃ (D=1.48) below 15° for 3-4 hrs. as directed (4) yields 6-nitro-3-chloro-p-cymene = 2-nitro-5-chloro-p-cymene [Beil. V-424], oil, b.p. 142-150° at 13 mm. (4) (which with piperidine for 30 min. at 100° yields (4) 2-nitro-5piperdino-p-cymene, oil, b.p. 146-148° at 32 mm. (4)).

 \bar{C} on dinitration by adding to 10 pts. conc. HNO₃ (D=1.5) below -5° during 15 min., then poured onto ice, yields (4) (9) a mixt. from which can be isolated 2,6-dinitro-3-chlorop-cymene, m.p. 105-106° (9), 102.5-103.5° (4) (which with piperidine (5 pts.) at 100° for 1½ hrs. yields 2,6-dinitro-3-piperidino-p-cymene, pale yel. ndls. from alc., m.p. 126-127° (9), 123-124° (4)).

[During this dinitration of C there is also formed a by-prod. formerly (4) supposed to be 2-chloro-3,5-dinitro-4-methylacetophenone but more recently (10) shown to be 3-chloro-4.6-dinitrotoluene, m.p. 90.0-90.5° (10); this prod. with piperidine gives (10) 3-piperidino-4.6-dinitrotoluene, m.p. 116-116.5° (10).]

3:8770 (1) Kobe, Okabe, Ramstad, Huemmer, J. Am. Chem. Soc. 63, 3251-3252 (1941). Fileti, Crosa, Gazz. chim. ital. 16, 288 (1886). (3) Junger, Klages, Ber. 29, 316 (1896). (4) Ganguly, R. J. W. LeFevre, J. Chem. Soc. 1934, 848-852. (5) C. G. LeFevre, R. J. W. LeFevre, R. W. Le K. W. Robertson, J. Chem. Soc. 1935, 483. (6) Vongerichten, Ber. 11, 364-369 (1878). (7)
 Frisch, Ger. 615,470, July 5, 1935; Cent. 1936, I 883; C.A. 29, 6252 (1935). (8) Livak, Carlson (to Dow Chem. Co.), U.S. 2,192,613, March 5, 1940; C.A. 34, 4396 (1940). (9) Qvist, Moilanen, Acta Acad. Aboensis, Math. et Phys. 13, No. 12, 10 pp. (1942); Cent. 1942, II 1337-1338; C.A. 37, 6254 (1943). (10) Qvist, Moilanen, Acta Acad. Aboensis, Math. et Phys. 14, No. 3, 9 pp. (1943); Cent. 1943, II 1268-1269; C.A. 38, 5491 (1944).

3:8775 2-CHLORO-4-ISOPROPYL-1-METHYLBENZENE $C_{10}H_{13}Cl$ Beil. V - 423 (2-Chloro-p-cymene) (CH₃)₂CH CH₃ V_1 - V_2 -(325)

B.P. 217.6°	at 760 mm.	(1)	$D_4^{17} = 1.0208$	(5)
216-218°	at 762 mm.	(2) (3)	1.0152 (?)	(2)
216-218° cor.	at 746 mm.	(4)		$n_{\rm D}^{17} = 1.51776 (5) (2)$
216-217°	at 761 mm.	(5)		
215-218°		(6)		
214-216°		(7)		
213-216°		(8)		
213-214°	at 764 mm.	(9)		
117°	at 35 mm.	(4)		
103-105°	at 19 mm.	(10)		
85-90°	at 5 mm.	(6)		

[For prepn. of \tilde{C} from carvacrol (2-hydroxy-p-cymene) (1:1760) with PCl₅ see (1) (11); from p-cymene (1:7505) with Cl₂ in pres. of I₂ (9) (3) (12) (8) (17) or Fe (6) (17) see indic. refs.; from 2-amino-p-cymene (cymidine) (carvacrylamine) [Beil. XII-1171, XII₁-(506)] via diazotization and use of Cu₂Cl₂ reactn. see (2) (9); from carvone (1:5540) (13) or eucarvone [Beil. VII-151, VII₁-(99)] (13) or carvenone [Beil. VII-78, VII₁-(66)] (10) with PCl₅ (cf. (14) (15)) see indic. refs.]

C on oxidn. with boilg. dil. HNO₃ yields (12) (8) (11) (10) 3-chloro-4-methylbenzoic acid (3-chloro-p-toluic acid) (3:4900), m.p. 199° (10), 196° (8), 194-195° (12).

 \bar{C} on dinitration with 10–12 pts. HNO₃ (D=15) below 0° (2) (16) (18) or with a mixt. of conc. or fumg. HNO₃ + fumg. H₂SO₄ as directed (2) (8) (6) yields 5,6-dinitro-2-chloro-p-cymene, cryst. from AcOH (2), dil. AcOH (2), EtOH (6), or dil. MeOH (16), m.p. 111.0–111.5° cor (18), 109.5–110.5° (2), 109.5° (8), 108–109° (6). [This prod. refluxed with 5–10 pts. piperidine for 20–60 min. at 100° gives 3,5-dinitro-2-piperidino-p-cymene, yel. ndls. from AcOH (2) or from dil. alc. (18) (16), m.p. 123–124° (16), 122.5–123.5° (18), 122–123° (2).] [Note that the original structure assigned by (6) to dinitro- \bar{C} has been confirmed by (18) despite intermediate contrary views (2) (16).]

[\bar{C} with Br₂ + Fe at ord. temp. yields (17) 5-bromo-2-chloro-p-cymene, b.p. 247° (17).]

3:8775 (1) Kobe, Okabe, Ramstad, Huemmer, J. Am. Chem. Soc. 63, 3251-3252 (1941). (2) Ganguly, R. J. W. LeFevre, J. Chem. Soc. 1934, 852-854. (3) Ganguly, R. J. W. LeFevre, J. Chem. Soc. 1934, 1699. (4) Fileti, Crosa, Gazz. chim. ital. 18, 299 (1888). (5) C. G. LeFevre, R. J. W. LeFevre, K. W. Robertson, J. Chem. Soc. 1935, 480-488. (6) Lubs, Young, J. Ind. Eng. Chem. 11, 1130-1133 (1919). (7) Junger, Klages, Ber. 29, 315 (1896). (8) Hintikka, Ann. Acad. Sci. Fennicae 19-A, No. 10, 6 pp. (1923), C.A. 19, 42 (1925). (9) R. J. W. LeFevre, J. Chem. Soc. 1933, 980-984. (10) Marsh, Hartridge, J. Chem. Soc. 73, 854-855 (1898).

(11) Fleischer, Kehulé, Ber. 6, 1090 (1873).
(12) Vongerichten, Ber. 10, 1249-1252 (1877).
(13) Klages, Kraith, Ber. 32, 2554, 2558, 2560 (1899).
(14) Semmler, Ber. 41, 4478 (1908).
(15) Wallach, Ann. 368, 15 (1909).
(16) R. J. W. LeFevre, J. Chem. Soc. 1933, 980.
(17) Varma, Srinivasan, J. Indian Chem. Soc. 13, 190-191 (1936).
(18) Qvist, Kajander, Acta Acad. Aboensis, Math. et Phys. 13, No. 10, 16 pp. (1942); Cent. 1942, II 26-28; C.A. 37, 4370-4372 (1943).

— p-CHLOROPHENOL CIOH C₆H₅OCl Beil. VI - 186 VI₁-(100) VI₂-(174)

B.P. 218-219° M.P. 42-43°

See 3:0475. Division A: Solids.

3: 8777
$$\gamma$$
-PHENYL- n -PROPYL CHLORIDE γ -Chloro- n -propylbenzene, hydrocinnamyl chloride) γ -CH₂.CH₂.CH₂.CH₂.Cl γ -CH₂.CH₂.Cl γ -CH₂.Cl γ -CH₂.CH₂.Cl γ -CH₂.Cl γ -CH₂.CH₂.Cl γ -CH₂.Cl γ -CH₂.CH₂.Cl γ -CH₂.Cl γ -CH₂.CH₂.Cl γ -CH₂.Cl γ -Cl γ -Cl

[For prepn. of \bar{C} from γ -phenyl-n-propyl alc. (hydrocinnamyl alc.) (1:6520) with fumg. HCl in s.t. at 130° (1) (15) or 140–150° (3), or in s.t. at 100° for 8 hrs. (77% yield (5)), or with ZnCl₂ + conc. HCl (40% yield (8)) (2) see indic. refs.; with SOCl₂ in ether (82% yield (9)) or pyridine (48.5% yield (10)) or dimethylaniline (70.5% yield (10)) see indic. refs. (for intermediate formn. of γ -phenyl-n-propyl chlorosulfite and bis-(γ -phenyl-n-propyl) sulfite in this reactn. see (11)); from γ -chloro-n-propyl p-toluenesulfonate (2 moles) with C₆H₅MgBr in ether (yield: 62% (6), 31% (12)) see indic. refs.; from C₆H₅CH₂MgCl with di-(β -chloroethyl) sulfate in ether (66% yield) see (4); from o-(γ -chloro-n-propyl)-aniline via diazotization and treatment with alk. + SnCl₂ (75% yield (3)) (13) see indic. refs.; from N-methyl-n-(γ -phenyl-n-propyl)benzamide with PCl₅ see (14).]

Č is not decomposed on boilg. with ZnCl₂ and does not react at 100° with AgOAc (1).

[$\bar{\mathbf{C}}$ boiled for 8 hrs. with excess 5% NaOMe in MeOH gives (86% yield (15)) γ -phenyl-n-propyl methyl ether [Beil. VI₁-(252)], b.p. 206.5° at 758.5 mm. u.c., b.p. 100–102° at 20 mm. (15); $\bar{\mathbf{C}}$ with KOH in EtOH refluxed 2 hrs. gives (1) γ -phenyl-n-propyl ethyl ether [Beil. VI-503], b.p. 224° cor.; $\bar{\mathbf{C}}$ boiled several hours with excess conc. alc. NaOC₆H₅ gives (100% yield (3)) γ -phenyl-n-propyl phenyl ether [Beil. VI-504, VI₁-252], b.p. 182–183° at 17 mm. (3).]

[$\tilde{\mathbf{C}}$ on boilg. several hours with alc. NaI yields (3) γ -phenyl-n-propyl iodide, b.p. 137–140° at 20 mm. (3) (for rate of reactn. of $\tilde{\mathbf{C}}$ with KI in acctone at 50° see (5)).]

[Č with activated Mg in dry ether gives (98% yield (9)) C₆H₅.CH₂.CH₂.CH₂.MgCl; for reactn. of this RMgCl cpd. with various carbonyl cpds., e.g., acrolein (10), ethyl phenyl ketone (9), or cyclopentanone (16), see indic. refs.]

[C with AlCl₃ in CS₂ or lgr. gives (17) about 10% hydrindene (1:7511), b.p. 177°, together with other products.]

[$\bar{\mathbf{C}}$ on mononitration with 4 vols. HNO₃ (D=1.5) below -10° gives over 90% yield (18) of γ -(p-nitrophenyl)-n-propyl chloride [Beil. V₁-191], b.p. 176–180° at 15 mm. with sl. dec. (18).]

3:8777 (1) Errera, Gazz. chim. ital. 16, 313-314 (1886). (2) Goebel, Wenzke, J. Am. Chem. Soc. 60, 698 (1938). (3) von Braun, Ber. 43, 2841-2842 (1910). (4) Suter, Evans, J. Am. Chem. Soc. 60, 536-537 (1938). (5) Conant, Kirner, J. Am. Chem. Soc. 46, 242, 249 (1924). (6) Rossander. Marvel, J. Am. Chem. Soc. 50, 1495 (1928). (7) Dunstan, Hiditch, Thole, J. Chem. Soc. 103, 140 (1913). (8) Norris, Taylor, J. Am. Chem. Soc. 46, 756 (1924). (9) Gilman, Harris, J. Am. Chem. Soc. 54, 2075 (1932). (10) Cohen, J. Chem. Soc. 1935, 433.

(11) Carré, Libermann, Compt. rend. 198, 274-276 (1934). (12) Gilman, Beaber, J. Am. Chem. Soc. 45, 842 (1923). (13) Merck, Ger. 239,076, Oct. 9, 1911; Cent. 1911, II 1393. (14) von Braun, Aust, Ber. 49, 507 (1916). (15) Straus, Berkow, Ann. 401, 151 (1913). (16) Denissenko, Ber. 69, 2186 (1936). (17) von Braun, Deutsch, Ber. 45, 1269 (1912).

B.P. 220°

53°

M.P. 28°

1 mm. (8)

at

See 3:0165. Division A: Solids.

3:8780 NEOPHYL CHLORIDE (1)
$$C_{10}H_{13}Cl$$
 Beil. V — $(\beta\text{-Chloro-}ter\text{-butyl})\text{benzene};$ $(\beta\text{-chloro-}\alpha,\alpha\text{-dimethyl})\text{ethylbenzene}$ CH_3 V_1 — C_2 CH_2Cl CH_3 V_2 -(320) CH_3 C_2 CH_3 C_2 CH_3 C_3 C_4 C_4 C_4 C_5 C_5 C_5 C_6 C_7 C_8 C_9 C_9

[For prepn. of \bar{C} from benzene (1:7400) + methallyl chloride (3-chloro-2-methylpropene-1) (3:7145) by condensation in presence of conc. H₂SO₄ (68% yield (1)) or HF (66% yield (2)) see (1) (2); for formn. from *ter*-butylbenzene (1:7460) by treatment with SO₂Cl₂ see (3); for formn. from corresp. alc. (2-methyl-2-phenylpropanol-1) with SOCl₂ see (5) (4).]

C htd. with 13% alc. KOH at 86° for 24 hrs. is unchanged (2); C refluxed 11½ hrs. with NaOEt in abs. alc. (1) or refluxed 9½ hrs. with pyridine (1) is recoverable to extent of 87-88% (1).

[For study of behavior of \bar{C} with Na, Na in liq. NH₃, NaEt, NaNH₂, etc., or on pyrolysis see (1).]

 \bar{C} with sublimed Mg (not comml. Mg even after activation) + a trace of I₂ yields (3) neophyl MgCl; this RMgCl on oxidation with O₂ gives (71.6% yield (1)) the corresp. alc., 2-methyl-2-phenylpropanol-1, b.p. 131° at 30 mm. (1), 122-123° at 20 mm. (5), n_D^{20} = 1.5261 (N-phenylcarbamate, m.p. 59-60° (5), 59.5-60.5° (1); N-(α -naphthyl)carbamate, m.p. 91.5-92.5° (1)). [For behavior of \bar{C} with C₆H₅MgBr in pres. of CoBr₂ see (8).]

- \oplus β -Phenylisovaleric acid: cryst from pet. eth., m.p. 57.5-58.5° (6), 58-59.5° (1). [From RMgCl on carbonation and subsequent hydrolysis; yield 81.6% (1).]
- β-Phenylisovaleranilide: m.p. 122-123° (3), 121-123° (6) [from RMgCl by reactn. with phenyl isocyanate (3)].
- p-Acetamino-(β-chloro-ter-butyl) benzene: m.p. 155-156° (7). [From C by nitration, reduction, and acetylation (7).]

3:8780 (1) Whitmore, Weisgerber, Shabica, J. Am. Chem. Soc. 65, 1469-1471 (1943). (2) Calcott, Tinker, Weinmayr, J. Am. Chem. Soc. 61, 1012 (1939). (3) Kharasch, Brown, J. Am. Chem. Soc. 61, 2147-2148 (1939). (4) Haller, Ramart, Compt. rend. 174, 1212; Cent. 1922, III 545. (5) Haller, Bauer, Ann. chim. (9) 9, 10-14 (1918). (6) Hoffmann, J. Am. Chem. Soc. 51, 2547 (1929). (7) Ipatieff, Schmerling, J. Am. Chem. Soc. 67, 1624 (1945). (8) Urry, Kharasch, J. Am. Chem. Soc. 66, 1438-1440 (1944).

3:8783 $d_{s}l_{-\alpha}$ -CHLORO-n-VALERIC ACID $C_{5}H_{9}O_{2}Cl$ Beil. II -302 Π_{1} — Π_{2} — Π_{2} —

B.P. F.P. 222° at 763 mm. (1) -15° (1) $D_{-}^{13.2} = 1.141$ (1) $n_{-}^{11} = 1.44807$ (1) 132-135° at 32 mm. (1)

Oil; insol. aq., sol. in alc., ether.

[For prepn. of \bar{C} from α -chloro-n-valeronitrile by hydrolysis with conc. HCl see (1) (2).] [The levorotatory isomer of \bar{C} , b.p. 80-84° at 1 mm., has been obtd. (3) from dextrorotatory 3-chlorohexene-1 by ozonolysis in CHCl₃, decompn. with aq., and Br₂/aq. oxidn. of the resultant aldehyde.]

- α-Chloro-n-valeramide: cryst. from alc. + aq. (3:1), m.p. 70-70.2° (4). [Prepd. indirectly from α-chloro-n-valeronitrile with conc. HCl (4).]
- ---- α -Chloro-n-valer-anilide: unreported.
- ---- α-Chloro-n-valero-p-toluidide: unreported.

3:8783 (1) Servais, Rec. trav. chim. 20, 45-46 (1901). (2) Henry, Bull. acad. roy. Belg. (3) 36, 241-262 (1898); Cent. 1898, I 194. (3) Levene, Haller, J. Biol. Chem. 83, 596 (1929). (4) Vandewijer, Bull. soc. chim. Belg. 45, 255 (1936).

--- 4-CHLORO-2-METHYLPHENOL OH C₇H₇OCl Beil. VI -(359) CH₃ VI₁-(174) VI₂-(332)

B.P. 220-225°

M.P. 48-49°

See 3:0780. Division A: Solids.

3:8784 6-CHLORO-2,4-DIMETHYLPHENOL C₈H₉OCl Beil. VI - 489 (5-Chloro-m-4-xylenol) OH VI₁-(241) VI₂—

B.P. 221-223° at 760 mm. (1) 100-101° at 17 mm. (2) 100-101° at 16 mm. (3)

86.5-87° at 9 mm. (2)

Oil with phenolic odor. - Sol. aq., eas. sol. org. solvents. - Volatile with steam.

[For prepn. of \bar{C} from 2,4-dimethylphenol (unsym.-m-xylenol) (1:1740) by chlorination with acet-N-chloro-2,4-dichloroanilide in AcOH contg. HCl at 15° as directed (1), or with SO₂Cl₂ in AcOH (3), see indic. refs.; from 6-amino-2,4-dimethylphenol hydrochloride [Beil. XIII-630, XIII₁-(245)] via diazotization and use of Cu₂Cl₂ reaction (77% yield) see (2); for formn. of \bar{C} from 2,4-dimethylquinol (m-xyloquinol) [Beil. VIII-22, VIII₁-(514)] by action of HCl (some of the isomeric 5-chloro-2,4-dimethylphenol (3:2460) also being formed) see (2) (4).]

[For studies of bactericidal action of C see (3) (5).]

The nitration of \tilde{C} has not been reported, and none of its mononitro- or dinitro-derivs. are known; for patent on sulfonation of \tilde{C} see (6).

Č in alc. soln. with FeCl₃ gives olive-green color turning brown on htg.

- ---- 6-Chloro-2,4-dimethylphenyl acetate: unreported.
- --- 6-Chloro-2,4-dimethylphenyl benzoate: oil (2).
- **© 6-Chloro-2,4-dimethylphenyl** p-nitrobenzoate: m.p. 94-94.5° (2). [From $\ddot{\mathbf{C}} + p$ -nitrobenzoyl chloride in pyridine (2).]
- © 6-Chloro-2,4-dimethylphenyl N-phenylcarbamate: m.p. 129-130° (2). [From C + phenyl isocyanate at 150-200° (2).]
- 3:8784 (1) Orton, King, J. Chem. Soc. 99, 1191 (1911). (2) Bamberger, Reber, Ber. 46, 793-795, 798-799 (1913). (3) Heicken, Angew. Chem. 52, 263-265 (1939). (4) Bamberger, Reber, Ber. 40, 2268 (1907). (5) Lockemann, Kunzmann, Angew. Chem. 46, 296-301 (1933). (6) Weiler, Better (to I.G.), Ger. 557,450, Aug. 24, 1931; Cent. 1932, II 2370-2371; [C.A. 27, 735 (1938)].

3:8785 1-CHLORODECANE
$$CH_3.(CH_2)_8.CH_2Cl$$
 $C_{10}H_{21}Cl$ Beil. I - 169 $I_1-I_{2-1}Cl$ $I_{2-1}Cl$ $I_{2-1}Cl$ $I_{2-1}Cl$ $I_{2-1}Cl$ $I_{2-1}Cl$ $I_{2-1}Cl$ $I_{3-1}Cl$ $I_{3-1}C$

```
B.P. 223.0-223.5° at 760 mm. (1) D_{25}^{25} = 0.8850 (4) n_{\rm D}^{25} = 1.4400 (4) 222-223^{\circ} at 760 mm. (7) D_{4}^{20} = 0.8696 (1) n_{\rm D}^{20} = 1.43799 (1) 180-190^{\circ} at 720 mm. (2) 0.8683 (7) 1.43731 (7) 130-140^{\circ} at 80 mm. (3) 122^{\circ} at 50 mm. (2) 137-142^{\circ} at 24 mm. (4) 100.8-101.0^{\circ} at 12 mm. (5) 106^{\circ} at 16 mm. (6)
```

Colorless oil with characteristic odor (1).

[For prepn. of \tilde{C} from decanol-1 (1:6275) with PCl₅ in CCl₄ see (1); with SOCl₂ + pyridine (80% yield (5)) or SOCl₂ without pyridine (91% yield (7)) see (5) (7); for prepn. from n-heptyl MgBr + γ -chloro-n-propyl p-toluenesulfonate sec (4).]

C htd. at 100° with aq. Ba(OH)₂ yields (2) decanol-1 (1:6275).

C with Mg in dry ether contg. trace of I2 gives (96% yield in 9 hrs. (8)) RMgCl.

3:8785 (1) Komppa, Talvitie, J. prakt Chem. (2) 135, 196 (1932). (2) Schultz, Ber. 42, 3610-3611 (1909). (3) Mabery, Am. Chem. J 19, 432 (1897). (4) Rossander, Marvel, J. Am. Chem. Soc. 50, 1493-1494 (1928). (5) Kohlrausch, Kóppl, Monatsh. 63, 269 (1933). (6) Rothstein, Bull. soc. chim. (5) 2, 84 (1935). (7) Vogel, J. Chem. Soc. 1943, 638, 641. (8) Houben, Boedler, Fischer, Ber. 69, 1768, 1779 (1936).

3:8787 HYDROCINNAMOYL CHLORIDE
$$C_9H_9OCl$$
 Beil. IX - 511 $(\beta$ -Phenylpropionyl chloride) $CH_2.CH_2.C=0$ Cl $CH_2.CH_2.C=0$ Cl B.P. B.P. $(contd.)$ D₂₁ = 1.135 (3) 225° at 760 mm. dec. (1) 112° at 15 mm. (7) 154-155° at 75 mm. (2) 113.5-114° at 13.5-14.5 mm. (8) 122° at 25 mm. (3) 117-119° at 13 mm. (9) (10) 121-122° at 22.5 mm. (4) 115-116° at 11-12 mm. (11) 133-135° at 21 mm. (23) 107° at 11-12 mm. (12) 122-123° at 20 mm. (25) 105° at 10 mm. (13) 115-118° at 16-17 mm. (5) 107.5° at 9 mm. (14) 116° at 15 mm. (6)

Colorless liq. with disagreeable odor; not solid even at -60° (3).

[For prepn. of \bar{C} from hydrocinnamic acid (1:0615) with PCl₅ (36% yield (8)) (15), with PCl₅ in CHCl₃ (yield: 95% (2), 90% (8), 75% (7)) (3), with PCl₃ in C₆H₆ (10), with SOCl₂ (yield: 100% (13) (4) (23), 88% (8), 85% (5)) (16) (17), or with oxally dichloride (3:5060) (98% yield (6)) see indic. refs.]

 \bar{C} with AlCl₃ in pet. ether (yield: 95% (13), 90% (18) (19)) (2) (20) (21) or \bar{C} with AlCl₃ in CS₂ (84.3% yield (25)) or \bar{C} with FeCl₃ in CS₂ (15) yields by ring closure and loss of HCl α -hydrindone (indanone-1) (1:5144), m.p. 42°.

[Č with Br₂ at 65-70° gives (74% yield (5)) α -bromo-hydrocinnamoyl chloride, b.p. 132-133° at 12 mm. (22), 113-115° at 5 mm., $D_{20}^{20} = 1.5538$, $n_{\rm D}^{20} = 1.5768$ (5) (amide, m.p. 126-127° (5)).]

[$\bar{\mathbf{C}}$ with NaN₃ in toluene yields (23) β -phenylethyl isocyanate, b.p. 112-114° at 15 mm. (23); $\bar{\mathbf{C}}$ with diazomethane in ether gives the corresp. diazo-ketone which according to treatment gives either (11) β -phenylethyl chloromethyl ketone (1-chloro-4-phenylbutanone-2) [Beil. VII₁-(168)], ndls. from C₆H₆, m.p. 84-85° (11), or (60% yield (24)) γ -phenyl-n-butyric acid, cryst. from lt. pet., m.p. 49-50° (24).]

Č on hydrolysis yields hydrocinnamic acid (1:0615), m.p. 48.7°; for the amide, anilide, p-toluidide, and other derivs. corresp. to Č see hydrocinnamic acid (1:0615).

3:8787 (1) Freundler, Bull. soc. chim. (3) 13, 834 (1895). (2) Kipping, J. Chem. Soc. 65, 484-486 (1894). (3) Taverne, Rec. trav. chim. 16, 39-40 (Note) (1897). (4) Ingold, Thorpe, J. Chem. Soc. 115, 149-150 (1919). (5) Shriner, Damschroder, J. Am. Chem. Soc. 60, 895 (1938). (6) Adams, Ulich, J. Am. Chem. Soc. 42, 604 (1920). (7) Freudenberg, Markert, Ber. 58, 1759 (1925). (8) Mohr, J. prakt. Chem. (2) 71, 322-324 (1905). (9) Hughes, Ber. 25, Referate, 747 (1892). (10) Rupe, Ann. 369, 319-320 (1909).

(11) Clibbens, Nierenstein, J. Chem. Soc. 107, 1493 (1907).
(12) Bergs, Ber. 67, 1621 (1934).
(13) Thiele, Wanscheidt, Ann. 376, 271-272 (1910).
(14) Schlenk, Bergmann, Ann. 463, 50 (1928).
(15) Wedekind, Ann. 253, 255-256 (1902).
(16) Haworth, Perkin, Pink, J. Chem. Soc. 127, 1714 (1925).
(17) Klarmann, J. Am. Chem. Soc. 48, 2363 (1926).
(18) Ingold, Piggott, J. Chem. Soc. 123, 1483 (1923).
(19) Amagat, Bull. soc. chm. (4) 41, 940-943 (1927).
(20) Haller, Bauer, Ann. chim. (9) 26, 341 (1921).

(21) Ramart, Amagat, Ann. chim. (10) 8, 320-321 (1927). (22) Fischer, Ber. 37, 3065 (1904). (23) Forster, Stötter, J. Chem. Soc. 99, 1338 (1911). (24) Litvan, Robinson, J. Chem. Soc. 1938, 1999. (25) Levin, Graham, Kolloff, J. Org. Chem. 9, 384 (1944).

B.P. 225°

M.P. 86°

See 3:2280. Division A: Solids.

3:8790 PHENOXYACETYL CHLORIDE

[For prepn. of \bar{C} from phenoxyacetic acid (1:0680) with PCl₅ (1) (4) (yield: 80% (2), 75% (3)), with PCl₃ (45% yield (3)), with SOCl₂ (100% yield (3)), or with phosgene + a nitrogen base or its salts (5) see indic. refs.]

Č htd. with alk. phenoxyacetate + POCl₃ in toluene yields (6) phenoxyacetic anhydride, ndls. from ether, m.p. 67-69° (6).

[C with MeOH yields methyl phenoxyacetate (1:4021), b.p. 245°; C with EtOH yields ethyl phenoxyacetate (1:4106), b.p. 251°; for reactn. of C with higher alcs. in prepn. of corresp. esters for use as textile assistants, e.g., n-dodecyl phenoxyacetate, m.p. 31° (7), n-tetradecyl phenoxyacetate, m.p. 39° (7), n-hexadecyl phenoxyacetate, m.p. 47° (7) (8), n-octadecyl phenoxyacetate, m.p. 55° (7), see indic. refs.; C with phenol yields (1) phenyl phenoxyacetate, m.p. 59°.]

[\bar{C} with AlCl₃ + C₆H₆ undergoes Friedel-Crafts reactn. yielding (1) (2) (9) mainly (9) phenoxymethyl phenyl ketone (ω -phenoxyacetophenone) [Beil. VIII-91], m.p. 72° (2) (not volatile with steam (2) (9)), together with a small proportion (15% (9)) of ring-closure product, viz., coumaranone [Beil. XVII-118, XVII₁-(59)], m.p. 101-102° (volatile with steam).]

[For reactn. of \bar{C} with dimethyl sodio-malonate in C_6H_6 see (10) (4); with K carbazole yielding N-(phenoxyacetyl)carbazole, m.p. 121-122°, see (11).]

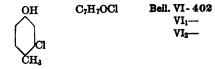
 $\ddot{\mathbf{C}}$ on hydrolysis yields phenoxyacetic acid (1:0680), m.p. 98-99° (for the amide, anilide, and other derivatives corresp. to $\ddot{\mathbf{C}}$ see 1:0680).

3:8790 (1) Vandevelde, Bull. acad. roy. Belg. (3) 35, 223-237 (1898); Cent. 1898, I 988. (2) Stoermer, Atenstädt, Ber. 35, 3561-356 (1902). (3) Blaise, Picard, Ann. chim. (8) 26, 274 (1912). (4) Gabriel, Ber. 46, 1346 (1913). (5) Soc. Chem. Ind. Basel, French 732,078, Sept. 13, 1932; Cent. 1934, I 287. (6) Schering (Chem. Fabrik. Aktien), Ger. 120,772, May 20, 1901; Cent. 1901, I 1304. (7) Henkel et Cie, French 746,434, May 29, 1933; Cent. 1933, II 1430. (8) I. R. Geigy, Swiss 165,401, 165,402, Jan. 16, 1934; Cent. 1934, I 3126. (9) Ramart-Lucas, Hoch, Bull. soc. chim. (4) 51, 837-838 (1932). (10) Pfeiffer, Willems, Ber. 62, 1245 (1929).

(11) Copisarow, J. Chem. Soc. 113, 818 (1918).

)

3-CHLORO-4-METHYLPHENOL



B.P. 228° at 760 mm.

M.P. 55°

See 3:1025. Division A: Solids.

3:8795 4-ISOPROPYLBENZYL CHLORIDE

(Cuminyl chloride; 1-chloromethyl-4isopropylbenzene)

	B.P.		F.P.			
	228° with part. dec.	(1)	-29°	(8)	$D_4^{21.5} = 1.020 \ \{1$	$n_{\rm D}^{21.5}=1.523 (1)$
	227-228°	(2)			_	
	226-229°	(3)				
	225-229°	(4)				
	116-118° at 22 mm.	(5)				
٠	110° cor. at 15 mm.	(1)				
	108-109° at 14 mm.	(6)				
	100° at 14 mm.	(7)				

Liq. with odor and lachrymatory effect less than that of benzyl chloride (3:8535) but with irritating effect on skin (1). — C on boilg. (4) (espec. in presence of ZnCl₂) partially dec. with forms. of a hydrocarbon C₂₀H₂₄ (probably 2,6-di-isopropyl-9,10-dihydroanthracene [Beil. V-654]), yel. pdr., m.p. 90° (4).

[For prepn. of \bar{C} from p-isopropylbenzene (cumene) (1:7440) with trioxymethylene (75% yield (1)) or formalin $(75\% \text{ yield (7)}) + \text{HCl} + \text{ZnCl}_2 \text{ sec (1) (7)}$; with chloromethyl methyl ether (3:7085) + SnCl₄ see (8); from p-cymeme (1:7505) by direct chlorination see (4) (3) (9); from cuminyl alc. [Beil. VI-543] with dry HCl (10) or const.-boilg. HCl (100% yield (2)) see (10) (2) (9).]

 \bar{C} with Zn + HCl reduces (10) to p-cymene (1:7507). — \bar{C} on boilg. with aq. Pb(NO₃)₂ soln. (7) or alk. Na₂Cr₂O₇ (12) yields p-isopropylbenzaldehyde (cuminaldehyde) (1:0234). — Č with aq. alk. presumably (no record) yields cuminyl alcohol [Beil. VI-543] but with alc. KOH gives (4) ethyl cuminyl ether [Beil. VI-544], b.p. 227° (4).

Č with Mg in dry ether yields (9) cuminyl MgCl accompanied by some bicumyl (4,4'disopropyldibenzyl) [Beil. V-623], m.p. 58° (9); the R.MgCl with aq. gives (74% yield (1)) p-cymene (1:7505); the R.Mg.Cl upon treatment with O₂ gas gives (71-80% yield (9)) cuminyl alcohol [Beil. VI-543], b.p. 246° cor. (9), 140° at 20 mm. (9); the R.Mg.Cl with CO₂ gives (73% yield (9)) after acidification p-isopropylphenylacetic acid (homocuminic ac.) [Beil. IX-561], m.p. 52°, b.p. 195° at 30 mm., 190° at 25 mm., $D_4^{15} = 1.039$, $n_D^{15} = 1.522$ (9). [The R.COOMgCl epd. if treated with isopropyl MgCl gives mainly (11) p-isopropylmalonic ac., m.p. 143.5° dec. (1).]

3:8795 (1) Bert, Bull. soc. chim. (4) 37, 1266-1268 (1925). (2) Norris, Mulliken, J. Am. Chem. Soc. 42, 2098 (1920). (3) Varma, Srinivasan, J. Indian Chem. Soc. 13, 191 (1936). (4) Errera, Gazz. chim. ital. 14, 277-283 (1884). (5) Jones, J. Chem. Soc. 1938, 1416. J. Chem. Soc. 1935, 1844. (7) Blanc, Bull. soc. chim. (4) 33, 317 (1923). (6) Baker, Nathan, (8) Darzens, Levy, Compt. rend. 194, 2057 (1932). (9) Bert, Bull. soc. chim. (4) 37, 1577-1583 (1925). (10) Paterno, Spica, Gazz. chim. ital. 9, 397-398 (1879).

(11) Ivanoff, Pchénitchny, Bull. soc. chim. (5) 1, 229 (1934). (12) Blanc, Ger. 347,583, Jan.

23, 1922; Cent. 1922, II 1138.

Care must be taken not to confuse C, the acid chloride of n-capric acid, with the corresponding relatives of n-caprylic acid (C_8) and of n-caproic acid (C_6); for this reason the name n-decanoyl chloride is preferred.

[For prepn. of C from n-decanoic acid (n-decylic acid) (n-capric acid) (1:0585) with PCl₅ (3), with PCl₃ (70% yield (1)), with POCl₃ (7), with oxalyl (di)chloride (3:5060) (5), or with SOCl₂ (6) (94% yield (4)) see indic. refs.]

[For use of C in prepn. of corresp. cellulose esters see (8) (9); for use in syntheses of various glycerides see (5) (6); for use in prepn. of derivs. of vanillylamine see (2) (10); for cat. hydrogenation to n-decylaldehyde (1:0222) see (11).

 $\bar{\mathbf{C}}$ on hydrolysis (or even slowly in moist air) yields n-decanoic acid (1:0585) q.v. (for the amide, anilide, p-toluidide, and other derivatives corresponding to \ddot{C} see 1:0585).

3:8800 (1) Deffett, Bull. soc. chim. Belg. 40, 389-391 (1931). (2) Ford-Moore, Phillips, Rec. trav. chim. 53, 856 (1934). (3) Krafft, Koenig, Ber. 23, 2385 (1890). (4) Fierz-David, Kuster, Helv. Chim. Acta 22, 86-89 (1939). (5) Averill, Roche, King, J. Am. Chem. Soc. 51, 868 (1929). (6) Robinson, Roche, King, J. Am. Chem. Soc. 54, 705-710 (1932). (7) Grimm, Ann. 157, 272-274 (1871). (8) Brit. 201,510, Sept. 19, 1923; Cent. 1923, IV 961. (9) Brit. 313,616, Aug. 8, 1929; Cent. 1929, II 2743. (10) Nelson, J. Am. Chem Soc. 42, 2125 (1919).

(11) Escourrou, Bull. soc. chim. (5) 6, 1180-1181 (1939).

PHENYL CHLOROACETATE C₈H₇O₂Cl Beil. VI - 153 VI₁-(87) Cl.CH₂.CO.O VI_{2} -(154) $n_0^{44} = 1.5146$ B.P. 230-235° M.P. 45°

See 3:0565. Division A: Solids.

B.P. 235° M.P. 57°

See 3:1535. Division A: Solids.

3:8803 1-CHLOROUNDECANE $CH_3.(CH_2)_9.CH_2Cl$ $C_{11}H_{23}Cl$ Beil. S.N. 10 (*n*-Undecyl chloride: 1-chlorohendecane)

B.P. 240-241° at 772 mm. (2)
$$D_4^{21.5} = 0.8570$$
 (1) $n_D^{21.5} = 1.4350$ (1) 117° at 16 mm. (1) $D_4^{20} = 0.8677$ (2) $n_D^{20} = 1.44003$ (2)

[For prepn. (80% yield (1)) from undecanol-1 $(1:5890) + \text{SOCl}_2 + \text{pyridine see (1)}$, or with SOCl₂ alone (89% yield) see (2).]

No other data on C are recorded.

3:8803 (1) Rothstein, Bull. soc. chim. (5) 2, 84 (1935). (2) Vogel, J. Chem. Soc. 1943, 638, 641.

B.P. 240-242° (1)

[For form. of \bar{C} from octamethylenediamine [Beil. IV-271] with NOCl see (1); from 1,8-diphenoxyoctane (see below) with fumg. HCl see (1).]

 \bar{C} htd. with sodium phenolate yields (1) (2) 1,8-diphenoxyoctane [Beil. VI-148; VI₁-(85)], colorless tbls., m.p. 83.5–84°, sol. in hot alc., in ether, or in C_6H_6 ; not volatile with steam. [This prod. splits with HCl to yield (1) \bar{C} ; with HBr to yield (1) 1,8-dibromooctane [Beil. I-160], m.p. 15–16°, b.p. 270–272° sl. dec., b.p. 150–161° at 20–25 mm. (1).]

Č refluxed with NaI in acctone for 4 hrs., solvent evaporated, ether-sol. portion of residual oil htd. for 4 hrs., with thiourea in isoamyl alc. gives (3) octamethylene bis-(ω , ω '-isothiourea hydrochloride), m.p. 185–186° (3).

3:8865 (1) Ssolonina, J. Russ. Phys.-Chem. Soc. 30, 620, 623 (1898); Cent. 1899, I 26. (2) Ssolonina, J. Russ. Phys.-Chem. Soc. 30, 822, 824 (1898); Cent. 1899, I 254. (3) Kawai, Hosono, Shikinami, Yonechi, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 16, Nos. 306-309, 9-16 (1931); Cent. 1831, II 1694; C.A. 25, 5665 (1931).

3:8810 1-CHLORODODECANE
$$CH_3$$
. $(CH_2)_{10}$. CH_2Cl $C_{12}H_{2\delta}Cl$ Beil. I — (n-Dodecyl chloride; I₁— n-lauryl chloride) I₂-(133)

B.P. 243-244° cor. (1)
$$D_4^{22} = 0.8673$$
 (3) $n_{\rm D}^{22} = 1.4421$ (3) $132-134^{\circ}$ at 18 mm. (2) $D_4^{20} = 0.8673$ (9) $n_{\rm D}^{20} = 1.44255$ (9) 130° at 15 mm. (3) $125-126^{\circ}$ at 10 mm. (4) 116.5° at 5 mm. (9)

[For prepn. (80% yield (3)) from dodecanol-1 (1:5900) + SOCl₂ + pyridine see (3); or with SOCl₂ in absence of pyridine (84% yield) see (9).]

C in alc. refluxed with thiourea for 4 days gives (5) S-n-dodecylisothiourea hydrochloride, m.p. 132-135° (5).

[For reactn. of C with liq. NH₃ see (6) (7); with various amines see (7).]

[For reactn. of \tilde{C} with KI see (1); for reactn. with Mg + ether see (2); for reaction of \tilde{C} with Li. Na, or K followed by CO_2 see (10).]

 \bar{C} htd. with pyridine in s.t. at 110° for 15 hrs. yields (8) n-dodecylpyridinium chloride, cryst. from alc. + ether or from C_6H_6 as monohydrate, m.p. 92° (8). [This quat. salt yields (8) on cat. hydrogenation N-(n-dodecyl)piperidinium hydrochloride, m.p. 188–189° (8).]

--n-Dodecyl mercuric chloride (C₁₂H₂₅HgCl); m.p. 114.0-114.5° (10). [Prepd. indirectly (10).]

3:8810 (1) Conant, Hussey, J. Am. Chem. Soc. 47, 485 (1925). (2) Oldham, Ubbelohde, J. Chem. Soc. 1938, 204. (3) Rothstein, Bull. soc. chim. (5) 2, 84 (1935). (4) Reed, Tartar, J. Am.

Chem. Soc. 57, 571 (1935). (5) Sprague, Johnson, J. Am. Chem. Soc. 59, 1838-1839 (1937). (6) Wibaut, Heiermann, Wagtendonk, Rec. trav. chim. 57, 456-458 (1938). (7) Westphal, Jerchel, Ber. 73, 1004-1011 (1940). (8) Karrer, Kahnt, Epstein, Jaffé, Ishil, Helv. Chim. Acta 21, 233-234 (1938). (9) Vogel, J. Chem. Soc. 1943, 638, 641. (10) Meals, J. Org. Chem. 9, 211-218 (1944).

3: 8820
$$\gamma$$
-PHENOXY- n -PROPYL CHLORIDE γ -Chloro- n -propyl phenyl ether) γ -Chloro- n -propyl phenyl ether) γ -Chloro- γ -PROPYL CHLORIDE γ -PROPYL

Colorless oil gradually turning yellowish in light.

[For prepn. of \bar{C} from γ -phenoxy-n-propyl alcohol (trimethylene glycol monophenyl ether) [Beil. VI-147, VI₁-(85)] with SOCl₂ + pyridine (88% yield) see (3).]

[For prepn. of C from 1-bromo-3-chloropropane (trimethylene glycol chlorobromide) (5) with potassium phenolate (1) or with alc. sodium phenolate (yields: 68% (6) (4), 55% (2)) see indic. refs.; note that by this method some trimethylene glycol diphenyl ether (1,3-diphenoxypropane) (1:7170), m.p. 61°, b.p. 338-340° cor., may also be formed.]

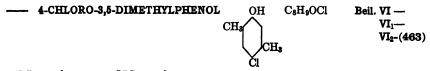
 $[\bar{C}$ with diethyl sodiomalonate in usual way gives (yields: 77% (2), 56% (6), 55% (4)) diethyl (γ -phenoxy-n-propyl)malonate [Beil. VI-168], b.p. 271° dec. at 140 mm. (4), 265–266° at 140 mm. (7), 216–219° at 20 mm. (6), m.p. 32° (7), 30° (4). — For analogous behavior of \bar{C} with diethyl sodio-methylmalonate see (7).]

[Č with Na in ether undergoes a complex decomposition giving (8) cf. (7) sodium phenolate, propylene, cyclopropane, hexamethylene glycol diphenyl ether, etc.]

[For study of rate of reactn. of C with KI in acetone at 50° and at 60° see (3).]

— N-(γ -Phenoxypropyl)phthalimide (phenyl γ -(phthalimido)-n-propyl ether) [Beil. XXI-472]: ndls. from alc., m. p. 91° (9), 88° (10). [Not reported from $\bar{\mathbf{C}}$ but obtd. in 80% yield (10) from γ -phenoxy-n-propylbromide with K phthalimide; also indirectly (9).]

3:8820 (1) Henry, Bull. soc. chim. (3) 15, 1224 (1896). (2) Gabriel, Ber. 25, 416-418 (1892). (3) Kirner, J. Am. Chem. Soc. 48, 2748-2749 (1926). (4) Granger, Ber. 28, 1198-1200 (1895). (5) Allen, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 157, Note 2 (1941); (18t ed.), 150-151, Note 2 (1932); 8, 53, Note 2 (1928). (6) Günther, Ber. 31, 2136-2137 (1898). (7) Funk, Ber. 26, 2569-2570 (1893). (8) Hamonet, Compt. rend. 136, 97 (1903); Bull. soc. chim. (3) 33, 535-536 (1905). (9) Manske, J. Am. Chem. Soc. 51, 1203 (1929). (10) Lohmann, Ber. 24, 2633 (1891).



B.P. 246° M.P. 115°

See 3:3505. Division A: Solids.

Beil. IX- 112

3:8830-3:8860

3:8830 2-CHLORO-4-n-BUTYLPHENOL

C₉H₉O₂Cl

[For prepn. of \bar{C} from p-n-butylphenol (1:1771) by chlorination with Cl_2 (3), SO_2Cl_2 (4) (5); or $ClSO_3H$ (5) see indic. refs.; for prepn. of \bar{C} from o-chlorophenyl propionate by rearr. with AlCl₃ in nitrobenzene to n-propyl 3-chloro-4-hydroxyphenyl ketone and subsequent reductn. to \bar{C} see (4) (1).]

[For studies of bactericidal characteristics of C see (1) (2) (6).]

Č with α -naphthoyl chloride (3:6930) yields (2) 4-n-butyl-2-chlorophenyl α -naphthoate, m.p. 44-46° (2).

3:8830 (1) Klarmann, Shternov, Gates, J. Am. Chem. Soc. 55, 2576-2589 (1933). (2) Blicke, Stockhaus, J. Am. Pharm. Assoc. 22, 1090-1092 (1933), Cent. 1934, I 1642, C.A. 28, 4839 (1934). (3) Klarmann (to Lehn & Fink Products Corp.), U.S. 2,010,595, Aug. 6, 1935, Cent. 1936, I 810; C.A. 29, 6608 (1935). (4) Klarmann (to Lehn & Fink Products Corp.), U.S. 2,139,550, Dec. 6, 1938; Cent. 1939, I 1807; C.A. 33, 2285 (1939). (5) Blicke (to Regents of Univ. of Michigan), U.S. 1,980,966, Nov. 13, 1934; Cent. 1935, I 3312; C.A. 29, 476 (1935). (6) Klarmann, Shternov, Gates, J. Lab. Clim. Med. 20, 40-47 (1934).

118-120° at 2 mm. (6)
Oil, insol. aq.; eas. sol. alc., ether.

5 mm. (5)

120-122° at

3:8860 β-CHLOROETHYL BENZOATE

[For prepn. of \overline{C} from ethylene chlorohydrin (3:5552) with BzCl (3:6240) on htg. (yields: 90% (1), 84.5% (6), 55% (2)) (5) see indic. refs.; from ethylene glycol (1:6465) with benzoic acid (1:0715) at 100° in pres. of HCl gas (7); from ethylene oxide (1:6105) with BzCl (3:6240) at 190° (8); from 1,4-dioxane (1:6400) with BzCl (3:6240) + TiCl₄ (2 moles) at 150-180° for 10 hrs. (70% yield (9)); from ethylene + BzOH (1:0715) + Cl₂ + cat. as directed (10) see indic. refs.]

[For formn. of \bar{C} from β -chloroethyl iminobenzoate on warming (3), from β -chloroethyl p-toluenesulfonate with $C_6H_5COOMgBr$ (5% yield (11)), or from bis-(β -chloroethyl) sulfate with NaOBz at 170° (61.5% yield (4)) see indic. refs.]

 \ddot{C} on htg. either alone or with SnCl₄ at 180–200° for 25 hrs. gives (9) ethylene glycol dibenzoate, m.p. 73°.

[$\ddot{\mathbf{C}}$ on a mononitration is claimed (1) to yield mainly β -chloroethyl m-nitrobenzoate, but this alleged prod. is not described either in the article or elsewhere in the literature.]

 \bar{C} with NaI (2 moles) in 90% alc. refluxed 6 hrs. gives (80% yield (1)) β -iodoethyl benzoate, b.p. 161–163° at 17 mm. (1).

 \tilde{C} with sec.-amines splits out HCl yielding the corresp. β -dialkylaminoethyl benzoate hydrochlorides [e.g., for reactn. of \tilde{C} with N-methylbenzylamine, N-methyl- β -phenylethylamine, N-methyl- γ -phenylpropylamine, and N-methyl- δ -phenylbutylamine see (12); with 4-methylpiperidine, 2-(β -phenylethyl)piperidine, and 4-(β -phenylethyl)piperidine see (13); with tetrahydroquinoline, tetrahydroisoquinoline, and cis- and trans-decahydroquinoline see (14)].

 $[\bar{\mathbf{C}}$ (1 mole) with N,N'-diphenylthiourea (thiocarbanilide) directly or in xylene at 130–150° for several hrs. gives a mixt. contg. N,N'-diphenylurea, phenylisothiocyanate, benzanilide, benzoic acid, and 2,3-diphenylthiazolidine, m.p. 136° (15).]

3:8860 (1) Zaki, J. Chem. Soc. 1930, 2271-2272. (2) Jones, Major, J. Am. Chem. Soc. 49, 1535-1536 (1927). (3) Gabriel, Heumann, Ber. 25, 2384 (1892). (4) Suter, Evans, J. Am. Chem. Soc. 60, 537 (1938). (5) Lynn, Lofgren, J. Am. Pharm. Assoc. 14, 970-972 (1925). (6) Kirner, J. Am. Chem. Soc. 48, 2751 (1926). (7) Simpson, Ann. 113, 120-121 (1860). (8) Altwegg, Landrivon (to Soc. Chim. Usines du Rhone), U.S. 1,393,191, Oct. 11, 1921; Cent. 1922, IV 947; C.A. 16, 422 (1922). (9) Goldfarb, Smorgonskii, J. Gen. Chem. (U.S. S.R.) 8, 1516-1522 (1938); Cent. 1939, II 4233, C.A. 33, 4593 (1939). (10) I.G., Brit. 460,720, March 4, 1937; Cent. 1937, I 4021; C.A. 31, 4675 (1937).

(11) Gilman, Beaber, J. Am. Chem. Soc. 45, 842 (1923).
(12) Cope, McElvain, J. Am. Chem. Soc. 53, 1589-1590 (1931).
(13) Bailey, McElvain, J. Am. Chem. Soc. 52, 1637-1638 (1930).
(14) Bailey, McElvain, J. Am. Chem. Soc. 52, 4013-4017 (1930).
(15) Olin, Dains, J. Am. Chem. Soc. 52, 3325 (1930).

— 4-CHLORORESORCINOL OH $C_6H_5O_2Cl$ Beil. S.N. 554 OH

B.P. 259–260° M.P. 105°

See 3:3100. Division A: Solids.

B.P. 258-262° dec. (1) 138-139° at 17 mm. (2)

Colorless liq. with agreeable odor; volatile with steam (1).

[For formn. of \bar{C} from 1,9-diaminononane (enneamethylenediamine) [Beil. IV-272] with NOCl (1), or from N,N' (bis-benzoylamino)nonane [Beil. IX-264, IX₁-(119)] with PCl₅ (60% yield (2)), or from 1,9-diphenoxynonane [Beil. VI-148] with HCl (1) see indic. refs.]

Č on htg. with sodium phenolate in alc. yields (1) 1,9-diphenoxynonane, white lfts., m.p. 62°, sol. in alc., ether, or C₆H₆ but not volatile with steam. [By loss of HCl during this etherification there is also formed a phenoxynonene (no constants) which is volatile with steam (1).]

3:8880 (1) Ssolonina, J. Russ. Phys.-Chem. Soc. 30, 606-632 (1898); Cent. 1899, I 26. (2) von Braun, Danziger, Ber. 45, 1972 (1912).

B.P. 260-263°

M.P. 57-58°

See 3:1130. Division A: Solids.

— 2-CHLOROHYDROQUINONE OH C₆H₅O₂Cl Beil. VI - 849 VI₁-(417) VI₂ (844)

B.P. 263°

M.P. 106°

See 3:3130. Division A: Solids.

B.P. 274° at 738 mm.

M.P. 34°

See 3:0300. Division A: Solids.

150-160° at 6 mm. (3) 87° at 0.15 mm. (4)

Pale yel. oil. — By soln. in 2 vols. 96% alc., cooling to -18° , and scratching, \tilde{C} has been obtd. in colorless cryst. from. (4).

[For prepn. (27% yield (2), 16% yield (4), 13-25% yield (3)) from diazotized m-chloro-aniline + C_6H_6 see (3) (4) (2).]

 \ddot{C} on oxidn. with CrO₃ in AcOH + V_2O_5 yields (5) *m*-chlorobenzoic acid (3:4392), m.p. 154°.

Č on nitration (no details (6)) gives a dinitro compd., 3-chloro-4,4'-dinitrobiphenyl, wooly flocks from alc., m.p. 202-203° (6) (9). [No other dinitro-3-chlorobiphenyls are recorded; of the possible mononitro-3-chlorobiphenyls only two (both prepd. indirectly) are known, viz., 4-nitro-3-chlorobiphenyl, m.p. 78.5-79.5° (7), and 3'-nitro-3-chlorobiphenyl, m.p. 101° (8).]

3:8940 (1) Hale, J. Am. Chem. Soc. 54, 4458-4459 (1932). (2), Gomberg, Bachmann, J. Am. Chem. Soc. 46, 2343 (1924). (3) Elks, Haworth, Hey, J. Chem. Soc. 1940, 1285. (4) Weissberger, Sängewald, Z. physik. Chem. B-20, 154 (1933). (5) Bellavita, Gazz. chim. ital. 65, 639 (1935). (6) Mascarelli, Gatti, Gazz. chim. ital. 63, 660 (1933). (7) Schoepfle, Truesdale, J. Am. Chem. Soc. 59, 376 (1937). (8) Mascarelli, Gatti, Atti accad. sci. Torino, 65, 143-147; Cent. 1930, II 1861. (9) Case, J. Am. Chem. Soc. 67, 116, 118 (1945).

--- 1-(CHLOROMETHYL)NAPHTHALENE

CH₂Cl C₁₁H₂Cl Beil. V - 566 V₁— V₂-(461)

B.P.291-292°

M.P. 32°

See 3:0250. Division A: Solids.

---- 4-CHLOROBIPHENYL

 $C_{12}H_9Cl$

Beil. V - 579 V₁---

 V_{2} -(483)

B.P. 291° at 745 mm.

M.P. 77°

See 3:1912. Division A: Solids.

--- 4-CHLOROPHTHALIC ANHYDRIDE

ORIDE O C₈H₃O₃Cl Beil. XVII - 483 XVII₁-(253)

B.P. 294.5° cor. at 720 mm.

M.P. 98°

See 3:2725. Division A: Solids.

---- 8-CHLORONAPHTHOL-2

Cl C₁₀H₇OCl

Beil. VI - 649

VI₁---VI₂-(604)

B.P. 307-308°

M.P. 101°

See 3:2965. Division A: Solids.

--- 6-CHLORO-2-PHENYLPHENOL

C₁₂H₉OCl

Beil, S.N. 539

B.P. 312° at 745 mm.

M.P. 71-72°

See 3:1757. Division A: Solids.

Beil, S.N. 539

3:8980 4-CHLORO-2-PHENYLPHENOL

(5-Chloro-2-hydroxybiphenyl)

C₁₂H₉OCl

[See also 6-chloro-2-phenylphenol (3:1757).]

Important Note: Through the year 1944 (and perhaps in some cases beyond) the chlorophenyl-phenol of m.p. $+ 11^{\circ}$ ($\tilde{\mathbb{C}}$) was regarded as having the structure 6-chloro-2-phenylphenol = 3-chloro-2-hydroxybiphenyl. In 1945, however, this view was corrected by the paper of Weissberger and Salminen (3); in this text, therefore, expression of the facts is reported in the light of their paper. Particular care is, therefore, required in consulting references prior to it since such material is universally expressed in the reverse sense of the present view.

[For prepn. of \bar{C} from 2-hydroxybiphenyl (1:1440) with Cl_2 (note that 6-chloro-2-phenylphenol (3:1757) is also formed) see (1) (4) (3), for prepn. of C from 5-amino-2-hydroxybiphenyl (5) by diazotization and use of Cu₂Cl₂ reaction (27% yield (3)) see indic. refs.]

C is sol. in aq. 25% NaOH at 60° but on cooling seps. NaA.4H₂O, m.p. 84-85° (1); anhydrous NaA, m.p. 280° (1) (4) (for use in sepn. of C from the isomeric 6-chloro-2phenylphenol (3:1757) see (1). [For form. of NaA in org. solvents such as MeOH, ether, or toluene see (8).1

The calcium salt of \bar{C} is more sol. in aq. than the corresp. deriv. of the isomeric 6-chloro-2-phenylphenol (3:1757) (use in sepn. (2)).

C on mononitration with HNO₃ in AcOH at 15-20° as directed gives (48% yield (3)) 5-chloro-2-hydroxy-3-nitrobiphenyl, yellow ndls., m.p. 57-58° (3).

[C on condensation with formaldehyde + morpholine yields (6) a prod. m.p. 125-126° (6).]

---- 4-Chloro-2-phenylphenyl benzoate: m.p. 86-87° (7). [Note that this prod. does not distinguish C from the isomeric 6-chloro-2-phenylphenol (3:1757) whose benzoate has m.p. 88.5°.1

3:8980 (1) Britton, Bryner (to Dow Chem. Co.), U.S. 1,921,727, Aug. 8, 1933; Cent. 1934, I 128-129; C.A. 27, 5086 (1933); Brit. 396,251, Aug. 24, 1933; Cent. 1934, I 128-129; C.A. 28, 578 (1934). (2) Rittler, Heller (to Chem. Fabrik von Heyden), Ger. 615,133, June 27, 1935; Cent. 1936, I 884; C.A. 29, 6247 (1935). (3) Weissberger, Salminen, J. Am. Chem. Soc. 67, 58-60 (4) Britton, Bryner (to Dow Chem. Co.), U.S. 1,969,963, Aug 14, 1934; C.A. 28, 6160 (5) Vorozhtsov, Troshchenko, J. Gen. Chem. (U.S.S.R.) 8, 431-437 (1938); Cent. 1940, II 2152; C.A. 32, 7907 (1938). (6) Bruson (to Rohm and Haas Co.), U.S. 2,040,039, May 5, 1936; Cent. 1936, II 1386-1387; C.A. 30, 4177 (1936). (7) Harris, Christiansen, J. Am. Pharm. Assoc. 24, 553-557 (1935). (8) Mills (to Dow Chem. Co.), U.S. 1,955,080, April 17, 1934; Cent. 1934, II 1991; C.A. 28, 3743 (1934).

1227

- 2-CHLOROBENZOPHENONE

B.P. 330° cor.

M.P. 45-46°

See 3:0715. Division A: Solids.

---- 4-CHLOROBENZOPHENONE

Cl C₁₃H₉OCl Beil. VII - 419 VII₁-(227)

B.P. 332° at 771 mm.

M.P. 77-78°

See 3:1914. Division A: Solids.

CHAPTER XX

DIVISION C. LIQUIDS WITH BOILING POINTS REPORTED ONLY UNDER REDUCED PRESSURE

3:9000-3:9299 (C₃-C₅ inclusive)

(Arranged in sequence of empirical formulas)

3: 9030 MALONYL DICHLORIDE
$$O=C-CH_2-C=O$$
 $C_3H_2O_2Cl_2$ Beil. II - 582 $II_{1^-}(252)$ $II_{2^-}(529)$

B.P. 58° at 27 mm. (1) (2) (3) $D_4^{22.9} = 1.4505$ (4) $n_D^{23.4} = 1.45973$ (4) 58° at 26 mm. (4) $D_4^{20} = 1.4509$ (5) $D_4^{20} = 1.4509$ (5) $D_4^{20} = 1.4509$ (5) $D_4^{20} = 1.4509$ (6) $D_4^{20} = 1.4639$ (7) at 15 mm. (6) $D_4^{20} = 1.4639$ (7) $D_4^{20} = 1.4639$ (8) $D_4^{20} = 1.4639$ (8) $D_4^{20} = 1.4639$ (9) $D_4^{20} = 1.4639$ (1) $D_4^{20} = 1.4639$ (1) $D_4^{20} = 1.4639$ (1) $D_4^{20} = 1.4639$ (2) $D_4^{20} = 1.4639$ (3) $D_4^{20} = 1.4639$ (4) $D_2^{20} = 1.4639$ (5) $D_4^{20} = 1.4639$ (5) $D_4^{20} = 1.4639$ (5) $D_4^{20} = 1.4639$ (6) $D_4^{20} = 1.4639$ (7) at 13 mm. (4)

Colorless liq. turning dark red on stdg. (6).

[For prepn. of \tilde{C} from malonic acid (1:0480) with SOCl₂ (yield 70% (8), 60% (6), 50% (9)) (1) (2) or with PCl₅ (yield: 68% (3), 36% (7)) see indic. refs.; for formn. of \tilde{C} from carbon suboxide with dry HCl gas see (10); for mfg. of \tilde{C} from methylene dichloride (3:5020) with CO, COS, or COCl₂ (3:5000) + cat. at 700° see (11).]

[\bar{C} in ether or EtOAc with Ag₂O, PbO, ZnO, etc., yields (8) carbon suboxide, b.p. +7°; \bar{C} treated at 0° with dry HBr gas yields (12) malonyl dibromide, b.p. 55–57° at 11 mm. (12); \bar{C} on cat. hydrogenation as specified (13) yields a condensation prod., m.p. 83°, of formyl-glutaconic acid.]

[C with acetone + CaCO₃ yields (14) mainly CH₃.CO.CH₂.CO.CH₂.CO.Cl [Beil. III₁-(263)] + a little phloroglucinol (1:1620) (the acid chloride itself, however, is quant. conv. to phloroglucinol by further htg. with CaCO₃).]

[\bar{C} with AlCl₃ + C₆H₆ yields (1) dibenzoylmethane (1:1480), m.p. 78°; for reactn. of \bar{C} with AlCl₃ + naphthalene (1:7200) yielding (15) (16) peri-naphthindandione (1,8-malonylnaphthalene) [Beil. VII₁-(391)] see indic. refs.; for reactn. of \bar{C} with acenaphthene (1:7225) yielding (15) (17) peri-acenaphtheneindandione (5,6-malonylacenaphthene) which on oxidn. gives (17) (18) naphthalene-1,4,5,8-tetracarboxylic acid [Beil. IX-1002, IX₁-(437)] see indic. refs.]

 \tilde{C} with 4 moles phenylhydrazine yields (2) malon-bis-(β -phenylhydrazide) [Beil. XV-272], m.p. 184° (2); \tilde{C} with 2 moles ethyl carbamate (urethane) in C_6H_6 refluxed until HCl is no longer evolved gives (85% yield {19}) malonyl-diurethane, cryst. from alc., m.p. 124° (19).

 $\tilde{\mathbf{C}}$ on hydrolysis with aq. yields malonic acid (1:0480). [Note that the half acid chloride of malonic acid has m.p. 65° dec. (20).] — For the amide, anilide, p-toluidide, and other derivs, corresp. to $\tilde{\mathbf{C}}$ see malonic acid (1:0480).

3:9030 (1) Auger, Ann. chim. (6) 22, 347-350 (1891). (2) Asher, Ber. 30, 1023-1024 (1897). (3) Clark, Bell. Trans. Roy. Soc. Can. (3), 27, III 97-107 (1933). (4) von Auwers, Schmidt, Ber. 46, 477-478 (1913). (5) Martin, Partington, J. Chem. Soc. 1936, 1181. (6) McMaster, Ahmann, J. Am. Chem. Soc. 50, 146 (1928). (7) Black, Shaw, Walker, J. Chem. Soc. 1931, 276. (8) Staudinger, Bereza, Ber. 41, 4463-4465 (1908). (9) Nightingale, Alexander, J. Am. Chem. Soc. 58, 794-796 (1936). (10) Diels, Wolf, Ber. 39, 696 (1906).

(11) Wiezevich, Frolich (to Standard Oil Development Co.), U.S. 2,062,344, Dec. 1, 1936; Cent. 1937, I 4863; C.A. 31, 708 (1937). (12) Fleischer, Hittle, Wolff, Ber. 53, 1848 (1920). (13) Fröschl, Maier, Monatsh. 59, 261, 269-270 (1932). (14) Komninos, Compt. rend. 167, 781 (1918); Bull. soc. chim. (4) 23, 452-455 (1918). (15) Fleischer, Retze, Ber. 55, 3282, 3285 (1922). (16) Badische Anilin und Soda Fabrik, Ger. 283,365, Apr. 10, 1915; Cent. 1915, I 965. (17) Eckert (to I.G.), Ger. 439,511, Jan. 14, 1927; Cent. 1927, I 1527. (18) Eckert (to Grasselli Dyestuffs Corp.), U.S. 1,612,103, Dec. 28, 1926; Cent. 1927, I 1527, C.A. 21, 593 (1927). (19) Basterfield, Woods, Whelen, J. Am. Chem. Soc. 49, 2945 (1927). (20) Staudinger, Ott, Ber. 41, 2211-2212 (1908).

3:9031
$$\alpha$$
-CHLOROACROLEIN (2-Chloropropen-2-al-1) CH_2 =C—CHO C_3H_3 OCl Beil. I — I_1 — I_2 —(785) B.P. 40° at 30 mm. (1) $D_2^{20} = 1.199$ (2) (3) $n_D^{20} = 1.463$ (2) (3) $D_2^{15} = 1.205$ (3) $D_2^{10} = 1.272$ (3)

Colorless strongly lachrymatory liq. with pronounced irritating effect on mucous membranes.

[For prepn. of \tilde{C} from acrolein (1:0115) in aq. with Cl_2 (50% yield (2)) or from α,β -dichloropropional dehyde (3:9034) by loss of 1 HCl with hot aq. NaOAc (27% yield (3)) (1) see indic. refs.]

C readily polymerizes.

 $[\bar{C} \text{ in CCl}_4 \text{ with Cl}_2 \text{ in cold adds 1 mole halogen giving (2) } \alpha,\alpha,\beta-\text{trichloropropionaldehyde } (3:9033).]$

[\bar{C} in dry ether with Br₂ in cold adds 1 mole halogen giving (2) α -chloro- α,β -dibromo-propionaldehyde, b.p. 105° at 55 mm., $D_{-}^{20} = 2.17$, $n_{D}^{20} = 1.548$.]

[For conversion of \bar{C} with EtOH to α -chloroacrolein diethylacetal, b.p. 158-160°, see (4).]

3:9031 (1) Muskat, Becker, J. Am. Chem. Soc. 52, 816-817 (1930). (2) Berlande, Bull. soc. chim. (4) 37, 1392-1393 (1925). (3) Moureu, Robin, Boisemenu, Ann. chim. (9) 15, 210-211 (1921). (4) The Distillers Co., Ltd., Staudinger, Tuerck, Lichtenstein, Brit. 554,570, July 9, 1943; C.A. 39, 312 (1945).

3:9082 d,l-α,β-DICHLOROPROPIONYL CHLORIDE C₃H₃OCl₃ Beil. S.N. 162

B.P.
$$52-54^{\circ}$$
 at 16 mm. (1) $D_4^{20} = 1.4757$ (2) $n_D^{20} = 1.47640$ (2) $43-44^{\circ}$ at 10 mm. (2)

[For prepn. of \bar{C} from α,β -dichloropropionic acid (3:0855) with SOCl₂ see (1) (2); for formn. of \bar{C} from glyceric acid (α,β -dihydroxypropionic acid) with PCl₅ see (4) (3) (5).]

[\bar{C} with alcohols yields alkyl α,β -dichloropropionates; e.g., cf. (1) (2) (3).]

 \bar{C} on hydrolysis yields α, β -dichloropropionic acid (3:0855) q.v.

3:9032 (1) Marvel, Dec, Cooke, Cowan, J. Am. Chem. Soc. 62, 3495-3498 (1940). (2) Leimu, Ber. 76, 1046, 1050 (1937). (3) Werigo, Werner, Ann. 170, 163-167 (1874). (4) Werigo, Okulitch, Ann. 167, 49 (1873). (5) Wichelhaus, Ann. 135, 253 (1865); 143, 3 (1867).

3:9032-A
$$\beta$$
, β -DICHLOROPROPIONYL CHLORIDE C₃H₃OCl₃ Beil. S.N. 162 Cl₂CHCH₂—C=O Cl

B.P. 43-44° at 10 mm. (1)
$$D_4^{20} = 1.4557$$
 (1) $n_D^{20} = 1.47378$ (1)

[For prepn. of \bar{C} from β,β -dichloropropionic acid (3:1058) with SOCl₂ at 75–80° for 3–4 hrs. see (1).]

[For study of rate of reaction of \bar{C} in dioxane with β -chloroethanol (3:5552) see (1).] \bar{C} on hydrolysis with aq. gives β,β -dichloropropionic acid (3:1058).

3:9032-A (1) Leimu, Ber. 70, 1046, 1050 (1937).

3:9033
$$\alpha_{1}\alpha_{1}\beta_{1}$$
-TRICHLOROPROPIONALDEHYDE $C_{3}H_{3}OCl_{3}$ Beil. I — C_{1} C_{1} C_{1} C_{1} C_{1} C_{2} $C_{3}H_{3}OCl_{3}$ Beil. I — C_{1} C_{2} $C_{3}H_{3}OCl_{3}$ Beil. I — C_{1} C_{2} $C_{3}H_{3}OCl_{3}$ Beil. I — C_{2} $C_{3}H_{3}OCl_{3}$ $C_{3}H$

[For prepn. of \bar{C} from α -chloroacrolein (3:9031) with Cl_2 in CCl_4 soln. (2), or for formn. of \bar{C} from β -(β '-chlorovinyl)acrylic acid dichloride (4,4,5-trichloropenten-2-oic acid-1) with ozone (1) see indic. refs.]

 \bar{C} on oxidn. with fumg. HNO₃ gives (2) (1) α,α,β -trichloropropionic acid (3:1275).

3:9033 (1) Muskat, Becker, J. Am. Chem. Soc. 52, 817-818 (1930). (2) Berlande, Bull. soc. chim. (4) 37, 1392 (1925).

3:9033-A
$$\alpha,\alpha$$
-DICHLOROPROPIONALDEHYDE Cl $C_3H_4OCl_2$ Beil. I-632 (2,2-Dichloropropanal-1) CH_3 — C — CHO I_1 — I_2 —

The physical constants of authentic pure C are unreported.

Note, however, that from n-propyl alc. (1:6150) by the action of Cl_2 there has been prepd. (1) a prod., m.p. 111-112° u.c., which is regarded (on very meager evidence) as a polymer of \bar{C} .

No further data on \bar{C} or its relatives can be found in the literature although the isomeric α,β -dichloropropional dehyde (acrolein dichloride) (3:9034) is well known.

3:9033-A (1) Spring, Tart, Bull. soc. chim. (3) 3, 402-405 (1890).

3: 9034
$$d_1$$
- α_1 -DICHLOROPROPIONALDEHYDE C_3 H $_4$ OCl $_2$ Beil. I - 632 (2,3-Dichloropropanal-1, CH $_2$ -CH $_2$ -CH $_3$ -CH $_4$ CH $_4$ -CHO I $_4$ -CHO

Colorless mobile liq. with strong odor suggesting chloral.

[For prepn. of \bar{C} from acrolein (1:0115) with Cl_2 in CCl_4 soln. in cold (74% yield (1)) cf. (3); for formn. of \bar{C} (together with oxalic acid) from 4,5-dichloropenten-2-oic acid (vinylacrylic acid dichloride) with ozone see (2).]

C with aq. forms a white solid (presumably a hydrate) but not further characterized (3) (1).

Č with abs. EtOH evolves heat and yields a prod. which analyzes correctly for the expected ethyl alcoholate but has been little studied (3).

C does not (3) combine with aq. NaHSO₃.

[Č with aq. NaOAc on htg. loses HCl giving (27% yield (1)) (2) 2-chloropropen-2-al-1 (α-chloroacrolein) (3:9031).

[\bar{C} with MeOH refluxed 6 hrs. gives (4) α,β -dichloropropionaldehyde dimethylacetal, b.p. 78–82° at 13 mm., $D_4^{18} = 1.182$, $n_D^{18} = 1.144$ (4); note, however, that \bar{C} with MeOH/NaOMe not only acetalizes but also loses 1 HCl giving (46% yield (4)) α -chloroacrolein dimethylacetal, b.p. 28° at 12 mm., $D_4^{19.5} = 1.081$, $n_D^{19.5} = 1.4305$ (4).]

[For reactn. of \tilde{C} with BrMgC=CMgBr yielding 4,5-dichloropentyn-1-ol-3, b.p. 90-91° at 12 mm., $D_4^{23}=1.306, n_D^{23}=1.500$ (5), see (5) (6).]

3:9034 (1) Moureu, Robin, Boismenu, Ann. chim. (9) 15, 209-211 (1921). (2) Muskat, Becker, J. Am. Chem. Soc 52, 816-817 (1930). (3) Aronstein, Ann. Suppl. 3, 190-192 (1864/5). (4) Naftali, Bull. soc. chim. (5) 4, 337 (1937). (5) Lespieau, Bull. soc. chim. (4) 43, 657-658 (1928). (6) Lespieau, Compl. rend. 179, 1606-1607 (1924), 203, 145 (1936).

3:9036 1,1,1,3-TETRACHLOROPROPANOL-2
$$C_3H_4OCl_4$$
 Beil. I — $(\beta,\beta,\beta,\beta'$ -Tetrachloroisopropyl alcohol) CH_2 — C — CCl_3 I₁— I₂-(385)

B.P. 95-96° at 17 mm. (1)
$$D_4^{20} = 1.610$$
 (2) $n_D^{20} = 1.51453$ (2) $87-89$ ° at 14 mm. (2)

Liq. with odor suggesting iodoform.

[For prepn. of \tilde{C} from 1,1,1,3-tetrachloropropanone-2 (unsym.-tetrachloroacetone) (3:6085) by reduction with $\Lambda l(OEt)_3$ or $Mg(OEt)_2$ or EtOMgCl see (2); from 3,3,3-trichloro-1,2-epoxypropane (γ,γ,γ -trichloropropylene oxide) (3:5760) (1) with conc. HCl on warming see (1).]

C with BzCl + dil. aq. alk. fails (1) to yield a crystn. benzoate.

3:9036 (1) Arndt, Eistert, Ber. 61, 1122 (1928). (2) Meerwein, von Bock, Kirschnick, Lens, Migge, J. prakt Chem. (2) 147, 212, 225 (1936).

3:9037 1,1,3,3-TETRACHLOROPROPANOL-2
$$C_3H_4OCl_4$$
 Beil. S.N. 24 $(\beta,\beta,\beta',\beta'$ -Tetrachloroisopropyl alcohol) Cl_2CH — CH — $CHCl_2$

B.P. 80-90° at 14 mm. (1)
$$D_4^{20} = 1.612$$
 (1) $n_D^{20} = 1.51334$ (1)

[For prepn. of \tilde{C} from 1,1,3,3-tetrachloropropanone-2 (sym.-tetrachloroacetone) (3:6050) by reduction with Al(OEt)₃, Mg(OEt)₂, or EtOMgCl see {1}.]

3:9037 (1) Meerwein, von Bock, Kirschnick, Lenz, Migge, J. prakt. Chem. (2) 147, 212, 225 (1936).

(Glycer " α-moi γ-chlore	HLOROPROI rol α-monochlo pochlorohydrii ppropylene gly	n,"	CH ₂ Cl C ₃ H ₂ H—C—OH CH ₂ OH	O ₂ Cl Beil. I - 473 I ₁ -(246) I ₂ -(537)
B.P. 141° 135° 129° 118.5-119.5° cor 119° 116° 113.5° 112-114° 101-105° 98-100° 92° cor. 83° 82-84° 81°	at 14 mm. at 11 mm. at 10.5 mm. at 10 mm. at 10 mm. at 3-4 mm. at 1 mm. at 1 mm. at 1 mm.	(2) 1 (3) 1 (45) (44) $D_4^{20} = 1$ (5) 1 (6) 1 (7) (76) (8) (9) $D_4^{17.5} = 1$ (1) (10) (11) Note. (12) 135.5–13 (13) 18 mm.	B.P. values of 1 36.0° at 20 mm. (6	$n_{\rm D}^{25} = 1.4811 \ (16)$ $1.4782 \ (15)$ $1.4781 \ (10)$ $1.4778 \ (15)$ $n_{\rm D}^{20} = 1.4811 \ (5)$ $1.4810 \ (13)$ $1.4809 \ (12)$ $1.4800 \ (15)$ $1.4794 \ (15)$ $n_{\rm D}^{17.5} = 1.4820 \ (6)$ 39° at 18 mm. (17), 34), and 130–131° at a material of doubtful
81° 80.9°	at 0.5 mm. at 0.53 mm.			

[See also 2-chloropropanediol-1,3 (glycerol β-monochlorohydrin) (3:9039).]

 \bar{C} is misc. with aq.; eas. sol. alc., ether, but alm. insol. pet. ether. — [For f.p./compn. data and diagram of system \bar{C} + aq. over range 0-60% \bar{C} see (19).]

USES OF C

The manifold uses of \bar{C} both as solvent and chemical intermediate cannot here be treated in detail [note, however, the following: for use of \bar{C} (sometimes together with ethylene glycol (1:6465) as solvent in nitration of various carbohydrates and related prods. see (20) (21); in cellulose nitrate lacquers see (22); in extraction of ligroin from spruce wood see (23); as rodent poison see (24)].

BIOCHEMICAL BEHAVIOR OF C

[For study of action of C on amylase (25), for effect on fermentation (26), for bactericidal action (27) (28) see indic. refs.]

PREPARATION OF C

 $\ddot{\mathbf{C}}$ may be prepared from four principal starting points, viz., glycerol (1:6540), 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358), 3-hydroxy-1,2-epoxypropane (glycidol), or allyl alcohol (1:6145); also from various miscellaneous starting points. — Note that by most of these methods a small proportion, e.g., 10-15%, of glycerol β -monochlorohydrin (3:9039) is also formed.

[For best working directions for lab. prepn. of C see (29).]

From glycerol (1:6540). With HCl without other acids. The earlier methods for prepn. of C from glycerol involved merely reaction with HCl under various circumstances [e.g., from glycerol satd. with HCl gas and htd. at 100° (30) (17), or 120° (32) cf. (15), 130° (19),

or at 150-170° under reduced press. (33), or in inert solvent such as dioxane or C itself (34) see indic. refs. and also (4); from glycerol with conc. HCl (9 moles) at 85° for 4 hrs. (9% yield (35)) or at 120° under press. (36) see indic. refs.].

With HCl in presence of organic acids. The reaction of glycerol with HCl is markedly facilitated by the presence of AcOH, other org. acids, or substances which yield such acids [e.g., for prepn. of \bar{C} from glycerol + AcOH with HCl gas (29) (1) (19) (37) (38) (39a) (yields: 86% (1) (19), 66% (29)) or with conc. aq. HCl (yields: 85–88% (16), 59–63% (29), 59% (9)) cf. (37) (39b) see indic. refs.; for prepn. of \bar{C} from glycerol + other org. acids (37) (39) or + esters of org. or inorg. acids (40) see indic. refs.; note also that further reactn. of \bar{C} with HCl leads to glycerol α,α' -dichlorohydrin (3:5985)].

With other reagents. [For prepn. of \bar{C} from glycerol with S_2Cl_2 (41) or with $SOCl_2$ + pyridine (42) see indic. refs.]

From 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358). [For prepn. of \overline{C} from epichlorohydrin with aq. at 100° (43) in s.t. (38) (31) or in s.t. at 125° (3) or on reflux. for 14 hrs. (80% yield (7)) see indic. refs.; this ring opening is greatly facilitated by pres. of dil. acids such as dil. H₂SO₄ (yields: 85-90% (44) (6), 80% (45)) or formic acid (66% yield (46)); for study of kinetics of this reactn. incl. influence of various acids and salts see (43) (3) (47) (48); for patent on use of dil. acids or acid-reacting salts see (49).]

From 3-hydroxy-1,2-epoxypropane (glycidol = epihydrin alc.). [For prepn. of \tilde{C} from glycidol with HCl (by oxide ring opening and addn.) under a wide variety of conditions see (4) (3) (50); yields may run as high as 90% (4).]

From allyl alcohol (1:6145) by addn. of HOCl. [For formn. of \bar{C} (together with glycerol β -monochlorohydrin (3:9039)) from allyl alc. by addn. of HOCl see text and corresp. citations under the β -isomer (3:9039).]

From miscellaneous starting points. [For prepn. of \bar{C} from propylene by addn. of HOCl see (51); from glyceryl triesters of hydroxy acids (e.g., castor oil) with HCl under various conditions see (52); from glycerol α -monochlorohydrin diacetate (3:6840) by alcoholysis with MeOH/HCl at 60° for 6 hrs. (yields: 86% (13), 81-85% (14)) see indic. refs.; from the reaction prod. of \bar{C} with acetone, i.e. from 4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (see below), by acid hydrolysis see (9) (5).]

CHEMICAL BEHAVIOR OF C WITH INORGANIC REACTANTS

Reduction of C. [C in aq. soln. with Na/Hg shaken 2 days at room temp. gives (53) cf. (31) propylene glycol (propanediol-1,2) (1:6455); note that reduction of C with conc. HI (which might be expected to yield isopropyl iodide) is so slow as to be useless for detn. of C (58).]

Oxidation of \tilde{C} . $[\tilde{C}$ in aq. soln. on oxidn. with conc. HNO₃ as directed (54) gives (yield not stated) β -chloro- α -hydroxypropionic acid (β -chlorolactic acid) [Beil. III-286, III₁-(110), III₂-(209)], eas. sol. aq., alc., ether, cryst. from C₆H₆ (54), m.p. 77° (54), 77-78° (55); for resolution of this acid into opt. act. forms, d-form, m.p. 91.5°, see (56). — For oxidation of \tilde{C} with HIO₄ giving (50% yield) chloroacetaldehyde hydrate (3:7212) see (146).]

[For study of inflammability of \bar{C} with solid KMnO₄ see (57); for titration of \bar{C} with Pb(OAc)₄ and use in detn. of \bar{C} in pres. of the isomeric glycerol β -monochlorohydrin (3:9039) see (12).]

Behavior of \tilde{C} with alkalies. \tilde{C} in the pres. of alkalies may react in at least two ways according to conditions: i.e., \tilde{C} may either undergo hydrolysis yielding glycerol (1:6540) or loss of HCl and consequent ring closure yielding 3-hydroxy-1,2-epoxypropane (epihydrin alc. = glycidol).

Hydrolysis of \bar{C} . [\bar{C} with aq. under reflux is slowly (33% in 70 hrs. (59)) hydrolyzed to

glycerol. — Č with aq. alk. (60) (61) (62) or alk. carbonate (61) (62) cf. (63) hydrolyzes to glycerol; for study of kinetics of alk. hydrol. see (60) (3) (4) (64) (65). — Note that Ç with alc. NaSH (66) or KSH (67) gives monothioglycerol [Beil. I-519].]

Dehydrochlorination of \bar{C} . [\bar{C} with alc. NaOH (68) (43) (4), or alc. KOH (16), or alc. NaOEt (16), or \bar{C} in dry ether with Na (16) (63) (50) (71), or \bar{C} with Na₂CO₃ + CaSO₄ (63), or \bar{C} in ether with BaO (31), or \bar{C} with 2 N aq. NaOH at ord. temp. for 10 min. (69), or \bar{C} with basic cpds. in alc. + C₆H₆ (70) gives (yields: 66% (68), 60–90% (16), 67% (4) 55% (71), 50–60% (63), 37% (43)) 3-hydroxy-1,2-epoxypropane (glycidol) [Beil. XVII-104, XVII₁-(50)], b.p. 160–161° (50), 65–66° at 2–25 mm (16), D_-^{25} = 1.1143 (16), n_D^{25} = 1.4302 (16) (corresp. N-phenylcarbamate, m.p. 60° (16); N-(α -naphthyl) carbamate, m.p. 102° (16)).

[Note that \tilde{C} in dil. aq. alk. loses HCl to give glycidol very much more rapidly (3) (4) than does the isomeric glycerol β -monochlorohydrm; for use of this property in detn. of purity of samples of \tilde{C} see (9).]

Behavior of C with salts of inorganic acids (for NaCN see below under salts of organic acids).

With alkali (or alk.-earth) volutes. [\bar{C} with alkali iodides (72a) or alk.-earth iodides (72b) at not above 90° in absence of light gives 3-iodopropanediol-1,2 (glycerol α -iodohydrin) [Beil. I₁-(246), I₂-(539)], m.p. 48-49° (72) (73), 49-50° (7) (corresp. bis-(p-nitrobenzoate), m.p. 102° (74), 102-103° (75)), note that this prod. comprises the pharmaceutical "Alival" (74) (75).]

With alkali phosphates. $[\bar{C}$ with aq. K_3PO_4 (76) or Na_3PO_4 (76) (77) cf. (78) (82) gives the di alkali salts of glycerol α -phosphoric acid [Bell. I-517, $I_{1-}(274)$, $I_{2-}(592)$].]

With alkali arsenites [For analogous behavior of C with Na₃AsO₃ see (79)]

Behavior of \tilde{C} with NH₃. \tilde{C} with NH₃ might be expected to yield 3-aminopropanediol-1,2; however, this prod. although known, is usually prepared from other sources. [For comments on reactn. of \tilde{C} with NH₃ see (80) (81).]

CHEMICAL BEHAVIOR OF C WITH ORGANIC REACTANTS

BEHAVIOR WITH ORGANIC HYDROXY COMPOUNDS

With monohydric alcohols. \tilde{C} with monohydric alcs. in pres. of corresp. alkoxide splits out alkali chloride giving the corresp. glycerol α -monoalkyl ethers.

[$\bar{\mathbf{C}}$ with MeOH/NaOMe gives (1) (83) (84) glycerol α -methyl ether (3-methoxypropanediol-1,2) [Beil. I-512, I₁-(271), I₂-(589)], b.p. 220° at 760 mm. (1) (15), 196° at 728 mm. (83), 135.5-136° at 40 mm (1) (15), 111-112° at 13 mm. (85), $D_4^{25} = 1.111$ (1) (15), $D_4^{17} = 1.1189$ (85), $n_D^{25} = 1.442$ (1) (15), $n_D^{17} = 1.4445$ (85) (corresp bis-(p-nitrobenzoate), m.p. 108° (86) (87) (15), corresp. bis-(N-phenylcarbamate), m.p. 118-119° (87)). — Note differences of these constants from those of the isomeric glycerol β -methyl ether (2-methoxy-propanediol-1,3) [Beil. I₂-(589)], viz., b.p. 232° at 760 mm. (1) (15), 148° at 40 mm. (1) (15), $D_4^{25} = 1.124$ (1) (15), $n_D^{25} = 1.446$ (1) (15) (corresp. bis-(P-nitrobenzoate), m.p. 155° (87) (15), corresp. bis-(P-phenylcarbamate), m.p. 102° (87)); note also that m.p.'s of mixts. of the two bis-(P-nitrobenzoates) (86) and of the two bis-(N-phenylcarbamates) (87) are depressed.]

[Č with EtOH/NaOEt gives (75% yield (1)) (88) glycerol α -ethyl ether (3-ethoxypropanediol-1,2) [Beil. I-512, I₂-(590)], b.p. 222° at 760 mm. (1) (15), 118-121° at 21 mm. (88), 114-116° at 10 mm. (15), 112-113° at 10 mm. (1); $D_4^{25} = 1.063$ (1), 1.058 (15); $n_D^{25} = 1.440$ (15), $n_D^{20} = 1.441$ (1) (corresp. bis-(N-phenylcarbamate), m.p. 103-104° (88)).]

[C with n-PrOH/NaO-n-Pr gives (88) (84) glycerol α-n-propyl ether (3-(n-propoxy)pro-

panediol-1,2) [Beil. I_1 -(272)], b.p. 122° at 22 mm. (84), 118-122° at 15 mm. (88), $D_4^{18} = 1.074$ (88), $D_5^{18} = 1.4400$ (88) (corresp. bis-(N-phenylcarbamate), m.p. 116° (88)).]

[\bar{C} with n-BuOH/NaO-n-Bu gives (88) glycerol α -n-butyl other (3-(n-butoxy))propanediol-1,2), b.p. 138-140° at 22 mm., $D_4^{18}=1.002, n_D^{18}=1.4463$ (corresp. bis-(N-phenylcarbamate), m.p. 94-95°).]

Certain of the glycerol α -monoalkyl ethers contg. long-chain alkyl radicals have special interest because of their occurrence in natural prods. Two such cases are represented by glycerol α -n-hexadecyl ether (chimyl alcohol) and glycerol α -n-octadecyl ether (batyl alcohol).

[\bar{C} with Na *n*-hexadecyl oxide fails (88), however, to yield $d_i l$ -glycerol α -*n*-hexadecyl ether (chimyl alcohol) [Beil. I₂-(590)], but prepns. by other methods (89) show following props.: m.p. 62-63° (89) (corresp. bis-(p-mtrobenzoate), m.p. 52-53° (89); corresp. bis-(N-phenylcarbamate), m.p. 92° (89)).]

[\ddot{C} with Na *n*-octadecyl oxide fails (88) to yield d,l-glycerol α -n-octadecyl ether (batyl alcohol) [Beil. I₂-(590)], but prepns by other methods (91) (89) (88) show following props.: m.p. 71-71.5° (89), 70-71° (91) (90) (89) (88) (corresp. bis-(p-nitrobenzoate), m.p. 73.5-74° (89); corresp. bis-(N-phenylcarbamate), m.p. 94.5-95° (89), 95-96° (88)).]

With polyhydric alcohols. $[\bar{C}$ with cellulose + NaOH gives (92) completely aq. soluble cellulose ethers; note, however, that the press of as little as 1% of 1,3-dichloropropanol-2 (glycerol α, α' -dichlorohydrin) (3:5985) suffices to render the ether completely aq. insoluble. — For use of \bar{C} in etherification of starch (93) (94), dextrin (94), etc., see indic. refs.]

With monohydric phenols. \tilde{C} with the sodium salts of monohydric phenols splits out NaCl yielding the corresp. glycerol α -aryl ethers.

[\bar{C} with phenol (1:1420) in EtOH/NaOEt (95), or \bar{C} with phenol + solid NaOH at 120° (96) (97), or \bar{C} with phenol + aq. NaOH at 100° for 2 hrs. (98) gives (yields: 61-64% (95), 59% (96)) glycerol α -phenyl ether (3-phenoxypropanediol-1,2) [Beil. VI-149, VI₁-(85)], m.p. 70° (95), 69° (99), 67-68° (96); note that this prod. on fusion changes to a second form, m.p. 53-54° (96) (97), but on stdg. at room temp. m.p. rises again to 68°.]

Corresponding condensations of \bar{C} with many other phenols are known but cannot be included here.

BEHAVIOR WITH CARBONYL COMPOUNDS

Č with carbonyl cpds. under appropriate conditions yields the corresp. cyclic acetals (see also under corresp. subheading of epichlorohydrin (3:5358).

With aldehydes. [\bar{C} with aq. formaldehyde soln. ("formalin") (1:0145) + H_3PO_4 on htg. gives (100) 4-(chloromethyl)-1,3-dioxolane [Beil. XIX-8, XIX₁-(610)], b.p. 126° at 750 mm. (100). — Note, however, that \bar{C} with paraformaldehyde (1:0080) + dry HCl gas reacts differently giving (101) 3-chloro-1,2-bis-(chloromethoxy) propane, although no constants on this prod. appear to have been reported.]

[C with acetaldehyde (1:0100) directly seems not have been recorded (cf. under epichlorohydrin (3:5358)): note, however, that \bar{C} with acetylene in pres. of HgSO₄ at 60-80° (102) or in pres. of BF₃/HgO/MeOH (103) gives (72% yield (103)) 4-(chloromethyl)-2-methyl-1,3-dioxolane [Beil. XIX₁-(610)], b.p. 148° (102), 147-149° (103), $D_4^{24} = 1.1720$ (103), $n_D^{24} = 1.4410$ (103).]

With ketones. [C with acetone (1:5400) in pres. of HCl (5), P_2O_5 (5), HCl + Na₂SO₄ (7), or H₂SO₄ + Na₂SO₄ (9) gives (60% yield (7)) 4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane ("acetone-glycerol α -chlorohydrin"), b.p. 157° at 767 mm., $D_4^{20} = 1.1079$, $n_D^{15} = 1.43750$ (7). — Note that this condensation occurs more readily than for the corresp. isomeric glycerol β -monochlorohydrin (3:9039) q.v. and has been employed (5) to enrich the proportion of the latter in mixtures of the two.]

[C with hexanone-2 directly has not been studied, but C with *n*-butylacetylene (1:8055) in pres. of Et₂O.BF₃/HgO/MeOH/trichloroacetic acid gives (104) 4-(chloromethyl)-2-*n*-butyl-2-methyl-1,3-dioxolane, b.p. 109° at 25 mm.]

[C with acetophenone (1:5515) in pres. of H₂SO₄ or HCl gives (105) a prod. presumably 4-(chloromethyl)-2-methyl-2-phenyl-1,3-dioxolane, b.p. 153-153.3° at 40 mm., which with

2 N HCl at 60° is hydrolyzed into its original components.]

BEHAVIOR OF C WITH SALTS OF ORGANIC ACIDS

 \bar{C} reacts with salts of organic acids to give in general the corresp. glycerol α -esters.

With salts of aliphatic monobasic acids. [\bar{C} with Na formate on htg. is claimed to yield (106) (45) glycerol α -monoformate [Beil. II-24, II₁-(19), II₂-(33)], but owing to the instability of this prod. the reliability of its supposed constants has been questioned (8).]

[\bar{C} with NaOAc or KOAc in s.t. at 150–160° yields (107) glyceryl α -acetate [Beil. II-146, II₁-(69), II₂-(159)], b.p. 129–131° at 3 mm., $D_4^{20}=1.2060$, $n_D^{20}=1.4517$ (108), but the reactn. is accompanied by some formn. of glyceryl diacetate and glyceryl triacetate.]

[For corresp. reactions of \bar{C} with sodium salts of *n*-butyric acid (1:1035), isobutyric acid (1:1030), *n*-valeric acid (1:1060), isovaleric acid (1:1050), and *n*-caproic acid (1:1130) see (8).

[\bar{C} with K laurate in s.t. at 180° under CO₂ (109) or \bar{C} with Na laurate at 130° (110) gives glyceryl α -laurate (" α -monolaurin") [Beil. II-362, II₁-(157), II₂-(320)], m.p. 63° (111), cf. (112), 62° (2).]

[\bar{C} with K myristate in s.t. at 180° under CO₂ (109), or \bar{C} with sodium myristate at 110–115° for 8–10 hrs. (110), gives (70% yield (110)) glyceryl α -myristate (" α -monomyristin") [Beil. II-366, II₁-(162), II₂-(327)], m.p. 68° (109) (113), 67.3° (111) cf. (112).]

[\bar{C} with K palmitate in s.t. at 180° under CO₂ (109), or \bar{C} with Pb palmitate at 112° under CO₂ (113), gives (50% yield (113)) glyceryl α -palmitate (" α -monopalmitin") [Beil. II-373, II₂-(338)], m.p. 74-75° (2), 77° (111) cf. (112).]

[\bar{C} with K stearate in s.t. at 180° under CO₂ (109), or \bar{C} with sodium stearate at 110–115° for 8–10 hrs. (110) cf. (114), gives glyceryl α -stearate (" α -monostearin"), m.p. 81.1° (111) cf. (112).]

With salts of amino acids. [For analogous forms. of corresp. glyceryl mono esters from \tilde{C} with sodium salts of aminoacetic acid (glycine) (115), α -aminopropionic acid (alanine) (115), α -amino-isocaproic acid (leucine) (116) see indic. refs.]

With alkali cyanides. [\bar{C} in 95% alc. with aq. KCN (or NaCN) in s.t. at 100° for 36 hrs., followed by hydrolysis, gives (9) 28% yield of the lactone of β , γ -dihydroxy-n-butyric acid (β -hydroxy-n-butyro- γ -lactone), m.p. 22.5-26° (9), accompanied by (23% yield (9)) the lactone of γ -hydroxyisocrotonic acid, m.p. +5° (9) (presumably formed by loss of H₂O from the former).] Cf. behavior of "glycerol β -monochlorohydrin" (3:9039).

BEHAVIOR OF Č WITH OTHER NON-NITROGENOUS ORGANIC REACTANTS

With alkyl halides (or their equivalents). [\bar{C} with MeI + silver oxide (15), or \bar{C} with methyl p-toluenesulfonate at 150° for 5 hrs. (117), or \bar{C} with diazomethane (118) gives the corresp. dimethyl ether, viz., 3-chloro-1,2-dimethoxypropane, b.p. 156-157° at 760 mm. (117), 156-158° (118), 156° (15), $D_4^{25} = 1.08$ (15), $n_2^{25} = 1.43$ (15).]

[Note that the corresp. diethyl ether, viz., 3-chloro-1,2-diethoxypropane, b.p. 69.8-70.4° at 14 mm., $D_4^{19} = 1.026$, $n_D^{20} = 1.4246$, has been prepd. indirectly (119).]

With RMgX cpds. [C with EtMgBr (2 moles) reacts in an obscure fashion yielding (120) hydroxyacetone (acetol) (1:5455). — C with iso-AmMgBr (4 moles) (perhaps acting through intermediate acetol) gives (25% yield (120)) 2,5-dimethylhexanediol-1,2 [Beil. I-491], b.p. 245-247° at 745 mm., 129-132° at 11 mm.]

[C with C₆H₅MgBr (4 moles) (perhaps acting through intermediate acetol) gives (120) (121) (60% yield (120)) 2-phenylpropanediol-1,2 [Beil. VI-930] accompanied by some 3-phenylpropanediol-1,2 [Beil. VI-929].]

BEHAVIOR OF C WITH AMINES

With primary amines. With aliphatic primary amines. [$\bar{\mathbb{C}}$ with n-heptadecylamine (122) or its hydrochloride gives a prod. which may be the expected N-(β , γ -dihydroxy-n-propyl)n-heptadecylamine.]

With aromatic primary amines. [Č with aniline (2 moles) + a little aq. refluxed for 1 hr., then neutralized, gives (63% yield (124)) $N-(\beta,\gamma-\text{dihydroxy-}n-\text{propyl})$ aniline [Beil. XII-183], b.p. 249-250° at 50 mm. (125), 200-203° (124), m.p. 42° (124), 52° (125).]

[$\bar{\mathbf{C}}$ with p-aminophenol gives (126) $N-(\beta,\gamma-\text{dihydroxy-}n\text{-propyl})-p$ -aminophenol, m.p. 192°, used as photographic developer (127); for analogous reactions of $\bar{\mathbf{C}}$ with p-anisidine giving $N-(\beta,\gamma-\text{dihydroxy-}n\text{-propyl})-p$ -anisidine, m.p. 75–76° see (126), or of $\bar{\mathbf{C}}$ with p-phenetidine giving $N-(\beta,\gamma-\text{dihydroxy-}n\text{-propyl})-p$ -phenetidine, m.p. 93° (126), 90–92° (128), see indic. refs.]

With secondary amines. With aliphatic secondary amines. [\bar{C} with Me₂NH + aq. NaOH at 20–40° (129) or \bar{C} with Me₂NH in s.t. at 100° for 5–6 hrs. (130) (131) cf. (132) gives 3-(dimethylamino)propanediol-1,2 [Beil. IV-302], b.p. 220° cor. at 749 mm. (130), 111° at 15 mm. (132). — \bar{C} with Et₂NH in s.t. at 100° for 5–6 hrs. (131) cf. (130) (132) gives 3-(diethylamino)propanediol-1,2 [Beil. IV-302], b.p. 233–235° at 748 mm. (130) (131), 106° at 3 mm. (132) (corresp. bis-(N-phenylcarbamate), m.p. 106.5° (133); corresp. bis-(N-phenylcarbamate)monohydrochloride, m.p. 109° (133)).]

With heterocyclic secondary amines. [$\bar{\mathbb{C}}$ with piperidine in s.t. at 100° for 4–5 hrs. (131, cf. (132) or in ord. flask at 100° for 1½ hrs. (134) gives 3-(piperidino)propanediol-1,2 [Beil. XX-34, XX₁-(12)], m.p. 83° (135) (132), 79–80° (136), 67–68° (134) (corresp. bis-(p-nitrobenzoate), m.p. 108° (135); corresp. bis-(N-phenylcarbamate)monohydrochloride ("Diothane"), m.p. 201–202° cor. (137), 197–198° u.c. (?) (133)). — Note that in prepn. of "Diothane" the influence of the purity of the piperidine has been studied (137); that 3-(piperidino)propanediol-1,2 yields a mono-(N-phenylcarbamate)monohydrochloride, m.p. 176–177° (133); for resolution of d,l-3-(piperidino)propanediol-1,2 into its opt. act. enantiomorphs and prepn. of the corresp. opt. act. "Diothanes" see (138).]

With tertiary amines. [\bar{C} with Me₃N anhydrous (139) or in aq. soln in s.t. at 100° for 8 hrs. (31) or in alc. soln. in s.t. at 100° for 6 hrs. (140) gives trimethyl- $(\beta,\gamma$ -dihydroxy-n-propyl)-ammonium chloride [Beil. IV-302]. — \bar{C} with Et₃N in s.t. at 100° for 8 hrs. gives (141) triethyl- $(\beta,\gamma$ -dihydroxy-n-propyl)-ammonium chloride [Beil. IV-303]. — For analogous behavior of \bar{C} with tri-n-propylamine, quinoline, and strychnine see (141). — For quat. salt from \bar{C} with N,N-dimethyl "stenyl" amine see (142).]

BEHAVIOR OF C WITH OTHER NITROGENOUS ORG. REACTANTS

[$\tilde{\mathbf{C}}$ with diazomethane gives (118) the corresp. dimethyl ether for which see above under behavior of $\tilde{\mathbf{C}}$ with alkyl halides.]

[C with aq. Na₂NCN stood for 12 hrs., then shaken with benzoyl chloride, gives (143) the tribenzoate, m.p. 130° of 5-(hydroxymethyl)-2-aminooxazoline; substitution of benzene-sulfonyl chloride for the benzoyl chloride yields (144) corresp. *tris*-(benzene-sulfonate), m.p. 158°.] Cf. behavior of epichlorohydrin (3:5358).

[—] Glycerol α -monochlorohydrin α' -acetate (γ -chloro- β -hydroxy-n-propyl acetate): b.p. 240° (see 3:6775).

- Glycerol α -monochlorohydrin β -acetate (β -chloro- β '-hydroxy-isopropyl acetate): b.p. 218° (see 3:6517).
- —— Glycerol α -monochlorohydrin α,β -diacetate: b.p. 245° (see 3:6840).
- —— Glycerol α -monochlorohydrin α' -benzoate: unreported.
- —— Glycerol α -monochlorohydrin β -benzoate: unreported.
- Glycerol α -monochlorohydrin α', β -dibenzoate: unreported.
- © Glycerol α -monochlorohydrin di-(p-nitrobenzoate): m.p. 108-109° u.c. (14), 108° (15), 107-108° (2). [From \bar{C} with p-nitrobenzoyl chloride (2 moles) in pyridine at room temp. for several days (93-96% yield (14)) or in CHCl₃ soln. with quinoline as acid acceptor (100% yield (2)); note that this prod. depresses m.p. (121-122°) of the corresp. deriv. of the isomeric glycerol β -monochlorohydrin (3:9039) (14).]
- Glycerol α -monochlorohydrin α' -(?)-(N-phenylcarbamate): m.p. 128-129° (16), 127-129° (9), 126° (42). [From \bar{C} with phenyl isocyanate in 7% yield (9); note that for the corresp. deriv. of glycerol β -monochlorohydrin (3:9039) the m.p. is 133-136°.]
- **D** N- $(\beta, \gamma$ -dihydroxy-n-propyl)phthalimide: m.p. 111.5-112.5° (145), 111° (46). [From \bar{C} with K phthalimide (100% yield (46)), but no details of conditions are stated.]
- 3:9038 (1) Fairbourne, Gibson, Stephens, J. Soc. Chem. Ind. 49, 1021-1023 (1930). (2) Fairbourne, Foster, J. Chem. Soc. 1926, 3148-3151. (3) Smith, Z. physik. Chem. 92, 717-735 (1917).
 (4) Smith, Z. physik. Chem. 94, 691-722 (1920). (5) Smith, Lindberg, Ber. 64, 511-515 (1931).
- Böeseken, Heimans, Rec. trav. chim. 42, 1106-1108 (1923), Bull. soc. chim. (4) 39, 1254 (1926).
 Fischer, Pfahler, Ber. 53, 1608-1609 (1920).
 Gilchrist, Schuette, J. Am. Chem. Soc. 53, 3480-3484 (1931).
 Glattfeld, Leavell, Spieth, Hutton, J. Am. Chem. Soc. 53, 3165-3171

(1931). (10) Gibson, J Soc. Chem. Ind 50, 971 (1931).

- (11) Walden, Swinne, Z. physik. Chem. 79, 721 (1912). (12) Sjoberg, Svensk Kem. Tid. 53, 390-400 (1941), Cent. 1942, I 2517-2518; C.A. 36, 2812 (1942). (13) Sjoberg, Svensk Kem. Tid. 53, 454-457 (1941); Cent. 1942, II 25, not in C.A. (14) Rider, J. Am. Chem. Soc. 54, 775-776 (1932). (15) Fairbourne, Gibson, Stephens, J. Chem. Soc. 1931, 446, 451-452. (16) Rider, Hill, J. Am. Chem. Soc. 52, 1521-1525 (1930) (17) Hanriot, Ann. Chim. (5) 17, 67-75 (1879). (18) Grun, von Skopnick, Ber. 42, 3750-3759 (1909). (19) Gibson, J. Soc. Chem. Ind. 50, 949-954 (1931). (20) Sturgis (to General Explosives Co), U.S. 1,473,685, Nov. 13, 1923; Cent. 1924, I 720; C.A. 18, 472 (1924).
- (21) Wrightsman (to du Pont Co.), U.S. 1,751,377, March 18, 1930, Cent. 1930, II 2476; C.A.
 24, 2605 (1930): U.S. 1,891,255, Dec. 20, 1932; Cent. 1933, I 1717; C.A. 27, 2036 (1933). (22)
 Rosenthal (to F. Bayer & Co.), Ger 406,426, Nov. 18, 1924, Cent. 1925, I 908; not in C.A. (23)
 Schütz, Cellulosechem. 19, 33-38 (1941); C.A. 36, 5008 (1942). (24) I G., Brit. 474,677, Dec. 2, 1937; Cent. 1938, I 2045, C.A. 32, 3004 (1938) French 805,557, Nov. 24, 1936; Cent. 1937, I 3397; C.A. 31, 4417 (1937). (25) Clark, Edwards, Trans. Roy. Soc. Can. (3) 28, III 107-125 (1934); Cent. 1935, I 2548; C.A. 29, 1112 (1935). (26) Simon, Buchem. Z. 253, 218-221 (1932). (27)
 Cooper, Forstner, Buchem. J. 18, 944 (1924). (28) Salumbein Compt. rend. 155, 368 (1912). (29) Conant, Quayle, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 294-296 (1941); (1st. ed.), 288-289 (1932), 2, 33-35 (1922). (30) Berthelot, Ann. 88, 311-312 (1853); Ann. chim. (3) 41, 296-297 (1854).
- (31) Hanriot, Ann. chim. (5) 17, 80, 100, 114 (1879). (32) Nivière, Compt. rend. 156, 1628 (1913); Bull. soc. chim. (4) 13, 893-894 (1913). (33) Sprengstoffwerke Nahnsen & Co., A.G., Ger. 254,709, Dec. 12, 1912; Cent. 1913, I 348, C.A. 8, 1190 (1914) Ger. 269,657, Jan. 88, 1914; Cent. 1914, I 713, C A. 8, 2253 (1914). (34) Britton, Slagh (to Dow Chem. Co.), U.S. 2,257,899, Oct. 7, 1941; C.A. 36, 498 (1942). (35) Norris, Mulliken, J. Am. Chem Soc. 42, 2096 (1920). (36) Deutsche Sprengstoff, A.G., Ger. 180,668, Jan. 29, 1907; Cent. 1907, I 774; C.A. 1, 1655 (1907). (37) Novelli, Anales farm. bioquim. (Buenos Aires) 1, 8-19 (1930); Cent. 1931, 250; C.A. 24, 5021 (1930). (38) Reboul, Ann. chim. (3) 60, 18-19 (1860). (39) Boehringer und Söhne, (a) Ger. 197,308 (b) Ger. 197,309; April 16, 1908; Cent. 1908, I 1655-1666; C.A. 2, 2429 (1908). (40) Chem. Fabrik Griesheim-Elektron, Ger. 238,341, Sept. 19, 1911; Cent. 1911, II 1679; C.A. 6, 1660 (1912).
- (41) Deutsche Sprengstoff, A.G., Ger. 229,872, Jan. 6, 1911; Cent. 1911, I 358; C.A. 5, 2557 (1911); Ger. 229,536, Dec. 22, 1910; Cent. 1911, I 274; C.A. 5, 2557 (1911); Ger. 201,230, Sept. 25, 1908; Cent. 1908, II 1218; C.A. 3, 377 (1910). (42) Carré, Mauclere, Compt. rend. 192, 1568 (1931).
 (43) Brönsted, Mary Kilpatrick, Martin Kilpatrick, J. Am. Chem. Soc. 51, 430-431, 445-446 (1929).
 (44) Fourneau, Ribas y Marques, Bull. soc. chim. (4) 39, 700 (1926). (45) Delaby,

Dubois, Compt. rend. 187, 767-769, 949-951 (1928); Bull. soc. chim. (4) 47, 570 (1930). (46) den Otter, Rec. trav. chim. 57, 18-20 (1938). (47) Banerjee, Sen, J. Indian Chem. Soc. 9, 509-518 (1932). (48) Smith, Wode, Widhe, Z. physik. Chem. 130, 157-162 (1927). (49) Groll, Hearne (to Shell Development Co.), U.S. 2,086,077, July 6, 1937; Cent. 1937, II 2433; C.A. 31, 5813 (1937). (50) Bigot, Ann. chim. (6) 22, 481-487 (1891).

(51) Curme, Young (to Carbide and Carbon Chem. Corpn.) Canadian 238,729, March 18, 1924; Cent. 1925, I 1129; not in C.A. (52) Grun, Ger. 272,337, March 27, 1914; Cent. 1914, I 1469–1470; C.A. 8, 2604 (1914): Ger. 227,901, Sept. 3, 1914; Cent. 1914, II 812; C.A. 9, 1096 (1915). (53) Lourenco, Ann. 120, 91 (1861). (54) Koelsch, J. Am. Chem. Soc. 52, 1105–1106 (1930). (55) von Richter, J. prakt. Chem. (2) 20, 193–195 (1879). (56) Tsunoo, Ber. 68, 1342 (1935). (57) Rathsburg, Gawlich, Chem. Ztp. 65, 426–427 (1941); Cent. 1942, I 651; C.A. 37, 3273 (1943). (58) Grün, Boedecker, Ber. 43, 1058, Note 1 (1910). (59) Olivier, Berger, Rec. trav. chim. 41, 639–640 (1921). (60) Drozdov, Chernov, J. Gen. Chem. (U.S.S.R.), 4, 1305–1309 (1934); Cent. 1936, I 4549; C.A. 29, 3306 (1935).

(61) Lewis (to du Pont Co.), U.S. 1,895,517, Jan. 31, 1933; Cent. 1933, I 2870; [C.A. 27, 2455 (1933)]. (62) Essex, Ward (to du Pont Co.), U.S. 1,626,398, April 26, 1927; Cent. 1928, I 410? [C.A. 21, 2136 (1927)]. (63) Kötz, Richter, J. prakt. Chem. (2) 111, 395-397 (1925). (64) Smith, Z. physik. Chem. 83, 349-352 (1912). (65) Smith, Lindberg, Ber. 61, 1709-1717 (1928). (66) Thiess, Müller (to M.L.B.), Ger. 405,384, Oct. 31, 1924; Cent. 1925, I 1527; not in C.A. (67) Carius, Ann. 124, 222-224 (1862). (68) Nef, Ann. 335, 232 (1904). (69) Groll, Hearne (to Shell Development Co.), U.S. 2,070,990, Feb. 16, 1937, Cent. 1937, II 2433; [C.A. 31, 2612 (1937)]. (70) Marple, Evans (to Shell Development Co.), U.S. 2,248,635, July 8, 1941; C.A. 35, 6599 (1941).

(71) Nivière, Bull. soc. chrm. (4) 15, 464-465 (1914). (72) Luders, (a) Ger. 291,541, April 20, 1916; Cent. 1916, I 913; C.A. 11, 1018 (1917); (b) Ger. 291,922, May 15. 1916; Cent. 1916, I 1210; C.A. 11, 1519 (1917). (73) Luders, Emmert, Deut. med. Wochschr. 41, 648-649 (1914); Cent. 1915, II 238. (74) Fairbourne, Stephens, J. Chem. Soc. 1932, 1973-1976. (75) Fischer, Ber. 53, 1625 (1920). (76) Bailly, Gaumé, Compt. rena. 178, 1192 (1924); Bull. soc. chrm. (4) 35, 590-91 (1924). (77) King, Pyman, J. Chem. Soc. 105, 1253 (1914). (78) Bailly, Ann. chrm. (9) 6, 127-137 (1916). (79) Oechslin (to Étab Poulenc Frères), Brit. 191,028, Feb. 14, 1923; Cent. 1923, IV 721; C.A. 17, 2887 (1923): French 556,366, July 19, 1923; Cent. 1923, IV 721; not in C.A. (80) Fairbourne, Gibson, Stephens. J. Soc. Chem. Ind. 49, 1069 (1930).

(81) Smith, Nilsson, J. prakt. Chem. (2) 162, 63-70 (1943). (82) Hill, Pyman, J. Chem. Soc. 1929, 2236-2238. (83) Grun, Bockish, Ber. 41, 3471 (1908). (84) Boehringer u. Söhne, Ger. 226,454, Oct. 4, 1910; Cent. 1910, II 1256; [C.A. 5, 1321 (1911)]. (85) Hibbert, Whelen, J. Am. Chem. Soc. 51, 1947 (1929). (86) Fairbourne, J. Chem. Soc. 1931, 2235. (87) Hibbert, Whelen, Carter, J. Am. Chem. Soc. 51, 302-306 (1929). (38) Davies, Heilbron, Owens, J. Chem. Soc. 1930, 2542-2546. (89) Baer, Fischer, J. Buol. Chem. 140, 397-410 (1941). (90) Davies, Heilbron, Jones, J. Chem. Soc. 1933, 167.

(91) Kornblum, Holmes, J. Am. Chem. Soc. 64, 3045-3046 (1942).
(92) Shorygin, Rymashevskaya, J. Gen. Chem. (U.S.S.R.) 8, 1903-1908 (1938); Cent. 1939, II 419, C A. 33, 5650 (1939); J. Gen. Chem. (U.S.S.R.) 7, 2428-2436 (1937); Cent. 1938, II 860; C A. 32, 1925 (1938).
(93) Shorygin, Makarov-Zemlyanskaya, Bilenko, Derevitskaya, Shematenkova, J. Gen. Chem. (U.S.S.R.) 8, 1910-1917 (1938), Cent. 1939, II 420; C.A. 33, 5814 (1939).
(94) Leuchs (to F. Bayer Co.), Ger. 408,714, Jan. 23, 1925, Cent. 1925, I 1820, not in C.A. (95) Wheeler, Willson, Org. Syntheses, Coll. Vol. 1 (2nd ed.), 296-298 (1941); (1st ed.), 290-291 (1932); 6, 48-50 (1926).
(96) Fairbourne, Stephens, J. Chem. Soc. 1932, 1972-1973.
(97) Stephens, J. Soc. Chem. Ind. 51, 375-378 (1932).
(98) Marle, J. Chem. Soc. 101, 310 (1912).
(99) Fourneau, J. pharm. chm. (7) 1, 55-61 (1910); Cent. 1910, I 1134; C.A. 4, 3070 (1910).
(100) Verley, Bull. soc. chm. (3) 21, 276-277 (1899).

(101) Blanchard, Bull. soc. chim. (4) 39, 1120 (1926). (102) Chem. Fabrik Griesheim-Elektron, Ger. 271,381, March 13, 1914; Cent. 1914, I 1316-1317; [C.A. 9, 356 (1915)]. (103) Nieuwland, Vogt, Foohey, J. Am. Chem. Soc. 52, 1020-1022 (1930). (104) Killian, Hennion, Nieuwland, J. Am. Chem. Soc. 58, 1658-1659 (1936). (105) Altwegg, Chermette (to Soc. Chim. Usines du Rhone), U.S. 1,572,176, Feb. 9, 1926; Cent. 1926, I 3370; [C.A. 20, 1243 (1926)]. (106) Van Romburgh, Rec. trav. chim. 1, 186-187 (1882). (107) Smith, Z. physik. Chem. 102, 64-65 (1922). (108) Schuette, Hale, J. Am. Chem. Soc. 52, 1979-1980 (1930). (109) Krafft, Ber. 36, 4341-4343 (1903). (110) Heiduschka, Schuster, J. prakt. Chem. (2) 120, 148-157 (1928).

(111) Averill, Roche, King, J. Am. Chem. Soc. 51, 869 (1929). (112) Young, Black, J. Am. Chem. Soc. 60, 2604 (1938). (113) Brash, J. Soc. Chem. Ind. 46, T. 481-482 (1927). (114) Veikhertz, Khim. Farm. Prom. 1932, 284-286; Cent. 1933, II 2661; [C.A. 27, 270 (1933)]. (115) Weizmann, Haskelberg, Compt. rend. 189, 105 (1929). (116) Fodor, Weizmann, Z. physiol. Chem. 154, 290-292 (1926). (117) Blanchard, Bull. soc. chim. (4) 41, 831 (1927). (118) Meer-

wein, Hins, Ann. 484, 17-18 (1930). (119) Meerwein, Hins, Hofmann, Kroning, Pfeil, J. prakt. Chem. (2) 147, 278 (1936/7). (120) Grignard, Compt. rend. 141, 45 (1905); Ann. chim. (8) 10, 31-40 (1907).

(121) Grignard, Ger. 164,883, Nov. 16, 1905; Cent. 1905, II 1751. (122) I.G., Brit, 358,114, Oct. 29, 1931; Cent. 1932, I 449; [C.A. 26, 4926 (1932)]. (123) I.G., Brit. 361,261, Dec. 10, 1931; Cent. 1932, I 1438; [C.A. 27, 1112 (1933)]; French 716,560, Dec. 23, 1931; Cent. 1932, I 1438; [C.A. 26, 2288 (1932)]. (124) Shoruigin, Smirnov, J. Gen. Chem. (U.S.S.R.) 4, 830-833 (1934); Cent. 1935, II 3763; C.A. 29, 2155 (1935). (125) Bamberger, Kitschelt, Ber. 27, 3425-3426 (1894). (126) Kolshorn, Ger. 346,385, Dec. 29, 1921, Ger. 346,386, Jan. 2, 1922; [Cent. 1922, II 574]; not in C.A.: Ger. 343,151, Oct. 28, 1921; [Cent. 1922, II 143]; not in C.A.: Brit. 145,614, June 29, 1920; C.A. 14, 3427 (1920); not in Cent.: Brit. 155,575/6, Jan. 13, 1921; Cent. 1921, II 601; C.A. 15, 1535 (1921): French 519,129, June 4, 1921; Cent. 1921, IV 803; not in C.A. (127) Kolshorn, Ger. 343,994, Nov. 12, 1921; Cent. 1922, II 604; not in C.A. (128) Bergmann, Ulpts, Camacho, Ber. 55, 2807-2809 (1922). (129) Alquist, Slagh (to Dow Chem. Co.), U.S. 2,147,226, 756-757 (1899).

(131) Roth, Ber. 15, 1149-1153 (1882). (132) Rider, Hill, J. Am. Chem. Soc. 52, 1528-1530 (1930). (133) Rider, J. Am. Chem. Soc. 52, 2115-2118 (1930); U.S. 2,004,132, June 11, 1935; Cent. 1935, II 3546; C.A. 29, 4902 (1935). (134) Magidson, Strukow, Arch. Pharm. 271, 1576-577 (1933). (135) Einhorn, Fiedler, Ladisch, Uhlfelder, Ann. 371, 158-161 (1910). (136) Pyman, J. Chem. Soc. 93, 1795 (1908). (137) Rider, Cook, J. Am. Chem. Soc. 59, 1741 (1937). (138) Rassch, Brode, J. Am. Chem. Soc. 64, 1112-1113 (1942). (139) Meyer, Ber. 2, 186-188 (1869). (140) Schmidt, Hartmann, Ann. 337, 102 (1904).

(141) Bienenthal, Ber. 33, 3500-3506 (1900). (142) du Pont Co., Brit. 477,981, Feb. 10, 1938; Cent. 1938, II 183; not in C.A. (143) Fromm, Pirk, Ann. 442, 143-144 (1925). (144) Fromm, Kapeller-Adler, Ann. 467, 253-254 (1928). (145) Gabriel, Ohle, Ber. 50, 824 (1917). (146) Hatch, Alexander, J. Am. Chem. Soc. 67, 688 (1945).

3:9039 2-CHLOROPROPANEDIOL-1,3
$$CH_2OH$$
 $C_3H_7O_2Cl$ Beil. I - 476 (Glycerol β -monochlorohydrin, " β -monochlorohydrin," H — C — Cl I_1 -(247) I_2 -(542) β -chlorotrimethylene glycol, β - β '-dihydroxyisopropyl chloride)

B.P.
$$[146^{\circ}]$$
 at 18 mm. (1) (2)] $D_{4}^{20} = 1.3219$ (4) $n_{D}^{20} = 1.4831$ (4) $124.5-125^{\circ}]$ at 14.5 mm. (3) 1.3217 (3) 1.3217 (3) $cf.$ (4) $122.5-123.5^{\circ}]$ at 13.5 mm. (5) $D_{4}^{0} = 1.3416$ 1.3375 (3)

Attention is directed to the fact that \bar{C} is in most respects extremely similar in physical constants and chemical behavior to the isomeric glycerol α -monochlorohydrin (3-chloropropanediol-1,2) (3:9038); that \bar{C} is very readily partially isomerized to the latter, and that, therefore, the homogeneity of all prepns. of \bar{C} or reactn. prods. derived from supposedly pure \bar{C} must be accepted with reserve. The literature of the two glycerol monochlorohydrins is seriously entangled, and reference to the original articles must be made for supporting details.

PREPARATION OF C

Č has been isolated (3) from the mixed glycerol monochlorohydrins by fractional hydrolysis and distillation; this isolation has been confirmed (4) (6) by methods based on the slower condensation of \bar{C} with acetone (see below). — The mixture of glycerol monochlorohydrins obtd. from glycerol (1:6540) with conc. HCl at 120° for 5 hrs. under press. contains (4) 13% \bar{C} .

[For formn. of \bar{C} (together with the isomeric α -monochlorohydrin) from a mixt. of monochlorohydrin diacetates with abs. MeOH contg. dry HCl gas see [7].]

[The mixture of the two glycerol monochlorohydrins obtd. from allyl alcohol (1:6145) by addn. of HOCl (1) (8) (5) cf. (6) (9) (10) (11) (13) or from epichlorohydrin (3:5358) q.v. by addn. of aq. in pres. of acids has been shown (12) to be essentially similar to that obtd. from glycerol with HCl, although different proportions of α - and β - isomers might be anticipated (3).]

CHEMICAL BEHAVIOR OF C

Reduction of \tilde{C} . [\tilde{C} with Na/Hg in aq. alc. HCl gives (8) trimethylene glycol (1:6490).] Behavior with aq. alkalies. [\tilde{C} with aq. alk. loses HCl and ring-closes to 3-hydroxy-1,2-epoxypropane (glycidol = epihydrin alcohol): this reactn. occurs with \tilde{C} very much more slowly than for the isomeric α -monochlorohydrin (3:9038); for its use in detn. of purity of \tilde{C} see (6) (3) (13) (14).]

Behavior with alkali cyanides. [\bar{C} in 95% alc. with aq. KCN (or NaCN) in s.t. at 100° for 36 hrs., followed by hydrolysis, does not (6) give the expected $\beta_1\beta'$ -dihydroxyisobutyric acid but instead gives (35% yield (6)) the lactone of $\beta_1\gamma$ -dihydroxy-n-butyric acid (β -hydroxy-n-butyro- γ -lactone), m.p. 22.5–26° (6), i.e., the same prod. similarly obtd. from glycerol α -monochlorohydrin (3:9038).]

Behavior with NaI. [\bar{C} with dry NaI in anhydrous acctone in s.t. at 100° for 12 hrs. gives (18% yield (15)) glycerol β -mono-iodohydrin, m.p. 52-53° (15).]

Behavior with acetone. [\bar{C} in acetone with P_2O_5 at 2-7° gives (57% yield (4)) a condensation prod., "acetone- β -chlorohydrin," $C_6H_{11}O_2Cl$, b.p. 161.5-162.2° cor. at 757 mm., $D_4^{15}=1.1344$, $n_D^{15}=1.4487$; this condensation occurs less readily, however, than the analogous reactn. for glycerol α -monochlorohydrin (3:9038), and removal of the latter by this means has been used (4) to enrich the proportion of \bar{C} in a mixt. of the two.]

- Glycerol β -monochlorohydrin α -acetate: oil, b.p. 230° at 760 mm., 230–234° cor. at 750 mm. (10), $D_{15}^{15} = 1.235$ (10). (See 3:6648.)
- Glycerol β -monochlorohydrin $\alpha_1\alpha'$ -diacetate: oil, b.p. 101–102° at 4 mm. (15).
- —— Glycerol β -monochlorohydrin α -benzoate: unreported.
- Glycerol β -monochlorohydrin α,α' -dibenzoate: oil, b.p. 210-211° at 1.5 mm. (15).
- Glycerol β-monochlorohydrin α,α'-bis-(p-nitrobenzoate): m.p. 121-122° (16) (7).
 [Prepd. indirectly; note that this prod. depresses the m.p. of authentic glycerol α-monochlorohydrin bis-(p-nitrobenzoate), m.p. 108-109° u.c. (7).]
- Glycerol β -monochlorohydrin α -(N-phenylcarbamate): m.p. 133-136° (6), 131-133° remelting at 133° (12). [From \bar{C} with phenyl isocyanate in 6% yield (6); note that, for the corresp. deriv. of glycerol α -monochlorohydrin, m.p. is 128-129° (12).]

3:9039 (1) Hanriot, Ann. chim. (5) 17, 73-75, 76-78 (1879). (2) Gibson, J. Soc. Chem. Ind. 56, 949-950 (1931). (3) Smith, Z. physik. Chem. 94, 723-736 (1920). (4) Smith, Lindberg, Ber. 64, 509-516 (1931). (5) Read, Hurst, J. Chem. Soc. 121, 996-999 (1922). (6) Glattfeld, Leavell, Spieth, Hutton, J. Am. Chem. Soc. 53, 3169-3171 (1931). (7) Rider, J. Am. Chem. Soc. 54, 773-776 (1932). (8) Henry, Ber. 5, 449 (1872): Bull. acad. roy. Belg. (3) 33, 110-114; Cent. 1897, I 741. (9) Essex, Ward (to du Pont Co.), U.S. 1,594,608, Aug. 3, 1926; Cent. 1926, II 1693; [C.A. 20, 3170-3171 (1926)]. (10) Wegscheider, Zmerzlikar, Monatsh. 34, 1071-1072 (1913).

[11] Brooks (to Standard Alcohol Co.), U.S. 2,311,023, Feb. 16, 1943; C.A. 37, 4407 (1943).
[12] Rider, Hill, J. Am. Chem. Soc. 52, 1521-1527 (1930).
[13] Smith, Z. physik. Chem. 92, 717-740 (1917).
[14] Smith, Lindberg, Ber. 61, 1712-1717 (1928).
[15] Glattfeld, Klass, J. Am. Chem. Soc. 55, 1114-1119 (1933).
[16] Fairbourne, Foster, J. Chem. Soc. 1926, 3150.

3:9040 1,4-DICHLOROBUTADI-YNE-1,8
$$C_4Cl_2$$
 Beil. I — (Dichlorobiacetylene) Cl — C = C — C = C — Cl I_1 — I_2 -(246)

M.P. 1-3° (1)

Long colorless ndls., which can be distilled under N_2 yielding a colorless oil (1). — \bar{C} has odor of dichloroacetylene; readily polymerizes to an insol. dark brown explosive material. — \bar{C} explodes at 73° (1).

[For prepn. of C from diacetylene [Beil. 1-266] by actn. of alk. hypochlorite soln. in cold and absence of light see (1) (2) (3).]

 \bar{C} dislyd. in CHCl₃ and stood 1 day with I₂ in CHCl₃ adds 2 moles I₂ yielding (1) 1,4-dichloro-1,2,3,4-tetraiodobutadiene-1,3, which after careful recrystn. from C₆H₆/pet. ether has m.p. 155-157° (1).

3:9010 (1) Straus, Kollek, Hauptmann, Ber. **63**, 1893–1894 (1930). (2) I.G., Brit. 333,946, Sept. 18, 1930; Cent. **1931**, I 523. (3) I.G., Ger. 495,787, April 17, 1930.

B.P. 125° at 70-80 mm. (1)

[From 2,3,4,5,5-pentachloropentadien-2,4-oic acid-1 [Beil. II-482] by boilg. with aq., then distilling with steam; the structure of the acid (and therefore of \bar{C}) is disputed (2). — For two other materials (b.p. 193-200° at 720 mm.) having the composition C₄HCl₅, obtd. from trichloroethylene (3:5170) with AlCl₃, but thought *not* to be identical with \bar{C} , see (3).]

3:9044 (1) Zincke, Küster, Ber. 26, 2113 (1893). (2) Zincke, Ann. 296, 143 (1897). (3) Kaufler, Ann. 433, 48-51 (1923).

3:9046 1,1,2,3,4,4-HEXACHLOROBUTENE-2 C₄H₂Cl₆ Beil. S.N. 11

(Liquid stereoisomer) Cl Cl Cl Cl

HC—C—C—C—H

B.P. 97-98° at 10 mm. (1)
$$D_{15}^{15} = 1.651$$
 (1) $n_{D}^{-} = 1.53313$ (1)

[See also solid stereoisomer (3:1945).]

Colorless oily liq. with agreeable odor.

[For formn. of \bar{C} (together with its solid stereoisomer (3:1945)) by actn. of Cl₂ upon the high-boilg fraction obtd. in the prepn. of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see (1); for formn. of \bar{C} from the liq. stereoisomer (3:6150) of 1,2,3,4-tetrachlorobutadiene-1,3 + Cl₂ see (1).]

8:9046 (1) Müller, Hüther, Ber. 64, 589-600 (1931); C.A. 25, 3956-3957 (1931).

1243

3:9048 HEXACHLOROBUTENE-X

C₄H₂Cl₆

Beil. S.N. 11

B.P. 106-107.5° at 14 mm. (1)

[For formn. of \tilde{C} from 1,1,2,2,3,4,4-heptachlorobutane (3:9056) with conc. aq. KOH see (1).]

Č reduces Tollens' reagt. (1).

3:9048 (1) Prins, Rec. trav. chim. 56, 125 (1937); Cent. 1937, I 3308; C.A. 31, 2999 (1937).

3:9050 HEXACHLOROBUTENE-Y

C₄H₂Cl₆ Beil. S.N. 11

B.P.

125.5° at 25 mm. (1)

M.P.

9.5-11° (1)
$$D_4^{20} = 1.6880$$
 (1) $n_D^{20} = 1.5442$ (1)

[For formn. of \bar{C} (together with other products) by actn. of F_2 on trichloroethylene (3:5170) see (1).]

 \bar{C} does not add Cl_2 or Br_2 in sunlight (1).

Č differs (1) in prop. from the solid stereoisomer (3:1945) of 1,1,2,3,4,4-hexachloro-butene-2.

3:9050 (1) Miller, J. Am. Chem. Soc. 62, 343 (1940).

3:9052 1,2,3-TRICHLOROBUTADIENE-1,3 Cl Cl Cl C4H₃Cl₃ Beil. S.N. 12

B.P. 33-34° at 7 mm. (1) (2)
$$D_A^{20} = 1.4060$$
 (1) $n_D^{20} = 1.5262$ (1)

[For prepn. of \tilde{C} from 1,2,2,3,4-pentachlorobutane (3:9070) (55% yield of \tilde{C} together with 25% yield 2,3,3,4-tetrachlorobutene-1 (3:9060)) with alc. KOH for 2 hrs. at room temp. see (1) (2).]

 \bar{C} after addition of hydroquinone can be distd. in vac. (1). — \bar{C} polymerizes more slowly than 2,3-dichlorobutadiene-1,3 (3:5220); under ordinary conditions \bar{C} changes in 10-12 days to a jelly-like mass contg. 50% unchanged \bar{C} ; after a month polymerization to a dark-colored soft friable mass is apparently complete (1).

3:9052 (1) Carothers, Berchet, J. Am. Chem. Soc. 55, 2004-2008 (1933). (2) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934, Cent. 1935, I 3724, C.A. 28, 5716 (1934).

3:9054 1,1,1,4,4-PENTACHLOROBUTENE-2 $C_4H_3Cl_5$ Beil. S.N. 11 Cl Cl

B.P.
$$78.5-80^{\circ}$$
 at 11 mm. (1) $D_{22}^{22}=1.611$ (1) $n_{\rm D}^{22}=1.5548$ (1) $76-77.9^{\circ}$ at 10 mm. (1) $D_{21}^{21}=1.612$ (1) $n_{\rm D}^{21}=1.5538$ (1)

[For prepn. of \bar{C} (in small yield and with much resinification (1)) from either trichloroethylene (3:5170) + 1,1,2-trichloroethane (3:5330) + AlCl₃ for 7 days at 40°, or from 1,2-dichloroethylene (3:5030) + 1,1,1,2-tetrachloroethane (3:5555) + AlCl₃ for 10 days at 40°, see (1).]

Č is volatile with steam (use in sepn. from accompanying resin (1).)

C reduces Tollens' soln, but not NH4OH/AgNO3 without alkali (1).

Č is not attacked by boilg. 0.1% KMnO₄ (1).

 $\bar{\mathbf{C}}$ on boilg. with excess N/10 alc. KOH splits off 2.34-2.6 moles HCl but $\bar{\mathbf{C}}$ cannot be titrated (1).

3:9054 (1) Prins, Rec. trav. chim. 56, 123-124 (1937).

B.P. 137.5° at 13.5 mm. (1)
$$D_{20}^{20} = 1.742$$
 (1) $n_{\rm D}^{20} = 1.5407$ (1) 97.5° at 2 mm. (1)

[For prepn. of C (60% yield (1) together with other products) from 1,2-dichloroethylene (3:5030) + pentachloroethane (3:5880) + AlCl₃ for 12 days at 40° see (1).

C in CCl4 gives with AlCl3 a yel. color; no HCl is evolved on boilg., and on addn. of water the solution is completely decolorized (1).

Č with Zn dust in alc. gives (50% yield (1)) of a trichlorobutadiene, b.p. 161°, 52° at 12 mm. (1).

3:9056 (1) Prins, Rec. trav. chim. 56, 124-125 (1937).

3:9057 1,2-DICHLOROBUTADIENE-1,3 Cl Cl C₄H₄Cl₂ Beil, S.N. 12 CH—CH—C—CH

B.P.
$$60-65^{\circ}$$
 at 105 mm. (4) $D_{15}^{15} = 1.207$ (1) $n_{D}^{15} = 1.5078$ (1) (5) $46.75-47.5^{\circ}$ at 85 mm. (5) $D_{4}^{15} = 1.199$ (5) $n_{D}^{7} = 1.4698$ (2)

(2)

C polymerizes slower than chloroprene (3:7080) yielding a rubberlike polymer which on vulcanization gives an ebonite-like subst. (1).

[For prepn. of C (56% yield (4)) from 1-chloro-2-vinylacetylene (3:7070) by treatment as directed at room temp. with conc. HCl + CuCl + NH₄Cl see (4); for formn. from vinylacetylene + Cl₂ see (3); for prepn. of C from 1,2,4-trichlorobutene-2 (3:9062) with EtOH/ KOH see (5).]

C on oxidn. with KMnO4 yields (3) oxalic acid dihydrate (1:0445). — C on ozonization in CCL (3) yields oxalic acid (1:0535) and formic acid (1:1005); under specified conditions. however. α,β-dichloroacrylic acid (3:2265), m.p. 85-86°, has been isolated (3).

C fails to add maleic anhydride (3). - [For behavior of C with HOBr or with HgO + $I_2 + MeOH see (6).$

3:9657 (1) Klebanskii, Tzyurikh, Dolgopol'skii, Bull. acad. sci., U.S.S.R. 1935, No. 2, 189-226; Rubber Chem. Tech. 9, 383-408 (1936); Cent. 1935, II 3844; C.A. 30, 1259 (1936). (2) Klebanskii. Volkenshtein, Orlova, J. Gen. Chem. (U.S.S.R.) 5, 1255-1267 (1935); Cent. 1936, I 3414; C.A. 30, 1025 (1936); J. prakt. Chem. (2) 145, 1-17 (1936). (3) du Pont Co., Brit. 389,122, April 4, 1933; Cent. 1934, II 2609. (4) Petrov, J. Gen. Chem. (U.S.S.R.) 13, 250-256 (1943); C.A. 38, 1467 (1944). (5) Petrov, J. Gen. Chem. (U.S.S.R.) 13, 102-107 (1943); C.A. 38, 329-330 (1944).

B.P. 82-83° at 17 mm. (1)

[For prepn. of C from 1,2-dichloroethylene (3:5030) by polymerization in pres. of peroxide cat. see (1).]

3:9058 (1) Bauer, U.S. 2,267,712, Dec. 30, 1941; C.A. 36, 2564 (1942).

3:9060 2,3,3,4-TETRACHLOROBUTENE-1 Cl Cl Cl C₄H₄Cl₄ Beil. S.N. 11 (1,2,2,3-Tetrachlorobutene-3)

 $D_4^{20} = 1.4602 (1)$ $n_D^{20} = 1.5133 (1)$ B.P. 41-42° at 7 mm. (1)

[For formn. of C (25% yield (1)) from 1,2,3,3,4-pentachlorobutane (3:9070) with MeOH/ KOH at room temp. for 2 hrs. (together with 55% yield 1,2,3-trichlorobutadiene-1,3 (3:9052)) see (1).]

 \bar{C} on oxidn. with excess aq. KMnO₄ yields (1) α, α, β -trichloropropionic acid (3:1275). m.p. 48-50°, Neut. Eq. 176.4 (calcd. 177.5) (1).

[A liquid, b.p. 90-110° at 25 mm., $D_4^{21} = 1.473$, $n_D^{21} = 1.514$, and believed to be a mixt. of tetrachlorobutenes, has been obtd. (2) from mon vinylacetylene + Cl₂; it may or may not have contained C.1

3:9060 (1) Berchet, Carothers, J. Am. Chem. Soc. 55, 2004-2008 (1933). (2) Rengert. Schumacher, Ber 73, 1025-1042 (1940); C.A. 35, 1027 (1941).

3:9062 1,2,4-TRICHLOROBUTENE-2 C₄H₅Cl₃ Beil. S.N. 11 (1,3,4-Trichlorobutene-2)

 $D_4^{20} = 1.3843$ (1) $n_D^{20} = 1.5175$ (1) B.P. 67-69° at 10 mm. (3) $D_4^{15} = 1.3575$ (3) $n_D^{15} = 1.5121$ (3) 64-65° at 10 mm. (1)

62-65° at 11 mm. (2)

[For formn. of C from 4-chlorobutadiene-1,2 (3:7225) + Cl₂ (together with 2,3,4trichlorobutene-1 (3:9064) and 1,2,2,3,4-pentachlorobutane) see (1) (2); for formn. of C from 2-chlorobutadiene-1,3 (Chloroprene) (3:7080) + Cl₂ (together with 2,3,4-trichlorobutene-1 (3:9064) and 1,2,2,3,4-pentachlorobutane (3:9070)) see (1) (2) (3),1

C with EtOH/KOH as directed (3) loses HCl giving 1,2-dichlorobutadiene-1,3 (3:9057). C on oxidn. with aq. KMnO₄ yields (1) (3) chloroacetic acid (3:1370), m.p. 63°, Neut. Eq. 95.1 (calcd. 94.5) (1).

3:9062 (1) Carothers, Berchet, J. Am. Chem. Soc. 55, 1628-1631 (1933). (2) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934; Cent. 1935, I 3724; C.A. 28, 5716 (1934). (3) Petrov. J. Gen. Chem. (U.S.S.R.) 13, 102-107 (1943); C.A. 38, 329 (1944).

B.P. 40-41° at 10 mm. (1)
$$D_4^{20} = 1.3430$$
 (1) $n_D^{20} = 1.4944$ (1) $37-41°$ at 10 mm. (2)

36-40° at 6 mm. (2)

[For formn. of \bar{C} from 4-chlorobutadiene-1,2 (3:7225) (together with 1,2,4-trichlorobutene-2 (3:9062)) especially at low temps., e.g., -60 to -70° , see (1). Note that at 40-60° \bar{C} formed by this reactn. reacts further with the by-product 1,2,4-trichlorobutene-2 (3:9062) to yield (1) as the principal product 1,2,3,3-tetrachlorobutane (3:9080) q.v.; for formn. of \bar{C} from 2-chlorobutadiene-1,3 (Chloroprene) (3:7080) with Cl_2 see (2) (3).]

C with alk. as specified (2) gives 2,3-dichlorobutadiene-1,3 (3:5220), b.p. 98° at 760 mm. (2).

 \bar{C} on htg. with 2 pts. aq. + calcd. amt. powdered CaCO₃ for 4 hrs. at 70° fails (4) to hydrolyze [diff. from 1,2-dichlorobutene-2 (3:5615) or 1,3-dichlorobutene-2 (3:5550)]. — \bar{C} does react, however, with hot aq. K_2CO_3 losing HCl and yielding (4) alm. 100% 2,3-dichlorobutadiene-1,3 polymer (4).

 \overline{C} on oxidn. with aq. KMnO₄ yields (1) α,β -dichloropropionic acid, (3:0855), m.p. 49–50°, Neut. Eq. 141 (calcd. 143) (1).

3:9064 (1) Carothers, Berchet, J. Am. Chem. Soc. 55, 1628-1631 (1933) (2) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934, Cent. 1935, I 3724, C.A. 28, 5716 (1934). (3) Coffmann (to du Pont), U.S. 1,964,720, July 3, 1934, Cent. 1934, II 3180; C.A. 28, 5080 (1934) (4) Tishchenko, J. Gen. Chem. (U.S. S.R.) 7, 658-662 (1937), Cent. 1937, II 371; C.A. 31, 5754 (1937).

3:9066 1,3-DICHLORO-2-(CHLOROMETHYL)PROPENE-1 $C_4H_5Cl_3$ Beil. I — CH_2Cl I_1 — I_2 -(181)

B.P. 62-64° at 9 mm. (1) (2)

[For formn. of \tilde{C} (together with other products) from 1,3-dichloro-2-chloromethyl-2-nitropropane [Beil. $I_{2^{-}}(92)$] with Na/Hg (2) or from 2-nitro-2-hydroxymethylpropanediol-1,3 [Beil. $I_{2^{-}}(596)$] with PCl₅ (1) see (1) (2).

Č on cat. hydrogenation with Pt black in alc. yields (2) 1,3-dichloro-2-methylpropane (3:7960), b.p. 45° at 10 mm.

 \bar{C} in CHCl₃ on shaking with Cl₂/aq. adds Cl₂ yielding (2) 1,1,2,3-tetrachloro-2-chloromethylpropane (3:9072), b.p. 99–101° at 12 mm. — \bar{C} with Br₂ in CHCl₃ adds Br₂ yielding (2) 1,2-dibromo-1,3-dichloro-2-(chloromethyl)propane, colorless odorless oil, b.p. 140° at 10 mm.

[For reactn. of C with sodio-malonic ester see (3).]

3:9066 (1) Kleinfeller, Ber. 62, 1585-1587 (1929). (2) Kleinfeller, Ber. 62, 1594-1595 (1929). (3) Kleinfeller, Frercks, J. prakt. Chem. (2) 138, 195-196 (1933).

B.P. 95.3-95.5° at 11 mm. (1)

[See also solid diastereoisomer (3:0750).]

[For prepn. of \bar{C} (30-50% yield of mixed solid and liquid stereomers (1)) from 1,2-dichloroethylene (3:5030) + 1,1,2-trichloroethane (3:5330) + 1% AlCl₃ for 5 days at 35-40° see (1).]

Č in CCl4 treated with AlCl3 gives a dark violet soln. which on boilg. evolves HCl (1).

 $\ddot{\mathbf{C}}$ in alc. treated wih Zn dust gives (60% yield (1)) 1-chlorobutadiene-1,3 (3:7210), b.p. 68° (1).

 \bar{C} dissolved in hot alc. and titrated with N/10 KOH splits off 1.51-1.59 moles HCl (1).

[A pentachlorobutane obtained (2) from trichloroethylene (3:5170) + 1,1-dichloroethane (3:5035) + AlCl₃ may or may not be identical with \bar{C} .]

3:9068 (1) Prins, Rec. trav. chim. **56**, 121-123 (1937). (2) Consortium für Elektrochem. Ind., Brit. **453**,414, Oct. 8, 1936; Cent. **1937**, I 1012.

3:9070 1,2,2,3,4-PENTACHLOROBUTANE Cl
$$C_4H_5Cl_5$$
 Beil. S.N. 10 (1,2,3,3,4-Pentachlorobutane) $H_2C-CH-C-CH_2$ Cl Cl Cl Cl Cl Cl B.P. 85° at 10 mm. (1) $D_4^{20}=1.5543$ (1) $n_D^{20}=1.5157$ (1) 78-84° at 9 mm. (2)

[For prepn. of \bar{C} from 1,3-dichlorobutene-2 (3:5550) by actn. of Cl_2 at low temps. (-60 to -70°), much HCl being evolved and 2,3,4-trichlorobutene-1 (3:9064) also being formed, see (1); note also that chlorination of 4-chlorobutadiene-1,2 (3:7225) gives mixts. of 2,3,4-trichlorobutene-1 (3:9064) and 1,2,4-trichlorobutene-2 (3:9062) which react further to yield \bar{C} (1).] [For patents on these processes see (2) (3).]

Č with alk. yields (2) both 1,2,3-trichlorobutadiene-1,3 (3:9052), b.p. 34° at 7 mm. (2), and 2,3,3,4-tetrachlorobutene-1 (3:9060), b.p. 42° at 7 mm. (2).

3:9070 (1) Carothers, Berchet, J. Am. Chem. Soc. 55, 1628–1631 (1933). (2) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934; Cent. 1935, I 3724; C.A. 28, 5716 (1934). (3) Coffmann (to du Pont), U.S. 1,964,720, July 3, 1934, Cent. 1934, II 3180; C.A. 28, 5080 (1934).

B.P. 99-101° at 12 mm. (1)

82-86° at 6 mm. (2)

[For prepn. of \bar{C} from 1,3-dichloro-2-(chloromethyl)propene-1 (3:9066) by shaking in CHCl₃ with Cl₂/aq. see (1).]

3:9072 (1) Kleinfeller, Ber. 62, 1595 (1929).

3:9074 2,3-DICHLOROBUTENE-1 Cl Cl C4H6Cl2 Beil. S.N. 11
$$CH_3 - C - C = CH_2$$

B.P. 111-113° at 2 mm. (1) $D_4^{18} = 1.1319$ (1) $n_C^{18} = 1.4503$ (1)

[For prepn. of \tilde{C} in 55% yield (1) from 2-chlorobutene-2 (3:7105) by treatment with 1 mole $Cl_2 + 1.5$ moles NaHCO₃ at 0° (accompanied by 45% yield 2,2,3-trichlorobutane (3:5680)) see (1); with Cl_2 in pres. of light and O_2 as directed see (2).]

3:9074 (1) Tishchenko, *J. Gen. Chem.* (U.S.S.R.) **8,** 1232-1246 (1938); Cent. **1939**, II 4223; C.A. **33,** 4190 (1939). (2) Hearne (to Shell Development Co.), U.S. 2,296,614, Sept. 22, 1942; C.A. **37,** 1129 (1943).

3:9078 1,2,2,3-TETRACHLOROBUTANE Cl Cl Cl C₄H₅Cl₄ Beil. I-119 CH₃—C—C—CH₂
$$I_1$$
— I_2 —

B.P. 63.0-63.5° at 11 mm. (1)

$$D_4^{18} = 1.4276 (1)$$
 $n_C^{18} = 1.4893 (1)$

[For prepn. (100% yield (1)) from 1,2-dichlorobutene-2 (3:5615) with 1 mole Cl_2 + 1.5 moles NaHCO₃ at 0° see (1).]

[The product obtained (2) cf. (3) from 2,2,3-trichlorobutanol-1 (3:1336) with PCl₅ may have been impure \bar{C} .]

3:9078 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) **8,** 1232-1246 (1938); C.A. **33,** 4190 (1939). (2) Garzarolli-Thurnlaekh, Ann. **213,** 372-373 (1882). (3) Norton, Noyes, Am. Chem. J. **10,** 432 (1888).

8:9080 1,2,3,3-TETRACHLOROBUTANE Cl Cl Cl C₄H₆Cl₄ Beil. S.N. 10

CH₃—C—C—CH₂

Cl H

B.P. 90° at 32 mm. (1)
$$D_4^{20} = 1.4204$$
 (1) $n_D^{20} = 1.4958$ (1) $55-57$ ° at 10 mm. (1)

[For formn. of \bar{C} (together with other products) from 1,3-dichlorobutenc-2 (3:5550) at 40-60° with Cl₂ see {1}. Note, however, that at very low temps. (-60 to -70°) much HCl is evolved during chlorination and the principal products are then 2,3,4-trichlorobutenc-1 (3:9064), b.p. 40-41° at 10 mm. {1}, and 1,2,3,3,4-pentachlorobutane (3:9070), b.p. 85° at 10 mm. {1}.] [For patents on this process see {2} {3}.]

3:9680 (1) Carothers, Berchet, J. Am. Chem. Soc. **55**, 1629–1631 (1933). (2) Coffman (to du Pont), U.S. 1,964,720, July 3, 1934; Cent. **1934**, II 3180; C.A. **28**, 5080 (1934). (3) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934; Cent. **1935**, I 3724; C.A. **28**, 5716 (1934).

B.P. 130-134° at 40 mm.

M.P. 73°

See 3:1760. Division A: Solids.

1249 LIQUIDS (WITH B.P. REPTD. AT RED. PRESS.) 3:9082-3:9086

3:9082 1,2,3,4-TETRACHLOROBUTANE (liquid isomer) $C_4H_6Cl_4$ Beil. I - 119 (Butadiene tetrachloride (liquid isomer); CH_2 —CH—CH— CH_2 I_1 -(38) erythrene tetrachloride (liquid isomer)) CH_2 CH_3 CH_4 CH_4 CH_5

B.P. 110-111° at 40 mm. (1) (2)

For formn. and reactns. see solid form, m.p. 73° (3:1760).

3:9082 (1) Muskat, Northrup, J. Am. Chem. Soc. 52, 4053-4055 (1930). (2) Muskat (to du Pont), U.S. 2,038,593, Apr. 28, 1936; Cent. 1936, II 3359; C.A. 30, 3912 (1936).

3:9084 1,1,3-TRICHLORO-2-(CHLOROMETHYL)PROPANE C4HaCla Beil, I --

$$\begin{array}{c} \operatorname{CH_2Cl} & \mathbf{I_1} \\ \downarrow & \mathbf{I_2} \\ \operatorname{ClCH_2-C-CHCl_2} \\ \downarrow & \operatorname{H} \end{array}$$

B.P. 77-80° at 9 mm. (1)

Oil with odor like CCl₄ but with irritating actn. on eyes. — Volatile with steam. [For formn. of \tilde{C} in small amt. (together with other products) from 2-nitro-2-hydroxymethylpropanediol-1,3 (nitro-isobutylglycerol) with PCl₅ see (1).]

3:9084 (1) Kleinfeller, Ber. 62, 1585 (1929).

3:9086 1,1,3-TRICHLOROBUTANE Cl $C_4H_7Cl_3$ Beil. S.N. 10 CH_3 —C— CH_2 - CH_2 . CH_2

B.P. 150° at 720 mm. (1)

A trichlorobutane which may have this structure has been reported (1) when vinyl chloride (3:7004) + AlCl₃ at 20° reacts with the material obtd. from ethylidene dichloride (3:5035) + AlCl₃ + chlorinated ethylenes.

3:9086 (1) Consortium für Elektrochem. Ind., Brit. 453,414, Sept. 10, 1936; Cent. 1937, I 1012; C.A. 31, 1046 (1937).

--- d,l- α,α' -DICHLOROSUCCINYL (DI)CHLORIDE $C_4H_2O_2Cl_4$ Beil. II ---CO--Cl II₁--H--C--Cl II₂-(558) Cl--C--Cl

B.P. 78.5° at 7 mm.

M.P. 39°

See 3:0395. Division A: Solids.

3:9087 meso-\alpha,\alpha'-DICHLOROSUCCINYL(DI)CHLORIDE C4H2O2Cl4 Beil. II - 619

CO—Cl
$$\Pi_{1}$$
-(267)
H—C—Cl Π_{2} -(558)
H—C—Cl Π_{2} -(558)

B.P. 105-106° at 45 mm. (1)

85-86° at 22 mm. (1)

79-80° at 15 mm. (2)

Colorless viscous lachrymatory oil.

[For prepn. of \bar{C} from fumaryl (di)chloride (3:5875) in CCl₄ soln. with Cl₂ in direct sunlight (100% yield (3)) (1) (2) see indic. refs.]

C with aq. reacts only very slowly on mere standing (1), but on continuous shaking with cooling readily hydrolyzes yielding (1) (2) meso-\alpha,\alpha'-dichlorosuccinic acid (3:4930).

[\bar{C} with C_6H_6 + AlCl₃ gives (60% yield (3)) meso-1,2-dichloro-1,2-dibenzoylethane (meso-2,3-dichloro-1,4-dipenylbutandione-1,4), m.p. 167° (4) (5), accompanied under certain conditions (3) by some α,β -dichloro- γ,γ -diphenylbutyrolacetone, m.p. 141-142° (3), presumably arising from reactn. of \bar{C} in the unsymmetrical (phthalide type) form.]

3:9087 (1) Michael, Tissot, J. prakt. Chem. (2) 46, 394-395 (1892). (2) Holmberg, J. prakt, Chem. (2) 84, 148 (1911). (3) Lutz, J. Am. Chem. Soc. 49, 1109-1110 (1927). (4) Conant, Lutz, J. Am. Chem. Soc. 47, 885-886 (1925). (5) Lutz, J. Am. Chem. Soc. 48, 2908, 2911 (1926).

B.P. 117-119° at 17 mm. (1)
$$D_4^{20} = 1.4397$$
 (1) $n_D^{20} = 1.4860$ (1) $93-96$ ° at 8 mm. (1)

Orange-colored liq. which fumes in air.

[For prepn. of \tilde{C} from acetylketene (ketene dimer) (2) (3) with Cl_2 in cold CCl_4 soln. see (1).]

 \bar{C} with aq. yields chloroacetone (3:5425) + CO_2 + HCl (note that this method gives chloroacetone free from higher chlorination products (3)).

[\bar{C} with excess abs. EtOH at 0° gives (1) (3) ethyl γ -chloroacetoacetate (3:6375).]

 \bar{C} with aniline in C_6H_6 yields (1) (3) γ -chloroacetoacetanilide, cryst. from ether, m.p. 140-141° (1).

3:9088 (1) Hurd, Abernathy, J. Am. Chem. Soc. 62, 1147-1148 (1940). (2) Hurd, Williams, J. Am. Chem. Soc. 58, 962-968 (1936). (3) Boese, Ind. Eng. Chem. 32, 16-22 (1940).

3:9092 DIGLYCOLOYL DICHLORIDE Cl C₄H₄O₃Cl₂ Beil. S.N. 220

CH₂—C=O

CH₂—C=O

B.P. 116° at 12 mm. (1)

Colorless oily liq. with odor suggesting succinyl dichloride (3:6200).

[For prepn. of C from diglycolic acid (1:0495) by susp. in CHCl₃ and treatment with PCl₅ see (1) (note also that insufficient PCl₅ leads (1) to diglycolic anhydride, m.p. 97°. b.p. 120° at 12 mm. (3)); for mfg. from α, α' -dichlorodimethyl ether (3:5245) by treatment at 25-50° and elevated press. with CO and suitable catalysts such as AlCl₂ or ZnCl₂ see (2).1

C with excess MeOH yields (1) (3) dimethyl diglycolate, m.p. 35° (3), 36° (1).

 $\bar{\mathbf{C}}$ with aq. readily hydrolyzes (1) yielding diglycolic acid (1:0495); for the anilide, ptoluidide, and other derivs. corresp. to C see the acid (1:0495).

3:9092 (1) Anschutz, Biernaux, Ann. 273, 64-65 (1893). (2) Scott (to du Pont Co.). U.S. 2,084,284, June 15, 1937; Cent. 1937, II 2261; C.A. 31, 5383 (1937). (3) Darapsky, Stauber, J. prakt. Chem. (2) 146, 212 (1936).

3:9094
$$\alpha_1\alpha_2\gamma$$
-TRICHLORO-n-BUTYRALDEHYDE Cl C₄H₅OCl₃ Beil. I-665 CH₂—CH₂—CHO I₁— I₂— Cl Cl

No physical consts. on \ddot{C} are reported; it is characterized only as a liquid which at -78° becomes a glassy solid (1). — Spar. sol. aq. (1).

[For prepn. of \bar{C} from α, γ -dichlorocrotonaldehyde [Beil. I-731], with dry HCl gas at 0° see (1).]

 \bar{C} oxidizes only very slowly in air but with fumg. HNO₃ in cold gives (1) $\alpha.\alpha.\gamma$ -trichloron-butyric acid (3:1831), m.p. 73-75° (1).

C does not add aq. to form a hydrate but on shaking with satd, aq. NaHSO3 soln, evolves heat and ppts. a NaHSO₃ cpd. (1).

C on boilg, with aq. contg. BaCO3 gives an amorphous prod., very easily sol, in aq. and possessing carbohydrate characteristics; for details see (2).

3:9094 (1) Natterer, Monatsh. 4, 551 (1883). (2) Natterer, Monatsh. 5, 251-255 (1884).

3:9096 METHYL
$$\alpha$$
-CHLOROACRYLATE Cl C₄H₅O₂Cl Beil. S.N. 163 CH₂—C—COOCH₃

B.P. 57-59° at 55 mm. (1) $D_4^{20} = 1.189$ (1) $n_D^{20} = 1.4420$ (11) 41-44° at 28 mm. (11) 1.4400 (1)

B.P.
$$57-59^{\circ}$$
 at 55 mm. (1) $D_4^{20} = 1.189$ (1) $n_D^{20} = 1.4420$ (11) $41-44^{\circ}$ at 28 mm. (11) 1.4400 (1)

[For prepn. of \bar{C} from methyl α,β -dichloropropionate (3:9103) by distn. with quinoline (yield: 73% (1), 60% (11)) or other dehydrochlorinating agent such as Na₂CO₃ (2) see indic. refs.; from trichloroethylene (3:5170) with CH₂O + MeOH + H₂SO₄ + CuCO₃ as directed (73% yield) see (10).]

IC readily polymerizes on standing, especially in light or pres. of peroxides (for study of polymers and polymerization see (1)). For examples of industrial prepn. and use of polymers of C for molding resins, etc., see (3) (4) (5) (6); for examples of co-polymers of C with butadiene-1,3 or chloroprene (7), styrene (8), or vinyl acetate (9) see indic. refs.]

For comments on other esters of \bar{C} see α -chloroacrylic acid (3:1445).

[For study of ester interchange of C with various alcohols see (11).]

3:9096 (1) Marvel, Cowan, J. Am. Chem. Soc. 61, 3156-3160 (1939). (2) Pollack (to Pittsburgh Plate Glass Co.), U.S. 2,245,547, June 10, 1941; C.A. 35, 5908 (1941); Brit. 536,806, May 28, 1941; C.A. 36, 1614 (1942). (3) Röhm & Haas Co., Brit. 411,860, June 13, 1934; Cent. 1935,

1252

C.A. 38, 1751 (1944).
(11) Frank, David, Drake, McPherson, J. Am. Chem. Soc. 66, 1509-1510 (1944).

3:9098 ACETOACETYL CHLORIDE
$$C_4H_5O_2Cl$$
 Beil. III — $(\beta$ -Keto- n -butyryl chloride) CH_3 — C — CH_2 — C = O III_1 — III_2 — O Cl

This compound cannot be preserved at temperatures above -20° (1) cf. (4); m.p. -50 to -51° (1).

[For prepn. of \tilde{C} from acetylketene (ketene dimer) (2) (3) (5) with dry HCl gas at -7 to -50° see (1).] [For anal. of \tilde{C} by reactn. with dil. alk. see (1).]

C on warming to room temp. undergoes bimolecular condensation with elimination of 2 HCl and yields (1) dehydroacetic acid (1:0700), m.p. 109°.

 $\bar{\mathbf{C}}$ in dry ether at -60° treated with abs. EtOH gives (27% yield (1)) ethyl acetoacetate (1:1710).

 \bar{C} in dry ether at -60° treated with aniline gives (49% yield (1)) acetoacetanilide [Beil. XII-518, XII₁-(275)], m.p. 85°; note, however, that \bar{C} with aniline at room temp. yields 1-phenyl-2,6-dimethylpyridone-4-carboxylic acid-3 (1-phenyllutidonecarboxylic acid-3) [Beil. XXII-303], m.p. 260–265° dec., Neut. Eq. calcd. 243, found 235 (1).

 \tilde{C} with C_6H_6 + AlCl₃ or with C_6H_6MgBr in ether at -50° gives (27% and 12% yield respectively (1)) benzoylacetone (1:1450), m.p. 59° (1).

3:9098 (1) Hurd, Kelso, J. Am. Chem. Soc. 62, 1548-1549 (1940). (2) Hurd, Abernathy, J. Am. Chem. Soc. 62, 1147-1148 (1940). (3) Hurd, Williams, J. Am. Chem. Soc. 58, 962-968 (1936). (4) Staudinger, Schotz, Ber. 53, 1109 Note 1 (1920). (5) Boese, Ind. Eng. Chem. 32, 16-22 (1940).

3:9098-A METHYL (CHLOROFORMYL)ACETATE
$$C_4H_5O_3Cl$$
 Beil. II - 582 (Carbomethoxyacetyl chloride) $COOCH_3$ II₁-(252) II_2 —

B.P. 57-59° at 12 mm. (1)

[See also ethyl (chloroformyl)acetate (3:9246).]

Note that \bar{C} is both an acid chloride and an ester; it comprises the half acid chloride/half methyl ester of malonic acid (1:0480).

[For prepn. of Č from potassium salt of methyl hydrogen malonate with SOCl₂ in dry ether (68% yield) see (1).]

Č on htg. or on repeated distn. or by action of quinoline in dry ether at 0° loses HCl and undergoes condensation to methyl 6-methoxy-2,4-diketo-2,3-dihydropyran-3-carboxylate [Beil. XVIII₁-(540)], ndls. from CHCl₃, m.p. 148-150° (1) cf. (2).

- \odot ω -(Carbomethoxyacet)anilide: ndls. from ether/pet. eth., m.p. 42-43° (1). [From $\ddot{\mathbf{C}}$ with aniline (1).]
- --- ω -(Carbomethoxyacet)-p-toluidide: unreported.
- 3:9098-A (1) Staudinger, Becker, Ber. 50, 1019-1020 (1917). (2) Leuchs, Ber. 39, 2643 (1906).

B.P. 130-140° at 12 mm. (1)
$$n_{\rm D}^{25}=1.4762$$
 (3) 89° at 1.75 mm. (2) 83° at 0.8 mm. (2) $D_4^{20}=1.532$ $n_{\rm D}^{20}=1.48378$ (2) 68° at 0.025 mm. (3) 1.4775 (3)

Note that \bar{C} may react either in the ester form (A) or the dioxolane form (B) and doubtless exists as a tautomeric equilibrium of both; in this equilibrium, however, form (A) probably predominates (2), but variations in the equilibrium may account for the observed variation in n_D^{20} (see above).

Colorless odorless oil, spar. sol. aq. (2). — \bar{C} on long stdg. is claimed (2) to disproportionate to ethylene glycol bis-(trichloroacetate) (not, however, otherwise described in the literature) and ethylene glycol (1:6465). — \bar{C} on attempted distn. at usual water-pump vac. (14-17 mm.) (3) or \bar{C} in presence of a trace of pyridine (3) decomposes yielding monomeric ethylene glycol carbonate [Beil. XIX-100], m.p. 38°, and CHCl₃ (3:5050).

[For prepn. of \bar{C} from ethylene glycol (1:6465) with trichloroacetyl chloride (3:5420) in 1,4-dioxane soln. (82% yield (2)) or from ethylene oxide (1:6105) with trichloroacetic acid (3:1150) (28% yield based on latter (1) (3)) see indic. refs.]

 \bar{C} on shaking with aq. and simultaneously titrating with N/10 aq. NaOH hydrolyzes to ethylene glycol (1:6465) and trichloroacetic acid (3:1150) as shown by Sap. Eq. of 207.8 (2) (calcd. 207.5).

[\bar{C} with diazomethane (1) best in CCl₄ soln. (2) gives (yields: 78% (2), 39% (1)) the methyl ether corresp. to structure (B), viz., 2-methoxy-2-(trichloromethyl)-1,3-dioxolane, pr. tbls. from alc., m.p. 78-78.5° (1), 77-78° (2) (4), b.p. 114-115° at 12 mm. (4), 112-113° at 10 mm. (1); this product although resistant to saponification by alkalies is hydrolyzed by dil. acids (4). — Note that the isomeric methyl ether corresponding to structure (A), viz., β -methoxyethyl trichloroacetate, although not obtainable from \bar{C} , has nevertheless been prepd. (82% yield (4)) from β -methoxyethanol (methyl "cellosolve") (1:6405 with trichloroacetyl chloride (3:5420), has quite different physical props., viz., m.p. 14.6-14.8° (4), b.p. 92-93° at 10 mm. (4), and is easily hydrolyzed (4) on shaking with aq. alone to β -methoxyethanol (1:6405) and trichloroacetic acid (3:1150). — Note also that the first of the above two methyl ethers, i.e., 2-methoxy-2-(trichloromethyl)-1,3-dioxolane, by trans-esterification with alcohols (e.g., EtOH (2), n-PrOH (4), n-BuOH (2)) can be converted to its higher homologs.]

 \bar{C} with acid chlorides gives esters corresp. to the acylic structure (A): e.g., \bar{C} with AcCl (3:7065) gives (71% yield (4)) the mixed ester, ethylene glycol acetate-trichloroacetate (β -acetoxyethyl trichloroacetate) b.p. 122° at 11 mm. (4); \bar{C} with SOCl₂ gives (70% yield (4)) β -chloroethyl trichloroacetate (3:6510).

3:9690 (1) Meerwein, Hins, Ann. 484, 16-17 (1930). (2) Meerwin, Sönke, J. prakt. Chem. (2) 137, 295-298, 308-311 (1933). (3) Hibbert, Grieg, Can. J. Research 4, 261-263 (1931). (4) Meerwin, Sönke, Ber. 64, 2375-2381 (1931).

3:9100
$$d_{i}l$$
- β -CHLORO- n -BUTYRYL CHLORIDE $C_{4}H_{0}OCl_{2}$ Beil. II - 278 CH_{3} -CH.CH₂.C=O II_{1} — II_{2} -(253) B.P. 67-69° at 41 mm. (1) $D_{4}^{20.25} = 1.2163$ (4) $n_{D}^{20} = 1.4525$ (3) 65-67° at 40 mm. (2) (3) 1.4511 (4) 40-41° at 12 mm. (2)

1254

[For prepn. of \tilde{C} from β -chloro-n-butyric acid (3:0035) with SOCl₂ (4) (6) (3) (90% yield (2)) see indic. refs.; from n-butyryl chloride (3:7370) with SO₂Cl₂ + dibenzoyl peroxide in CCl₄ (55% yield \tilde{C} + 15% α - (3:5570) and 30% γ - (3:5970) isomers (3)) or with Cl₂ in CCl₄ (1) see indic. refs |

[C with methyl p-tolyl ether (1:7495) + AlCl₃ in CS₂ yields (4) 3-(β-chloro-n-butyryl)-4-methylphenol (b.p. 167-170° at 20 mm. (4)) which in alc. soln. on addn. of dil. Na₂CO₃ loses HCl yielding 2,6-dimethylchromanone, m.p. 54-55° (5).]

 \bar{C} with benzene + AlCl₃ in CS₂ yields (6) (by Friedel-Crafts reactn. of both halogen atoms) β -phenylbutyrophenone (phenyl β -phenyl-n-propyl ketone) [Beil. VII-453], m.p. 74° (6).

 \bar{C} on hydrolysis with aq. yields β -chloro-n-butyric acid (3:0035) q.v. (note, however, that hydrolysis with alk. will cause loss of HCl and formn. of crotonic acid (1:0425).

For the anilide, p-toluidide, and other derivs corresp. to \bar{C} see β -chloro-n-butyric acid (3:0035).

3:9100 (1) Michael, Ber. 34, 4052 (1901). (2) Abderhalden, Fleischmann, Fermentforschung, 10, 203 (1928); Cent. 1929, I 2318; C.A. 23, 1388 (1929). (3) Kharasch, Brown, J. Am. Chem. Soc. 62, 928 (1940). (4) von Auwers, Ann. 421, 37-39 (1921). (5) von Auwers, Ber. 52, 128 (1919). (6) von Auwers, Muller, J. prakt. Chem. (2) 137, 128 (1933).

3:9101
$$\beta$$
-CHLORO-ISOBUTYRYL CHLORIDE $C_4H_6OCl_2$ Beil. II - 295 CH_2 —CH--C=O II_1 — II_2 —

B.P. 171–172° at 765 mm. (1) $n_D^{20} = 1.4542$ (2) $n_D^{20} = 1.4542$ (2)

Because of the serious disagreement in b.p. and the lack of data to decide between them, $\ddot{\mathbf{C}}$ is placed in this division.

[For prepn. of \bar{C} from isobutyryl chloride (3:7270) with Cl_2 in CCl_4 soln. (30-40% yield \bar{C} + 60-70% α -isomer (3:5385) (1)), with Cl_2 in activating light (3) (6), or with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 (80% yield \bar{C} + 20% α -isomer (3:5385) (2)), see indic. refs.; for formn. of \bar{C} from phosgene (3:5000) + propylene + cat. see (5).]

Č as liq. with dehydrohalogenating cat. loses HCl giving (4) α-methacryloyl chloride.

 \ddot{C} with aniline gives (1) (2) β -chloro-isobutyranilide, m.p. 109.0-109.5° (2), 104-105° (1); note that the isomeric α -dichloro-isobutyranilide has m.p. 71-71.5° (2), 69-70° (1).

3:9101 (1) Michael, Garner, Ber. 34, 4054-4055 (1901). (2) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940). (3) Schmidt, Schloffer (to I.G.), Ger. 738,398, July 15, 1943; C.A. 38, 392 (1944). (4) I.G., French 873, 389, July 7, 1942; Cent. 1942, II 2535; not in C.A. (5) Reid (to du Pont Co.), U.S. 2,028,012, Jan. 14, 1936; Cent. 1936, II 866; C.A. 30, 1387 (1936). (6) Schmidt, Schloffer (to I.G.), Ger. 738,398, July 15, 1943; C.A. 38, 3992 (1944).

3:9102
$$\alpha,\beta$$
-DICHLORO- n -BUTYRALDEHYDE $C_4H_6OCl_2$ Beil. I — (Crotonaldehyde dichloride; Cl Cl Cl I_1 — I_2 —(724)

B.P.
$$58-60^{\circ}$$
 at 20 mm. (1) $D_{1}^{21} = 1.2666$ (1) $n_{D_{1}}^{21} = 1.4618$ (1) $48-49^{\circ}$ at 13 mm. (2) $D_{1}^{45} = 1.2716$ (1)

Colorless liq. with odor suggesting chloral. — \bar{C} on exposure to light or on distn. at ord. press. turns brown and decomposes with evoln. of HCl. — \bar{C} is insol. aq.; sol. alc., ether, CHCl₃, or CCl₄.

[For prepn. of \bar{C} from crotonaldehyde (1:0150) with Cl₂ directly at -5° (3) cf. (4), or in CCl₄ soln. at 0° (98% yield (1)), or in CS₂ in freezing mixt. (2) see indic. refs.]

C with NaHSO₃ soln. gives (2) a crystn. addn. compound.

[$\bar{\rm C}$ in McOH contg. 1% HCl gas refluxed 4 hours gives (40% yield (5)) α,β -dichloro-n-butyraldehyde dimethylacetal, oil, b.p. 86–90° at 13 mm., $D_{\rm D}^{19.5}=1.179, n_{\rm D}^{19.5}=1.4498$ (5); note that the presumably corresp. behavior of $\bar{\rm C}$ with EtOH and the α,β -dichloro-n-butyral-dehyde diethylacetal are unreported.]

[\tilde{C} with ethylene glycol (1:6465) at 160° for 1 hour even in absence of cat. gives (50.3% yield (3)) corresp. cyclic acetal, viz., 2-(α,β -dichloro-n-propyl)-1,3-dioxolane, b.p. 100–105° at 13–15 mm. (3).]

[Č with aq. NaOAc on distn. with steam splits out 1 HCl giving (70-80% yield (6)) (1) (3) (7) \(\alpha\)-chlorocrotonaldehyde (3:8117), b.p. 147-150° at 760 mm. (3).

[$\bar{\rm C}$ with EtMgBr in dry ether followed by usual hydrolysis gives (80% yield (2)) 4,5-dichlorohexanol-3 [Beil. I-439], b.p. 88-93° at 12 mm., $D_4^{19}=1.1685$, $n_D^{19}=1.4709$ (2). — Similarly, $\bar{\rm C}$ with ${\rm C_6H_5MgBr}$ gives (66% yield (2)) α,β -dichloro-n-propyl-phenyl-carbinol, b.p. 162-168° at 14 mm., $D_4^{15}=1.2355$, $n_D^{15}=1.5500$ (2).]

[Note that suitable oxidn. of \bar{C} would be expected to yield either or both crotonic acid dichloride (3:1375), m.p. 63°, or isocrotonic acid dichloride (3:1903), m.p. 78°, but that such oxidation has not actually been reported.]

[For use of C as component of insecticides see (8).]

- α,β -Dichloro-n-butyraldoxime: oil, not further characterized (2).
- α,β-Dichloro-n-butyraldehyde phenylhydrazone: unreported. [Note, however, that C̄ reacts vigorously with phenylhydrazine (2).]
- \bigcirc α,β -Dichloro-n-butyraldehyde semicarbazone: m.p. 96-97° (2).

3:9102 (1) Moureu, Murat, Tampier, Bull. soc. chim. (4) 29, 31-32 (1921). (2) Helferich, Besler, Ber. 57, 1277-1278 (1924). (3) Hibbert, Houghton, Taylor, J. Am. Chem. Soc. 51, 613 (1929). (4) Zeisel, Monatsh. 7, 360 (1886). (5) Naftali, Bull. soc. chim. (5) 4, 338 (1937). (6) Chattaway, Irving, Outhwaite, J. Chem. Soc. 1933, 994. (7) Chem. Fabrik vorm. Weilerter-Meer, Ger. 351, 137, April 3, 1922; Cent. 1922, IV 155; not in C.A. (8) Soc. des Usines Chim. Rhône-Poulenc, Ger. 528, 194, June 26, 1931; Cent. 1931, II 1910; [C.A. 25, 4653 (1931)].

3:9103 METHYL
$$d,l$$
- α,β -DICHLOROPROPIONATE $C_4H_6O_2Cl_2$ Beil. S.N. 162 CH_2 — CH — $COOCH_3$

$$CI$$

$$CI$$

B.P. 72-75° at 21 mm. (1)

[For prepn. of \bar{C} from technical methyl acrylate (1:3025) in MeOH soln. below 40° by treatment with Cl₂ (85% yield) see (1).]

 \tilde{C} on distn. with quinoline (2), with dimethylaniline (1), with quinaldine (1), or with other dehydrohalogenating agents (such as Na₂CO₃ (3)) (4) loses HCl giving (73% yield (2)) methyl α -chloroacrylate (3:9096).

 \ddot{C} on boilg. with 20% HCl hydrolyzes (1) yielding MeOH (1:6120) and α,β -dichloropropionic acid (3:0855) g.v.

3:9163 (1) Marvel, Dec, Cooke, Cowan, J. Am. Chem. Soc. 62, 3495-3498 (1940). (2) Marvel, Cowan, J. Am. Chem. Soc. 61, 3158 (1939). (3) Pollack (to Pittsburgh Plate Glass Co.), U.S. 2,245,547, June 10, 1941; C.A. 35, 5908 (1941); Brit. 536,806, May 28, 1941; C.A. 36, 1614 (1942). (4) Bauer, Lauth (to Rohm, Hass Co.), Ger. 648,820, June 23, 1937; Cent. 1937, II 2072.

3: 9105 2,3-DICHLORODIOXANE O
$$C_4H_6O_2Cl_2$$
 Beil. S.N. 2668 H_2C CHCl $H_$

 $\bar{\mathbf{C}}$ is theoretically capable of existing in *cis* and *trans* forms; collateral evidence exists that both may actually be present, but they have not yet been isolated as such.

88-89°

85°

82°

at 16-17 mm.

at

at

(3)

15 mm. (4)

14 mm. (5)

Although comml. \bar{C} is liq. extremely pure samples may, after inoculation (9), be obtd. in cryst. form.

[For prepn. of \bar{C} from 1,4-dioxane (1:6400) by actn. of Cl_2 at 90° in presence of catalyst such as $SnCl_2$ or I_2 (96.6% yield (6)), or with Cl_2 at 90° for 16 hrs. without catalyst (61% yield (4)), see (6) (4) (7).]

[For studies of further chlorination of \bar{C} see (3) (8); for studies of reaction of \bar{C} with alcohols and phenols see (5) (9) (2) (10) (11) (17); for studies of reaction of \bar{C} with R.MgX cpds. see (12) (13) (4) (14) (15); for reaction of \bar{C} with Mg + I₂ yielding dioxadiene see (16).]

Č on boiling with aq. for 10 min. gives clear soln. containing hydrolysis products, viz., ethylene glycol (1:6465) and glycxal. After cooling, making alk., and shaking with BzCl the former can be converted to ethylene glycol dibenzoate (1:2293), extracted with ether, recrystd. from MeOH, m.p. 73° (70-72° (3)); another portion of the aq. soln. of hydrolysis products gives on treatment with p-nitrophenylhydrazine hydrochloride a 97% yield of glycxal-p-nitrophenylosazone, yel. cryst., m.p. 306° (310°) (3).

3:9105 (1) Médard, J. chim. phys. 33, 627 (1936). (2) Baker, Shannon, J. Chem. Soc. 1933, 1598. (3) Butler, Cretcher, J. Am. Chem. Soc. 54, 2987-2988 (1932). (4) Summerbell, Bauer, J. Am. Chem. Soc. 57, 2365 (1935). (5) Böeseken, Tellegen, Henriquez, Rec. trav. chim. 50, 909-914 (1931). (6) Kucera, Carpenter, J. Am. Chem. Soc. 57, 2346-2347 (1935). (7) Lintner, Scheuerman (to I.G.), Ger. 705,435, March 20, 1941; C.A. 36, 1955 (1942); Ger. 717,953, Feb. 12, 1942; C.A. 38, 2350 (1944). (8) Böeseken, Tellegen, Henriquez, J.Am. Chem. Soc. 55, 1284-1288 (1933). (9) Böeseken, Tellegen, Matha, Rec. trav. chim. 52, 1067-1072 (1933). (10) Böeseken, Tellegen, Plusje, Rec. trav. chim. 57, 73-78 (1938).

(11) Tellegen, Rec. trav. chim. 57, 667-672 (1938). (12) Summerbell, Christ, J. Am. Chem. Soc. 54, 3777-3778 (1932). (13) Christ, Summerbell, J. Am. Chem. Soc. 55, 4547-4548 (1933). (14) Summerbell, Bauer, J. Am. Chem. Soc. 58, 759-761 (1936). (15) Summerbell, Umhoefer, J. Am. Chem. Soc. 61, 3016-3019 (1939). (16) Summerbell, Unhoefer, J. Am. Chem. Soc. 61, 3020-3022 (1939). (17) McNally, Schmitt (to Eastman Kodak Co.), U.S. 2,069,962, Feb. 9, 1937; Cent. 1937, I 4056. (18) Bitler, Nicholl (to Kay-Fries Chemicals, Inc.), U.S. 2,327,855, Aug. 24, 1943; C.A. 38, 752 (1944).

3:9107 \$\textit{\beta-HYDROXYETHYL DICHLOROACETATE C4H}_6O_3Cl_2\$ (A) Beil. S.N. 160 (2-Hydroxy-2-(dichloromethyl)-1,3-dioxolane) (B) Beil. S.N. 2691

HOCH₂.CH₂.O.CO.CHCl₂
$$CH_2$$
—O CH_2 —O $CHCl_2$

(A) (B)

B.P. 106° at 0.08 mm. (1) (3)
$$D_4^{20} = 1.438$$
 (2) $n_D^{25} = 1.4730$ (1) 82° at 0.5 mm. (2) 1.429 (2) $n_D^{22} = 1.4743$ (3) $n_D^{22} = 1.4743$ (3) $n_D^{20} = 1.47345$ (2) 1.47263 (2)

Note that C may react either in the acyclic ester form (A) or the dioxolane form (B) and doubtless exists as a tautomeric equilibrium of both; in such an equilibrium, however, form (A) greatly predominates (2); but variations may account for the variation in constants (see above).

Colorless oil, spar. sol. aq. — \bar{C} on long stdg. is claimed (2) to disproportionate to ethylene glycol bis-(dichloroacetate) (not, however, further described in the literature) and ethylene glycol (1:6465).

[For prepn. of \bar{C} from ethylene glycol (1:6465) with dichloroacetyl chloride (3:5290) in 1,4-dioxane soln. (75% yield (2)) or from ethylene oxide (1:6105) with dichloroacetic acid (3:6208) (yields: 34% (2), 15% (1)) see indic. refs.]

 \bar{C} on shaking with aq. and simultaneously titrating with N/10 aq. NaOH hydrolyzes to ethylene glycol (1:6465) and dichloroacetic acid (3:6208) as shown by Sap. Eq. of 170.8 (2) (calcd. 173).

[\bar{C} with diazomethane gives not only the methyl ethers of both forms (A) and (B) but also other unexpected products including ethylene glycol (1:6465), ethylene glycol dimethyl ether (1:6141), methyl dichloroacetate (3:5655), etc. Note that the methyl ether of structure (B), viz., 2-methoxy-2-(dichloromethyl)-1,3-dioxolane, has b.p 91-92.5° at 9 mm. (2), $D_4^{20}=1.387$ (2), $n_D^{20}=1.47032$, and is stable to aq. alk.; that corresp. to the acyclic structure (A), viz., β -methoxyethyl dichloroacetate (methyl-" cellosolve" dichloroacetate), best prepared (100% yield (2)) from β -methoxyethanol (1:6405) with dichloroacetyl chloride (3:5290) in CHCl₃), has b.p. 55-56° at 0.5 mm. (2), $D_4^{20}=1.309$ (2), $n_D^{20}=1.45157$ (2).]

3:9107 (1) Allen, Hibbert, J. Am. Chem. Soc. 56, 1399 (1934). (2) Meerwein, Sonke, J. prakt. Chem. (2) 137, 298-301, 311-316 (1933). (3) Hibbert, Greig, Can. J. Research 4, 262 (1931).

3:9109 \(\alpha\)-CHLORO-n-BUTYRALDEHYDE \(\Chi_4\)H7OCl Beil. S.N. 87 (2-Chlorobutanal-1) \(CH_3\).CH2.CH2.CH.CHO

No record of this compound can be found in the literature. However, for the isomeric β -chloro-n-butyraldehyde (3:9110), γ -chloro-n-butyraldehyde (3:9111), and α -chloro-isobutyraldehyde (3:7235) see indic. refs.

3:9110 β -CHLORO-n-BUTYRALDEHYDE C_4H_7OCl Beil. I — (3-Chlorobutanal-1) CH_3 -CH.CH $_2$ -CHO I_1 — I_2 -(724)

B.P. 28-33° at 13 mm. (1)

[See also the trimer of \ddot{C} (3:2650).]

Spar. sol. aq. but misc. with org. solvents.

[For prepn. of C from crotonaldehyde (1:0150) with 1 mole HCl in ether (50% yield) see (1).]

 $\bar{\mathbf{C}}$ is difficult to preserve because of rapid polymerization to its trimer, para- β -chloro-n-butyraldehyde (3:2650), m.p. 96-97°. [The product supposed by (2) to have been $\bar{\mathbf{C}}$ was actually (1) this trimer.]

[$\bar{\mathbf{C}}$ with 3 moles acetaldehyde (1:0100) in the cold gives (53% yield (1)) 2,4-dimethyl-6-(β -chloro-n-propyl)trioxane-1,3,5 [Beil. S.N. 2952], b.p. 83-85° at 13 mm., $D_4^{19} = 1.0937$, $n_1^{19} = 1.4373$ (1).]

[$\bar{\mathbf{C}}$ with excess EtMgBr yields (1) 5-chlorohexanol-3 [Beil. I₂-(438)] b.p. 78-79° at 13 mm., $D_1^{19} = 1.0012$, $n_D^{19} = 1.4433$ (1), together with other products.]

Č with methylhydrazine in dry ether yields (3) 1,5-dimethylpyrazoline, b.p. 124-132° (picrate, m.p. 112-113° (3)).

3:9110 (1) Helferich, Besler, *Ber.* **57**, 1280 (1924). (2) Kekulé, *Ann.* **162**, 100–102 (1872). (3) von Auwers, Heimke, *Ann.* **458**, 204 (1927).

3:9111
$$\gamma$$
-CHLORO- n -BUTYRALDEHYDE C_4H_7OCl Beil. S.N. 87 (4-Chlorobutanal-1) $CH_2.CH_2.CH_2.CH_2$ Cl

B.P. 50-51° at 13 mm. (1)
$$D_{15}^{8.5} = 1.107$$
 (1) $n_{D}^{8.5} = 1.44662$ (1)

[For prepn. of \overline{C} from 5-chloropentanediol-1,5 (1) by oxidn. with Pb(OAc)₄ see (1).] \overline{C} polymerizes readily on htg. (1).

- \bigcirc γ -Chloro-n-butyraldoxime: m.p. 74.5° (1).
- D γ-Chloro-n-butyraldehyde p-nitrophenylhydrazone: m.p. 110° (1).
- ① γ-Chloro-n-butyraldehyde 2,4-dinitrophenylhydrazone: m.p. 134-135° (1).

3:9111 (1) Paul, Compt. rend. 215, 303-305 (1942); C.A. 38, 4907 (1944).

No physical constants for C are recorded.

[For prepn. of Č from 3-chloro-2-methylpropen-2-ol-1 (3:8340) by treatment with acids as specified see (1).]

No other record of C appears in the literature.

3:9112 (1) N. V. de Bataafsche Petroleum Maatschappij, French 763,286, April 26, 1934; Cent. **1934** II 1531; [C.A. **28**, 5077 (1934)].

3:9113 d,l-2-CHLOROBUTEN-3-OL-1

CaHrOCl Beil, S.N. 25

B.P. 69.5-70.0° at 30 mm. (1) (2) 66.5-67.0° at 30 mm. (3)

 $n_{\rm D}^{20}=1.4665~(1)~(2)$

[See also 1-chlorobuten-3-ol-2 (3:8110).]

[For prepn. of \tilde{C} from 3,4-epoxybutene-1 (1) (2) with conc. HCl (2 moles) in ether below 5° (61% yield (2)) or with cold conc. HCl (60% yield (3)) see indic. refs.; note that by these methods \tilde{C} is accompanied by a small amt. (2% (2)) of 4-chlorobuten-2-ol-1 (1-chlorobuten-2-ol-4) (3:9114).]

C with Br₂ gives (3) 2-chloro-3,4-dibromobutanol-1, b.p. 133.5-135.5° at 10 mm. (3).

 \bar{C} with KOH (3) loses HCl, ring-closing to 3,4-epoxybutene-1, b.p. 67° at 750 mm. (3), 65.0-65.8° at 739 mm. (2); $D_{\underline{4}}^{20} = 0.8745$ (2) (3); $n_{\underline{D}}^{20} = 1.4170$ (2) cf. (3).

[For study of hydrolysis of C with aq. NaOH see (1).]

- 2-Methoxybuten-3-ol-1 (\bar{C} methyl ether): b.p. 70° at 50 mm. (2); $n_D^{20} = 1.4290$ (2): corresp. 3,5-dinitrobenzoate, m.p. 68-71° (2). [From \bar{C} with MeOH/NaOMe refluxed 30 min. (52% yield (2)).]
- —— 1-Chlorobuten-3-yl-1 acetate: b.p. 79.5-80° at 30 mm. (3). [Note that with KOH this prod. loses AcOH, ring-closing (3) to 3,4 epoxybutene-1 (above).]
- —— 1-Chlorobuten-3-yl-1 3,5-dinitrobenzoate: m.p. 65.6° u.c. (2). [Note that this prod. depresses m.p. of corresp. deriv. (m.p. 61.5-63.5° u.c.) from 1-chlorobuten-3-ol-2 (3:8110).]

3:9113 (1) Kadesch, J. Am. Chem. Soc. 68, 46-48 (1946). (2) Kadesch, J. Am. Chem. Soc. 68, 41-45 (1946). (3) Petrov, J. Gen. Chem. (U.S.S.R.) 11, 991-995 (1941), C.A. 37, 1699 (1943).

3:9114 4-CHLOROBUTEN-2-OL-1 C₄H₇OCl Beil. S.N. 25 (1-Chlorobuten-2-ol-4)

 $n_{\rm D}^{20.5} = 1.4792 \,(1)$

64-65° at 2 mm. (2) 54-55° at 2 mm. (1)

 $n_{\rm D}^{20} = 1.4845 (2)$

[For form. of \bar{C} in small amount (18.6% yield (2)) from 3,4-epoxybutene-1 with HCl see (1) (2); note that the main product of this reaction is 2-chlorobuten-3-ol-1 (3:9113) (1) (2).] [For study of hydrolysis of \bar{C} with aq. or aq. NaOH see (2).]

---- 4-Chlorobuten-2-vl-1 3.5-dinitrobenzoate: unreported.

6 4-Chlorobuten-2-yl-1 $N-(\alpha$ -naphthyl)carbamate: m.p. 88-89° (1).

3:9114 (1) Kadesch, J. Am. Chem. Soc. 68, 45 (1946). (2) Kadesch, J. Am. Chem. Soc. 68, 46-48 (1946).

3:9115 d,l-3-CHLOROBUTEN-3-OL-2 Cl OH C₄H₇OCl Beil. S.N. 25

B.P. $53-57^{\circ}$ at 19 mm. (1) $D_4^{23} = 1.1138$ (1) $n_C^{23} = 1.46232$ (1) $67-68^{\circ}$ at 19 mm. (1)

[For prepn. of \tilde{C} from either the low-boilg. (3:5360) or high-boilg. (3:5615) stereoisomers of 1,2-dichlorobutene-2 (together with 2-chlorobutene-2-ol-1 (3:8240)) by hydrolysis with 2 pts. aq. + 1 mole CaCO₃ for 4 hrs. at 70° see {1}; note that \tilde{C} is formed by virtue of allylic transposition during the process and that *Cent*. and *C.A.* do not agree on the boilg. pt. (orig. inaccessible).

3-Chlorobuten-3-yl-2 $N-(\alpha-naphthyl)$ carbamate: m.p. $92-92.5^{\circ}$ (1).

3:9115 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 658-662 (1937); Cent. 1937, II 371; C.A. 31, 5754 (1937).

3:9130 d,l-
$$\alpha$$
-CHLORO- n -BUTYRIC ACID C₄H₇O₂Cl Beil. II - 276 CH₃—CH₂.CH.COOH II₁-(123) II₂-(253)

B.P. 109.5° at 24 mm. (1)
$$D_4^{20} = 1.1796$$
 (13) $n_{D_1}^{20} = 1.4411$ (13) 101.25° at 15 mm. (2)

Viscous liq.; spar. sol. cold aq.; eas. sol. hot aq.

[For prepn. of \bar{C} from diethyl α -ethyl- α -chloromalonate by hydrolysis and subsequent htg. of the resultant α -ethyl- α -chloromalonic acid (90% yield (1)) (2) see indic. refs.; from n-butyric acid (1:1035) with SO₂Cl₂ + acetyl chloride (3:7065) (3) or with SO₂Cl₂ + dibenzoyl peroxide in CCl₄ (10% \bar{C} + 45% β - (3:0035) and 45% γ - (3:0020) isomers) see (4); from n-butyric acid with Cl₂ and suitable cat. see (5); from α -chloro-n-butyryl chloride (3:5570) by hydrolysis with aq. see (7).]

 \bar{C} with SOCl₂ (1) yields α -chloro-n-butyryl chloride (3:5570), b.p. 129-132°.

 $[\bar{C} \text{ (in the form of Ca$\bar{A}_2)} \text{ on cat. hydrogenation with Pd/Ba$SO_4 in aq. alc. is completely converted (6) to n-butyric acid; <math>\bar{C}$ itself is only partially (6) reduced.]

[For study of rate of hydrolysis of the halogen in NaĀ by aq. at 70° see (8).]

- Methyl d_{i} - α -chloro-n-butyrate: b.p. 145-146° at 756 mm. (See 3:8103.)
- Ethyl d,l-α-chloro-n-butyrate: b.p. 163-164° at 760 mm. (See 3:8307.) For study of rate of esterification of C with EtOH see (9).]
- \bigcirc d₁- α -Chloro-n-butyramide: cryst. from C₆H₆, m.p. 81° (10), 78.4-78.9° (11). [From methyl α -chloro-n-butyrate (3:8103) with conc. aq. NH₄OH (60% yield (10)).]
- \bigoplus d_il- α -Chloro-n-butyranilide: m.p. not reported. [From α -chloro-n-butyryl chloride (3:5570) with aniline (1).]
- \bigcirc d.l- α -Chloro-n-butyro- ϕ -toluidide: m.p. 98° (12).

3:9130 (1) Blaise, Bull. soc. chim. (4) 15, 668 (1914). (2) Cloves, Ann. 319, 357-358 (1901). (3) Blank, Ger. 157,816, Jan. 18, 1905; Cent. 1905, I 414. (4) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940). (5) Bass (to Dow Chem. Co.), U.S. 2,010,685, Aug. 6, 1935; Cent. 1936, I 880; C.A. 29, 6608 (1935). (6) Paal, Schiedewitz, Ber. 62, 1937-1938 (1929). (7) Markownikow, Ann. 163, 241 (1870). (8) Simpson, J. Am. Chem. Soc. 40, 679 (1918). (9) Lichty, Ann. 319, 372 (1901). (10) De Boosere, Bull. soc. chim. Belg. 32, 44-45 (1923).

Vandewijer, Bull. soc. chim. Belg. 45, 255 (1936). (12) Wolffenstein, Rolle, Ber, 41, 736 (1908).
 Schjanberg, Z. physik. Chem. A-172, 231 (1935).

--- d,l- β -CHLORO-n-BUTYRIC ACID C₄H₇O₂Cl Beil. II - 277 CH₃--CH.CH₂.COOH II₁-(123) II₂-(253)

B.P. 116° at 22 mm. M.P. 16-16.5° $D_{4}^{20} = 1.1898$ $n_{D}^{20} = 1.4421$

See 3:0035. Division A: Solids.

B.P. 196° at 22 mm. M.P. 16° $D_4^{20} = 1.2236$ $n_D^{20} = 1.4512$

See 3:0020. Division A: Solids.

$$\alpha$$
-CHLORO-ISOBUTYRIC ACID CH₃ C₄H₇O₂Cl Beil. II - 294 II₁-- CH₃ C₄H₇O₂Cl Beil. II - 294 II₂-- CI

B.P. 118° at 50 mm. M.P. 31°

See 3:0235. Division A: Solids.

3:9132
$$\beta$$
-CHLORO-ISOBUTYRIC ACID $C_4H_7O_2Cl$ Beil. S.N. 162 CH_2 — CH — $COOH$ Cl CH_2

B.P. 128-133° at 50 mm. (1)

[For prepn. of \bar{C} from isobutyric acid (1:1030) with Cl_2 in pres. of S (2) (3) or in activating light (1) (note that some α -chloro-isobutyric acid (3:0235) is also formed) see indic. refs.; for prepn. of \bar{C} from isobutyric acid (1:1030) with SO_2Cl_2 in presence of dibenzoyl peroxide in CCl_4 soln. (85% yield \bar{C} + 15% α -isomer) see (4).]

 \bar{C} should by conventional means such as SOCl₂, etc., be convertible to the corresp. β -chloroisobutyryl chloride (3:9101), but no record of such transformation appears in the literature, the expected product having been prepd. by indirect means.

- Methyl β-chloroisobutyrate: b.p. 151-155° at 750 mm., 85-90° at 60 mm., D_{15}^{15} = 1.1101 n_D^{15} = 1.4297 (1). [From \bar{C} in MeOH with H₂SO₄ in 70% yield (1) cf. (3); note that this prod. on htg. with quinoline (1) or passing over hot silica gel (3) loses HCl giving (87% yield (1)) methyl methacrylate.]
- Ethyl β -chloroisobutyrate: b.p. 56-58° at 10 mm. (5). [From ethyl β -hydroxyisobutyrate with PCl₅ in dry ether (40% yield (5)).]
- ---- B-Chloroisobutyramide: unreported.
- ---- β-Chloroisobutyranilide: m.p. 109.0-109.5° (4), 104-105° (6).
- ---- β-Chloroisobutyr-p-toluidide: unreported.

3:9132 (1) Zal'kind, Markov, J. Applied Chem. (U S.S.R.) 10, 1042-1044 (1937); Cent. 1938, II 2421; C.A. 32, 1652 (1938); note that in C.A. reference isobutyric acid has been erroneously rendered as "isooleic acid" and chloroisobutyric acid as "chloroisooleic acid" throughout. (2) Loder, Ries (to du Pont Co.), U.S. 2,043,670, June 9, 1936; Cent. 1936, II 2229; C.A. 30,5240 (1936). (3) Loder (to du Pont Co.), Brit. 428,223, June 6, 1935; Cent. 1936, I 179; C.A. 29,6607 (1935). (4) Kharsch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940). (5) Rydon. J. Chem. Soc. 1936, 1448. (6) Michael, Garner, Ber. 34, 4054-4055 (1901).

3:9140 β-METHOXYETHYL CHLOROFORMATE C₄H₇O₃Cl Beil. S.N. 199 (Methyl "cellosolve" chloroformate; CH₃.O.CH₂.CH₂.O.CO.Cl β-methoxyethyl chlorocarbonate)

B.P. 58.7° at 13 mm. (1)
$$D_{abs.}^{25} = 1.1905$$
 (1) $n_D^{25} = 1.4163$ (1)

Colorless liq. insol. aq.

[For prepn. (93% yield (1)) from β -methoxyethanol (methyl "cellosolve") (1:6405) + phosgene (3:5000) see (1).]

D β -Methoxyethyl carbamate: from \tilde{C} + aq. NH₄OH in poor yield (13.3% (1)); m.p. 46.8° (1).

3:9140 (1) Ashburn, Collett, Lazzell, J. Am. Chem. Soc. 60, 2933-2934 (1938).

3:9145 1,3-DICHLOROBUTANOL-2 H H
$$C_4H_8OCl_2$$
 Beil. I-373 CH_3-C CH_2 CH_2 CH_3 CH_3 CH_3 CH_4 CH_5 CH

B.P. 63-64° at 10 mm. (1)
$$n_{\rm D}^{20}=1.4766$$
 (1) $D_{\rm D}^{15}=1.2870$ (1) $n_{\rm D}^{15}=1.4790$ (1)

[For prepn. of \bar{C} from 3-chloro-1,2-epoxybutane (α -chloroethylethylene oxide) or from 1-chloro-2,3-epoxybutane (α -(chloromethyl)- α -methylethylene oxide) by addn. of HCl see (1); for possibly similar processes cf. (2).]

C on oxidn. gives (1) 1,3-dichlorobutanone-2 (3:5900).

—— 1,3-Dichloro-sec.-butyl acetate: b.p. 82.5-83.5° at 10 mm.,
$$D_4^{20} = 1.2185$$
, $D_4^{15} = 1.2229$; $n_D^{20} = 1.4530$, $n_D^{15} = 1.4550$ (1).

3:9145 (1) Petrov, J. Am. Chem. (U.S S R.) **11**, 713-721 (1941); Cent. **1942**, I 2867; C.A. **36**, 404 (1942). (2) Zikes, Monatsh. **6**, 348-355 (1885).

3:9150
$$\alpha,\beta'$$
-DICHLORODIETHYL ETHER Cl C₄H₈OCl₂ Beil. I — I₁— I₂-(674) Cl₃— C H O Cl.CH₂.CH₂

B.P. 55-57° at 17 mm. (1)
$$D_4^{20} = 1.1867$$
 (2) $n_D^{20} = 1.4473$ (2) $D_{19}^{19} = 1.1823$ (1) $n_D^{16.2} = 1.4497$ (1)

Colorless liq. fumg. in air and decomposing on distn. at ord. press. (1).

[For prepn. (60%) yield (2)) from ethylene chlorohydrin (3:5552) + acetaldehyde (1:0100) (2) or paraldehyde (1:0170) (1) + dry HCl see (1) (2).]

 \bar{C} rapidly dis. in cold aq. yielding by hydrolysis β -chloroethanol (3:5552), acetaldehyde (1:0100), and HCl (1).

3:9150 (1) Grignard, Purdy, Bull. soc. chim. (4) 31, 984-985 (1922). (2) Lingo, Henze, J. Am. Chem. Soc. 61, 1574-1575 (1939).

[For prepn. of \bar{C} (83% yield (1)) by saponification of the corresp. trichloroacetate obtd. by chlorination of *n*-butyl trichloroacetate (3:6315) see (1).]

 \bar{C} with SOCl₂ + pyridine gives (1) 1,2-dichlorobutane (3:7680), b.p. 127°, $n_D^{25} = 1.4420$ (1).

- ---- β-Chloro-n-butyl acetate: unreported.
- --- B-Chloro-n-butyl benzoate: unreported.
- ---- β-Chloro-n-butyl p-nitrobenzoate: unreported.
- ---- β-Chloro-n-butyl 3,5-dinitrobenzoate: unreported.
- \bigcirc β -Chloro-n-butyl N-phenylcarbamate: m.p. $52.5-53.5^{\circ}$ (1).
- ---- 2-(N-Phthalimino)butanol-1: unreported.
- 3:9160 (1) Waddle, Adkins, J. Am. Chem. Soc. 61, 3363 (1939).

3:9165 3-CHLOROBUTANOL-1 H C₄H₉OCl Beil. S.N. 24
$$(\gamma$$
-Chloro- n -butyl alcohol) CH₃—C—CH₂.CH₂OH C l B.P. 67–68° at 15 mm. (1) $D_4^{20} = 1.06218$ (1) $n_D^{20} = 1.44464$ (1) 61° at 10 mm. (2)

C on distn. at atm. press. or on htg. with quinoline loses HCl and yields crotonyl alc. CH₃.CH=CH.CH₂OH, b.p. 120-121° at 755 mm., $D_4^{20} = 0.85306$, $n_D^{20} = 1.42976$ (Nphenylcarbamate, m.p. 79.4-80°) (1).

[For prepn. of \bar{C} from butanediol-1,3 (1:6482) + HCl see (1) (3); from γ -chloro-n-butyl butyrate by hydrol. with HCl see (2); from $C_3H_6 + 30\%$ CH₂O + HCl at 50° see (4).]

[C over Al₂O₃ at 250° gives (3) butadiene-1,3.]

- ---- γ-Chloro-n-butyl acetate: unreported.
- ---- γ-Chloro-n-butyl benzoate: unreported.
- ---- γ-Chloro-n-butyl p-nitrobenzoate: unreported.
- ---- γ-Chloro-n-butyl 3,5-dinitrobenzoate: unreported.
- ---- γ-Chloro-n-butyl N-phenylcarbamate: unreported.
- --- 3-(N-Phthalimino)butanol-1: unreported.

3:9165 (1) Verhulst, Bull. soc. chim. Belg. 40, 85-90 (1931). (2) Heyse (to I.G.), Ger. 524,435, May 7, 1931; Cent. 1931, II 767. (3) Runge, Müller-Cunradi (to I.G.), Ger. 578,038, June 12, 1933, Cent. 1933, II 935. (4) I.G., Brit. 465,467, June 3, 1937; Cent. 1937, II 1445.

3:9170 4-CHLOROBUTANOL-1 (δ-Chloro-n-butyl alcohol, tetramethylene chlorohydri	010112.0112.0112.0112.011	Beil. I — I ₁ — I ₂ -(398)
B.P. 84-85° at 16 mm. (1) 86° at 15.mm. (2) 81-82° at 14 mm. (3) (4) 72-75° at 10 mm. (5) 70-71° at 7 mm. (4) 64-65° at 3 mm. (6) 57° at 0.5 mm. (7)	$D_4^{25} = 1.125$ (5) $D_4^{20} = 1.0883$ (1) 1.0867 (8)	$n_{\rm D}^{25} = 1.4551$ (5) $n_{\rm D}^{20} = 1.4518$ (1) 1.4529 (8)

Colorless liq. — On distn. above 16 mm. splits off HCl (1) (2) yielding tetrahydrofuran, b.p. 63°.

[For prepn. from tetrahydrofuran [Beil. XVII-10] by actn. of HCl gas (yield; 54-57%

- (3) (4) (8)) see (3) (4) (8); from tetramethylene glycol (1:6516) with SOCl₂ + pyridine (47% yield (1)) or S_2 Cl₂ (2) see (1) (2); from δ -chlorobutyl acetate by alcoholysis with MeOH (80% yield) see (6); for mfg. from ethylene oxide + C_2 H_{δ}Cl + AlCl₃ (or other catalysts) see (9).]
- \bar{C} (2 moles) treated with PBr₃ (1 mole) gives (98% yield (3)) tetramethylene chlorobromide, b.p. 175–176°, $D_4^{20}=1.488, n_D^{20}=1.4885$ (3). [For study of reaction of \bar{C} with HBr see (7).]
 - ---- δ -Chloro-n-butyl acetate: oil, b.p. 92-93° at 22 mm. (6), 92-94° at 22 mm. (10); $D_4^{20} = 1.0805$ (6); $n_D^{20} = 1.43439$ (6). [From tetrahydrofuran [Beil. XVII-10] with AcCl (6) as directed cf. (10) or with AcOH + HCl + cat. (11).]
 - --- δ -Chloro-n-butyl benzoate: oil, b.p. 140-142.5° at 4 mm., $D_4^{20} = 1.1429$, $n_D^{20} = 1.52028$ (6). [From tetrahydrofuran [Beil. XVII-10] with benzoyl chloride + ZnCl₂ (54.5% yield (6)).]
 - ----- δ-Chloro-n-butyl p-nitrobenzoate: oil, b.p. 205-206° at 7 mm. (12). [From tetra-hydrofuran [Beil. XVII-10] with p-nitrobenzoyl chloride + SnCl₂ (12).]
 - ---- δ-Chloro-n-butyl 3,5-dinitrobenzoate: unreported.
 - . Φ δ-Chlorobutyl N-phenylcarbamate: cryst. from pet. eth. (1); m.p. 54° (1), 54-55° (5).
 - \bigcirc \$\delta\$-Chlorobutyl N-(\alpha-naphthyl)carbamate: cryst. from pet. eth. (1); m.p. 69-70° (1), 69° (3), 66° (2).
- 3:9176 (1) Kirner, Richter, J. Am. Chem. Soc. 51, 2505-2506 (1929). (2) Bennett, Heathcoat, J. Chem. Soc. 1929, 272. (3) Starr, Hixon, J. Am. Chem. Soc. 56, 1595-1596 (1934). (4) Starr, Hixon, Org. Syntheses, Coll. Vol. 2 (1st ed.), 571-572 (1943). (5) Waddle, Adkins, J. Am. Chem. Soc. 61, 3363 (1939). (6) Cloke, Pilgrim, J. Am. Chem. Soc. 61, 2667-2669 (1939). (7) Bennett, Reynolds, J. Chem. Soc. 1935, 139. (8) Yur'ev, Minacher, Samurskaya, J. Gen. Chem. (U.S.S.R.) 9, 1710-1716 (1939); C.A. 34, 3731 (1940). (9) I.G., Brit. 354,992, Sept. 10, 1931; Cent. 1931, II 3545. (10) Manchen, Schmidt (to I.G.), Ger. 736,428, May 6, 1943; C.A. 38, 2966 (1944); U.S. 2,314,454, March 23, 1943; C.A. 37, 5078 (1943).
- (11) Seidenfaden, Bröker (to I.G.), Ger. 725,528, Aug. 13, 1942; C.A. 37, 5985 (1943). (12) Smorgonskii, Gold'farb, J. Gen. Chem. (U.S.S.R.) 10, 1113-1119 (1940); C.A. 35, 4011 (1941).

3:9175
$$d$$
, l -C-CHLOROBUTANOL-2 H C₄H₉OCl Beil. I — (1-Chlorobutanol-3) ClCH₂-C-CH₃ I_{1} -(188) I_{2} —

B.P. 70° at 13 mm. (1)

[For prepn. from 3-chloropropanal-1 (β-chloropropionaldehyde) (3:5576) + CH₃MgI see (1) (2).]

[4-Phthalimidobutanol-2, cryst. from pet. eth., m.p. 47-48°, although never recorded by reactn. of \tilde{C} with K phthalimide, has been prepd. indirectly (3).]

3:9175 (1) Fourneau, Ramart-Lucas, Bull. soc. chim. (4) 25, 367 (1919). (2) Backer, Bilt, Rec. trav. chim. 54, 69-70 (1935). (3) Robinson, Suginome, J. Chem. Soc. 1932, 308.

[For prepn. (76% yield (1)) via hydrolysis of the corresp. trichloroacetate (obtd. by chlorination of isobutyl trichloroacetate) see (1).]

- \bigcirc β -Chloro- α -methyl-n-propyl N-phenylcarbamate; m.p. 63.5-64° (1).
- 3:9180 (1) Waddle, Adkins, J. Am. Chem. Soc. 61, 3363 (1939).
- 3:9185 2-(β -CHLOROETHOXY)ETHANOL-1 C₄H₉O₂Cl Beil. I 467 (Diethylene glycol chlorohydrin; CH₂—CH₂—O—CH₂—CH₂OH I₁— ethylene glycol mono- β -chloroethyl cher; β -chloroethyl β -hydroxyethyl Cl ether; β -chloro- β -hydroxydiethyl ether)
 - B.P. 180-185° (1) 92-100° at 12 mm. (2) 93-96° at 11 mm. (3)

Colorless mobile highly refractive liq. — Very sol. aq. but can be salted out by addition of K_2CO_3 . — Misc. with alc. or ether. [For study of toxicity see (11).]

[For prepn. of \bar{C} from ethylene chlorohydrin (3:5552) with ethylene oxide (1:6105) at 140° (4) in pres. of SnCl₄, AlCl₃, etc. (2), or acidified hydrosilicate cat. (3), or conc. H₂SO₄ (30-35% yield (5)) (together with numerous other prods.), or with ethylene glycol (1:6465) + HCl gas as directed (1) see indic. refs.; for prepn. from ethylene oxide (1:6105) satd. with HCl gas see (4); for formn. of \bar{C} during extractn. of lignin from pine wood by means of ethylene chlorohydrin + HCl see (6).]

[For use of quat. salts obtd. from \bar{C} by treatment with oleic acid followed by pyridine or from \bar{C} with *n*-octadecylamine followed by pyridine and chloroacetic acid see (7); for use of \bar{C} as rat poison see (8).]

- [\bar{C} with hot aq. alk. ring-closes with loss of HCl giving (90-95% yield (9)) 1,4-dioxane (1:6400).]
- [Č (1 mole) with Me₂NH (3 moles) in C₆H₆ in s.t. at 120° for 8 hrs. gives (75% yield (5)) 2-(β -dimethylaminoethoxy)ethanol-1, b.p. 95° at 15 mm. (\bar{B} .picrolonate, m.p. 110°; \bar{B} .m-nitrobenzoate.HCl, m.p. 142°) (5).]
 - ---- 2-(β-Chloroethoxy) ethyl acetate; oil, b.p. 94-95° at 11 mm. (6).
 - 2-(β -Chloroethoxy)ethyl p-toluenesulfonate: oil; consts. not reported. [From \bar{C} (1 mole) with p-toluenesulfonyl chloride (0.75 mole) at 142° for 10 hrs. (yield 59% (10)); for use in introduction of 2-(β -chloroethoxyethyl) group see (10).]
- 3:9185 (1) Lourenco, Ann. chim. (3) 67, 290-292 (1863). (2) Haussmann, Göts, Ger. 670,419, Jan. 18, 1939; Cent. 1939, II 560; C.A. 33, 3031 (1939). (3) I.G., Brit. 354,357, Sept. 3, 1931; Cent. 1931, II 2657; C.A. 26, 3885 (1932). (4) Wurts, Ann. chim. (3) 69, 338-341 (1863). (5) Fourneau, Ribas, Bull. soc. chim. (4) 41, 1046-1051 (1927). (6) Freudenberg, Acker, Ber. 74, 1406 (1941). (7) I.G., Brit. 474,671, Dec. 2, 1937; Cent. 1938, 2063; C.A. 32, 3518 (1938): French 19,000, Oct. 7, 1937; Cent. 1938, 2063; C.A. 32, 2653 (1938). (8) I.G., Brit. 474,677, Dec. 2, 1937; Cent. 1938, I 2045; C.A. 32, 3064 (1938): French 805,557, Nov. 24, 1936; Cent. 1937, I 3397; C.A. 31, 4417 (1937). (9) Webel (to I.G.), Ger. 526,478, Oct. 8, 1932; Cent. 1933, I 1019; C.A. 27, 737 (1933). (10) Butler, Renfrew, Cretcher, Souther, J. Am. Chem. Soc. 59, 228-229 (1937).
 - (11) Smyth, Carpenter, J. Ind. Hyg. Toxicol. 26, 269-273 (1944).

3:9190 d,l-3-CHLORO-2-METHYLPROPANEDIOL-1,2 $C_4H_9O_2Cl$ Beil. S.N. 30 $(\beta$ -Methylglycerol- α -monochlorohydrin) CH_2Cl

B.P. 80° at 1.6 mm. (1)
$$D_4^{20} = 1.2362$$
 (1) $n_D^{20} = 1.4748$ (1)

Colorless viscous liq., misc. in all proportions with aq., alc., ether (1).

[For prepn. of \bar{C} from 1-chloro-2-methyl-2,3-epoxypropane (" β -methylepichlorohydrin") (3:7657) by warming with 0.1% aq. H₂SO₄ (95% yield (1)) see (1) (2).]

 \overline{C} with aq. 15% NaOH at 10–20° reacts very rapidly (by loss of HCl and ring closure) giving (70% yield (1)) (3) by ether extraction 2,3-epoxy-2-methylpropanol-1 (β-methylglycidol), colorless liq. misc. with aq., alc., or ether, b.p. 68° at 25 mm., $D_4^{20}=1.0420$, $n_D^{20}=1.4299$ (1). [This prod. on further hydration in the aq. soln. yields 2-methylpropanetriol-1,2,3 (β-methylglycerol), b.p. 115–120° at 1.6 mm., $D_4^{20}=1.1863$, $n_D^{20}=1.4730$ (1).]

3:9190 (1) Hearne, DeJong, *Ind. Eng. Chem.* **33**, 940-943 (1941). (2) Groll, Hearne (to Shell Development Co.), U.S. 2,086,077, July 6, 1937; *Cent.* **1937**, II 2433; *C.A.* **31**, 5813 (1937). (3) Groll, Hearne (to Shell Development Co.), U.S. 2,070,990, Feb. 16, 1937; *Cent.* **1937**, II 2433; *C.A.* **31**, 2612 (1937).

3:9195 1-CHLORO-2-(CHLOROMETHYL)BUTADIENE-1,3
$$C_5H_6Cl_2$$
 Beil. I — CH_2Cl I_1 — CH_2 —

No physical constants on C are cited by the abstract journals.

[For formn. of C from 2-(chloromethyl)-1,2,3-trichlorobutane (3:5230) with boilg. alc. KOH (2-(chloromethyl)-1,3-dichlorobutene-1 (3:9201) is also formed) see (1),

C readily polymerizes (1).

C with maleic anhydride (1:0625) forms addn. prods. (1).

3:9195 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1116-1132 (1936); Cent. 1937, I 573; C.A. 31, 1003 (1937).

3:9200 1-CHLORO-2-METHYLBUTADIENE-1,3 C_5H_7Cl Beil. S.N. 12 ("Isoprene monochloride") CH_3 Cl H_2C —CH—C—CH

B.P. 50.4° at 100 mm. (1)
$$D_4^{20} = 0.9710$$
 (1) $n_D^{20} = 1.4792$ (1)

Č has pleasant odor resembling isoprene.

[For prepn. of \bar{C} (38% yield (1) together with other products) from 2-methylbutadiene-1,3 (isoprene) with Cl_2 in CCl_4 see (1); for formn. of \bar{C} (30% yield (2) together with other products) from 1,2,3-trichloro-2-methylbutane (3:6100) with 2 moles of quinoline at 185– 225° see (2).]

Č with 4 pts. liq. SO₂ gives (1) 1-chloro-2-methylbutene-2 1,4-sulfone, white rhombic plates from water (which effectively separates the accompanying tar), or from ether, m.p. 73° cor. (1). [This prod. is a potent sternutator and skin irritant; its soly. in aq. is about

2.4 g. at 15° and 7.2 g. per 100 ml. aq.; in boilg. aq. it gives a tar, and aq. solns. are therefore concd. under reduced press.; on htg. to 140° under 100 mm. press. it regenerates (77% yield) \tilde{C} and thus constitutes a convenient means for storing \tilde{C} in stable form. (1).]

C polymerizes at a rate comparable to that of isoprene (for details see (1)).

Č (6 g.) + 1,4-naphthoquinone (1:9040) (3.5 g.) htd. under N₂ for 4 hrs. at 80° gives (1) on cooling 1-chloro-2-methyltetrahydroanthraquinone, pale yel. ndls. from acetone, colorless ndls. from alc., m.p. 146° cor. (1); this prod. on oxidn. with air in alc. NaOH yields 1-chloro-2-methylanthraquinone, cryst. from AcOH or alc., m.p. 171-172° cor. (1) (3) [dif. from 3-chloropentadiene-1,3 (3:7360) q.v.].

C with maleic anhydride (1:0625) evolves HCl and yields (2) a dianhydride.

3:9200 (1) Jones, Williams, J. Chem. Soc. 1934, 829-835. (2) Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1116-1132 (1936); Cent. 1937, I 573; C.A. 31, 1003 (1937). (3) Keimatsu, Hirano, J. Pharm. Soc. Japan, 49, 140-147 (1929); C.A. 23, 3466 (1929).

3:9201 2-(CHLOROMETHYL)-1,3-DICHLOROBUTENE-1 C₅H₇Cl₈ Beil. S.N. 11

$$D_4^{12} = 1.33$$
 (1) $n_C^{12} = 1.4975$ (1)

[For prepn. of \bar{C} from 2-(chloromethyl)1,2,3-trichlorobutane (3:5230) by loss of HCl with boilg. alc. KOH (1-chloro-2-(chloromethyl)butadiene-1,3 (3:9195) is also formed) see (2); for formn. of \bar{C} from 3-chloro-2-(chloromethyl)butene-1 (3:9206) with Cl₂ + NaHCO₃ at 0° (yield 6% \bar{C} together with 90% 2-(chloromethyl)-1,2,3-trichlorobutane (3:5230)) see (1).]

C on ozonolysis yields (2) 1,3-dichlorobutanone-2 (3:5900) and formic acid (1:1005).

3:9201 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938), Cent. 1939, II 4223; C.A. 33, 4190 (1939). (2) Tishchenko. J. Gen. Chem. (U.S.S.R.) 6, 1116-1132 (1936); Cent. 1937, I 573; C.A. 31, 1003 (1937).

3:9202 2,5-DICHLOROPENTENE-2

$$D_4^{14.5} = 1.1182 (1) \quad n_C^{14.5} = 1.4683 (1)$$

[For prepn. of \bar{C} (92% yield (1)) from cyclopropyl methyl ketone [Beil. VII-7, VII₁-(5)] with PCl₅ below 20° see (1); for formn. of \bar{C} from 5-chloropentanone-2 (see below) with excess 50% KOH see (1).]

C with conc. H₂SO₄ gives (43% yield (1)) 5-chloropentanone-2 (3:9267).

 $\bar{\rm C}$ cannot be hydrolyzed with aq. + CaCO₃ but on protracted reflux (210 hrs.) with excess KOAc in abs. alc. gives 2-chloro-5-acetoxypentene-2, b.p. 81.5° at 13 mm., D_4^{15} = 1.0800, n_{Cl}^{15} = 1.4499 (1).

C on oxidn, with 3% KMnO4 gives (1) acetic acid (1:1010) and acrylic acid (1:1020).

 $\ddot{\mathbf{C}}$ on ozonolysis yields (1) β -chloropropionic acid (3:0460).

3:9202 (1) D'yakonov, J. Gen. Chem. (U.S.S.R.) 10, 414-412 (1940); C.A. 34, 7861 (1940).

3:9204 1,4-DICHLORO-2-METHYLBUTENE-2 $C_5H_8Cl_2$ Beil. S.N. 11 Cl Cl Cl Cl CH_2 —CH=C— CH_2

B.P. 93° at 50 mm. (1)
$$D_4^{20} = 1.1526$$
 (1) $n_D^{20} = 1.4932$ (1) 56° at 10 mm. (1)

Colorless lachrymatory liquid. — Sol. in cold conc. H₂SO₄ with yel.-br. color.

[For prepn. from 2-methylbutadiene-1,3 (isoprene) (1:8020) in CCl₄ by treatment with Cl₂ see (1) (1-chloro-2-methylbutadiene-1,3 (3:9200) is also formed (1)).]

C in alc. added dropwise to a suspension of Zn dust in hot alc. gives (77% yield (1)) 2-methylbutadiene-1,3 (isoprene) (1:8020), b.p. 34°.

 \overline{C} on oxidn. with KMnO₄ in acctone at -5° gives (1) 1,4-dichloro-2-methylbutanediol-2,3, ndls. from ether, m.p. 106.5° cor. (1).

Č in CHCl₃ treated with O₃, then with aq., yields (1) chloroacetone (3:5425) and chloroacetaldehyde (3:7212); ozonolysis of Č without solvent followed by KMnO₄ oxidn. gives (1) chloroacetic acid (3:1370).

3:9204 (1) Jones, Williams, J. Chem. Soc. 1934, 829-834.

3:9206 d,l-3-CHLORO-2-(CHLOROMETHYL)BUTENE-1 C₅H₈Cl₂ Beil. S.N. 11

B.P. 39-40° at 7 mm. (1)
$$D_4^{18} = 1.1328$$
 (1) $n_C^{18} = 1.4713$ (1)

[For form. of \bar{C} from 3-chloro-2-methylbutene-1 (3:7300) with $Cl_2 + NaHCO_3$ at 0° see (1) (yield of \bar{C} is 35% accompanied by 30% 1,3-dichloro-2-methylbutene-2 (3:8170) and 30% 1,2,3-trichloro-2-methylbutane (3:6100)) (1).]

Č upon ozonolysis yields (1) 1,3-dichlorobutanone-2 (3:5900).

3:9206 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4223; C.A. 33, 4190 (1939).

1,3-DICHLORO-2,2-bis-(CHLOROMETHYL)PROPANE C5H8Cl4 Beil. I - 141

$$\begin{array}{ccc} & \text{CH}_2\text{Cl} & \text{I}_1-\\ & \text{ClCH}_2-\text{C-CH}_2\text{Cl} & \text{I}_2-(\textbf{104}) \\ & \text{CH}_2\text{Cl} & & \end{array}$$

1268

B.P. 110° at 12 mm. M.P. 97°

See 3:2675. Division A: Solids.

3:9214 2-(CHLOROMETHYL)BUTENE-1 CH₂Cl C₅H₉Cl Beil. I - 211 (β -Ethylallyl chloride) CH₃.CH₂—C=CH₂ I₁— I₂-(187)

C has not been obtd. in pure form.

[For formn. of C together with 1-chloro-2-methylbutene-1 (3:7303) + 1-chloro-2-methylbutene-2 (3:7485) from 1-chloro-2-methylbutanol-2 (3:8175) by distn. with anhydrous

oxalic acid see (1); for formn, of C (together with other products) from 2-methylbutene-1 (1:8210) by actn. of Cl₂ see (2).]

[For behavior of C with NaI in acetone see (2); for use in prepn. of unsatd. cellulose ethers see (3).1

C with O₃ followed by hydrolysis yields (2) chloromethyl ethyl ketone (3:8012).

3:9214 (1) Chalmers, Trans. Roy. Soc. Can. (3) 22, III 73, 76 (1928). (2) Gutner, Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1062-1067 (1938); Cent. 1939, II 4221; C.A. 33, 3755 (1939). (3) Hahn (to du Pont), U.S. 2,082,797, June 8, 1937; Cent. 1937, II 3838; C.A. 31, 5577 (1937).

No physical constants of C have been reported.

[For formn. of C from diisoamyl sulfide [Beil. I-405, I₁-(200), I₂-(435)] by action of Cl₂ see (1).]

 \tilde{C} on htg. in a s.t. for 5 hrs. at 110° with Ag₂O + ag. yields (1) isovaleric acid (1:1050). 3:9216 (1) Spring, Lecrenier, Bull. soc. chim. (2) 48, 627 (1887).

3:9218 d,l-1,3-DICHLORO-2-(CHLOROMETHYL)BUTANE C₅H₉Cl₃ Beil. S.N. 10

[For formn. of C from 1,3-dichloro-2-methylbutane (3:9228) or from 3-chloro-2-methylbutene-1 (3:7300) with Cl₂ see (1).]

C with Cl₂ as specified (1) yields 1,2,3-trichloro-(2-chloromethyl)butane (3:5230).

C with KOH or with quinoline gives (1) only resins.

3:9218 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1116-1132 (1936); Cent. 1937, I 573; C.A. **31.** 1003 (1937).

B.P. 80.4° at 60 mm. (1)
$$D_4^{20} = 1.0834$$
 (1) $n_D^{20} = 1.4485$ (1)

[For prepn. of C (30% yield (1) together with other products) from 1-chloropentane (3:7460) by vapor-phase photochemical chlorination see (1).]

Č on refluxing 24 hrs. with NaI in acetone gives (90% yield (1)) 3-chloro-1-iodopentane, b.p. 50.5° at 2.5 mm., $D_{-}^{20} = 1.6611$, $n_{\rm D}^{20} = 1.5229$ (1). (A small amt. of 1,3-diiodopentane, b.p. 80-82° at 2.5 mm., is also formed (1).) [For reactn. of 3-chloro-1-iodopentane with diethylamine to give (74% yield) 3-chloropentyl-diethylamine HCl, m.p. 98.5°, see (1).]

3:9220 (1) Hass, Huffman, J. Am. Chem. Soc. 63, 1233-1235 (1941).

B.P. 88.1° at 60 mm. (1)
$$D_4^{20} = 1.0840$$
 (1) $n_D^{20} = 1.4503$ (1)

69-70° at 28 mm. (3) 59-61° at 17 mm. (2)

58–60° at 15 mm. (2) r prepn. of \bar{C} (31% yield (1) together with other prods.) from 1-ch

[For prepn. of \tilde{C} (31% yield (1) together with other prods.) from 1-chloropentane (3:7460) by vapor-phase photochemical chlorination see (1); from 2-methyltetrahydrofuran [Beil. XVII-12] on htg. in s.t. for 4 hrs. at 60° with 2 vols. conc. HCl (2) or from pentanediol-1,4 by treatment in boilg. aq. with HCl (2) see indic. refs. — For formn. of \tilde{C} (together with other prods.) from pentane (1:8505) + Cl₂ see (3).]

 \tilde{C} on boilg, with aq. (2) or aq. K_2CO_3 (3) yields pentanediol-1,4 [Beil. I-480] [bis-(N-phenylcarbamate), m.p. 125-125.5° (3)].

 \vec{C} on refluxing 24 hrs. with NaI in acetone gives (90% yield (1)) 4-chloro-1-iodopentane, b.p. 61.3° at 3.5 mm., $D_{\rm c}^{20}=1.6580$, $n_{\rm D}^{20}=1.5248$ (1) (a small amt. of 1,4-diiodopentane, b.p. 100° at 5 mm. is also formed (1)). [For reactn. of 4-chloro-iodopentane with diethylamine to give (42% yield) 4-chloropentyl-diethylamine hydrochloride, m.p. 99°, see (1).]

3:9224 (1) Hass, Huffman, J. Am. Chem. Soc. 63, 1233-1235 (1941). (2) Fröbe, Hochstetter, Monatsh. 23, 1087-1088 (1902). (3) Lemke, Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 1995-1998 (1937); Cent. 1939, I 2398; C.A. 32, 482 (1938).

3:9228 d,l-1,3-DICHLORO-2-METHYLBUTANE $C_5H_{10}Cl_2$ Beil S.N. 10

Note that C has never been reported; the prod. originally supposed by (1) to have been C was later (2) found to be 2-(chloromethyl)-3-chlorobutene-1 (3:9206) q.y.

By chlorination of opt. act. 1-chloro-2-methylbutane with SO₂Cl₂ in pres. of benzoyl peroxide followed by subsequent fractionation (3) both opt. act. forms of \bar{C} are alleged to have been obtd.; dextro form, b.p. 155° at 760 mm. (calcd.), 91° at 100 mm. (obs.); levo form, b.p. 153° at 760 mm. (calcd.), 89.2° at 100 mm. (obs.) (3). Note, however, that in (3) the authors were apparently unaware of the correction mentioned above.

3:9228 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 6, 1116-1132 (1936); Cent. 1937, I 573; C.A. 31, 1003 (1937). (2) Tishchenko, J. Gen. Chem. 8, 1232-1246 (1938); Cent. 1939, II 4222. (3) Brown, Kharasch, Chao, J. Am. Chem. Soc. 62, 3437 (1940).

3:9230 d,l-3,8-DICHLORO-2-METHYLBUTANE $C_8H_{10}Cl_2$ Beil. I -135 I_1 — CH_3 —C—C— CH_3 I_2 — I_2 —

No data on physical properties of C appear to be recorded.

[For prepn. of \bar{C} from isopropyl methyl ketone (1:5410) with PCl₅ see (1).]

C with alc. KOH at 130° yields (1) isopropylacetylene (1:8010), b.p. 28°.

3:9230 (1) Béhal, Ann. chim. (6) 15, 285-286 (1888).

B.P. 64° at 35 mm. (1) 45° at 12 mm. (2)

[For prepn. of \bar{C} from tiglic acid (1:0420) with PCl₃ (yield 90% (1)) (2) see indic. refs.] \bar{C} with hydrazine hydrate (2 moles) yields (3) N,N'-ditiglylhydrazide, m.p. 182-183° (3). \bar{C} on hydrolysis yields tiglic acid (1:0420), m.p. 64.5-65°, q.v. for the corresp. amide, anilide, v-toluidide, and other derivs.

3:9240 (1) Barger, Martin, Mitchell, J. Chem. Soc. **1937**, 1822. (2) Blaise, Bagard, Ann. chim. (8) **11**, 120 (1907). (3) Freri, Atti X° congr. intern. chim. **3**, 150–154 (1939); Cent. **1939**, II 3975; C.A. **34**, 100 (1940).

3:9242 ETHYL
$$\alpha$$
-CHLOROACRYLATE Cl C₅H₇O₂Cl Beil. S.N. 163 CH₂=C-COOC₂H₅ B.P. 51-53° at 18 mm. (1) $n_D^{20} = 1.4384$ (1)

[For prepn. of \bar{C} from ethyl α,β -dichloropropionate (3:6090) by htg. with dimethylaniline, quinoline, or quinaldine at 100° for 10 min. under N_2 (81% yield) see (1).

See also α -chloroacrylic acid (3:1445) and methyl α -chloroacrylate (3:9096).

3:9242 (1) Marvel, Dec, Cooke, Cowan, J. Am. Chem. Soc. 62, 3495-3498 (1940).

3: 9244 METHYL
$$\beta$$
-CHLOROCROTONATE $C_6H_7O_2Cl$ Beil. II — CH₃—C—Cl II₁-(189) II₂-(396) H—C—COOCH₃

B.P. 64–67° at 14 mm. (1) $D_4^{22\ 3}=1.1555$ (1) $D_4^{21\ 4}=1.1564$ (1) $n_D^{21\ 4}=1.46275$ (1) $D_4^{20}=1.157$ (1)

[See also methyl B-chloroisocrotonate (3:8028).]

[For prepn. of \tilde{C} from β -chlorocrotonic acid (3:2625) in MeOH (1:6120) with dry HCl see (1).]

 $[\bar{C}]$ with Na salt of benzyl mercaptan gives (2) methyl β -(benzylmercapto)crotonate, cryst. from ether and MeOH, m.p. 69–70° (2), 73° (3), also obtd. (78% yield (3)) from Na thioenolate of methyl β -mercaptocrotonate with benzyl chloride (3:8535); note that this (and also other, analogous products) are also obtd. starting with the stereoisomeric methyl β -chloroisocrotonate (3:8028) q.v.

3:9244 (1) von Auwers, Ber. 45, 2806-2807 (1912). (2) Scheibler, Voss, Ber. 53, 384 (1920). (3) Scheibler, Topouzada, Schulze, J. prakt. Chem. (2) 124, 20 (1940).

See also methyl (chloroformyl)acetate (3:9098-A).1

63-64° at 10 mm. (4)

Note that \tilde{C} is both an acid chloride and an ester; it comprises the half acid chloride/half ethyl ester of malonic acid (1:0480).

[For prepn. of Č from ethyl hydrogen malonate with SOCl₂ (3) or better from potassium ethyl malonate with SOCl₂ at 0° (1) or in ether (4) (yields: 70% (1), 45% (4)) of. (5) or with PCl₅ (6) see indic. refs.]

Č boils at ord. press. about 170–180° with serious decompn. (3). — Č on repeated distn. even under reduced press. (4) or Č with quinoline in dry ether at 0° (4) loses HCl and undergoes condensation yielding ethyl 6-ethoxy-2,4-diketo-2,3-dihydropyran-3-carboxylate [Beil. XVIII₁-(540)], cryst, from CS₂, m.p. 85–86° (4) cf. (7).

[For behavior of C with 2,4-dimethylpyrryl MgBr (8), with indolyl MgBr (5), with indolyl MgI (9), or with imidazolyl MgBr (10) see indic. refs.]

[For behavior of C with atoxyl see (1).]

[\bar{C} with urea (2 moles) reacts as an acid chloride giving (2) ethyl malonurate [Beil. III-66], m.p. 128° (2). — \bar{C} with thioformamide condenses with loss of H_2O + HCl giving (11) (12) (13) ethyl thiazole-5-carboxylate, b.p. 103.5-104.5° at 12 mm. (13), which on hydrolysis gives thiazole-5-carboxylic acid, m.p. 196-197° cor. (11).]

```
—— ω-(Carbethoxyacet)anilide: unreported.

Φ ω-(Carbethoxyacet)-p-toluidide: m.p. 83° (4).
```

3:9246 (1) Morgan, Walton, J. Chem. Soc. 1931, 1744-1745. (2) Boehringer und Söhne, Ger. 193,447, Dec. 28, 1907; Cent. 1908, I 1000; C.A. 2, 1862-1863 (1908). (3) Marguery, Bull. soc. chim. (3) 33, 546-547 (1905). (4) Staudinger, Becker, Ber. 50, 1023 (1917). (5) Oddo, Albanese, Gazz. chim. ital. 57, 833-834 (1927). (6) van't Hoff, Ber. 7, 1572 (1874). (7) Leuchs, Ber. 39, 2642-2643 (1906). (8) Ingraffia, Gazz. chim. ital. 64, 780-782 (1934). (9) Majima, Shigematsu, Rokkaku, Ber. 57, 1454-1455 (1924). (10) Oddo, Quintino, Gazz. chim. ital. 58, 595-596 (1928).

(11) Erlenmeyer, von Meyenburg, Helv. Chim. Acta 20, 205 (1937). (12) Soc. Chem. Ind. Basel, Swiss 192,849, Nov. 16, 1937; Cent. 1938, I 3659; C.A. 32, 4285 (1938). (13) Soc. Chem. Ind. Basel, Ger. 658,353, March 29, 1938, Cent. 1938, II 354; C.A. 32, 4727 (1938).

Note that \bar{C} is both an acid chloride and an ester; \bar{C} is an important reagent for introducing the three-carbon radical —CH₂.CH₂.COOH.

[For prepr. of \bar{C} from methyl hydrogen succinate, m.p. 58° (itself obtd. (yields: 95–96% (3), 83% (4) (1)) from succinic anhydride (1:0710) with MeOH (1:6120)) by action of SOCl₂ (yields: 100% (6), 90–93% (3), 90% (5)) or of PCl₅ (92.5% yield (4)) see indic. refs. Note that \bar{C} on distr. (except at low press.) tends to lose MeCl (3:7005) giving (3). succinic anhydride (1:0710).

Examples of utility of \bar{C} in synthesis include the following: \bar{C} + ethyl sodio-acetoacetate (6); \bar{C} + ethyl sodio- α -acetyl-n-undecanoate (7); \bar{C} + ethyl sodio- α -acetyl- γ -phenoxy-n-butyrate (8); \bar{C} + ethyl sodio- γ -phenoxy-propylacetoacetate (9); \bar{C} + methyl γ -(6-methoxy-1-naphthyl)butyrate (10); \bar{C} + methyl sodio- α -acetyl-propionate (11); \bar{C} + 1-methyl-cyclohexene-1 (5); \bar{C} + ethyl α -acetyl-n-tridecanoate (1); \bar{C} + Cd diisoamyl (4).]

- β -(Carbomethoxy) propionamide: unreported.
- \oplus β -(Carbomethoxy)propionanilide: ndls. from ether or lt. pet./C₆H₆, m.p. 97-99° (1). [From \bar{C} with aniline (1).]
- 3:9247 (1) G. M. Robinson, R. Robinson, J. Chem. Soc. 127, 180 (1925). (2) Clutterbeck, R. Robinson, Biochem. J., 19, 385-396 (1925); Cent. 1925, II 1516. (3) Cason, Org. Syntheses 25, 19-22 (1945). (4) Cason, J. Am. Chem. Soc. 64, 1107 (1942). (5) Nenitzescu, Cioranescu, Przemetzky, Ber. 73, 314 (1940). (6) Ruggli, Maeder, Helv. Chim. Acta 25, 943 (1942); C.A. 37, 1714-1715 (1943). (7) G. Robinson, Robinson, J. Chem. Soc. 1926, 2206. (8) R. Robinson, Watt, J. Chem. Soc. 1934, 1539. (9) Barger, R. Robinson, Smith, J. Chem. Soc. 1937, 724. (10) R. Robinson, Thompson, J. Chem. Soc. 1938, 2011.
 - (11) R. Robinson, Seijo, J. Chem. Soc. 1941, 585.

3:9250 β-METHOXYETHYL TRICHLOROACETATE C₅H₇O₃Cl₃ Beil. S.N. 160 (Methyl "cellosolve" trichloroacetate) CH₂OCH₃

B.P. M.P. 98.0-99.5° at 17 mm. (2) 14.6-14.8° (1) $D_4^{20} = 1.3866$ (3) $n_D^{20} = 1.45626$ (2) 92-93° at 10 mm. (1) 1.3826 (2) 1.45823 (2) 61° at 0.9 mm. (3)

Colorless liq. with agreeable odor.

[For prepn. (82% yield (1)) from β -methoxyethanol (1:6405) + trichloroacetyl chloride (3:5420) see (1).]

Č on shaking with ac. is smoothly saponified (1) to β -methoxyethanol (1:6405) + tri-chloroacetic ac. (3:1150).

3:9256 (1) Meerwein, Sönke, Ber. 64, 2379 (1931). (2) Palomaa, Salmi, Korte, Ber. 72, 797 (1939). (3) Meerwein, Sönke, J. prakt. Chem. (2) 137, 309 (1933).

3:9260 d,l- γ -CHLORO-n-VALERYL CHLORIDE C_5H_8 OCl₂ Beil. II — CH₃.CH.CH₂.CH₂—C=O II₁-(132) C_1 II₂—

B.P. 61° at 8 mm. (1)

[For prepn. of C from γ -chloro-n-valeric acid (3:9270) with sl. excess of SOCl₂ (100% yield) see (1).]

 $[\bar{C}]$ with EtZnI at -15° to -20° yields (2) γ -chloro-n-butyl ethyl ketone (6-chlorohepta-

none-3) [Beil. I₁-(359)], b.p. 79° at 13 mm. (2) (semicarbazone, m.p. 129-129.5° (2), pnitrophenylhydrazone, unrecryst. oil (2)); \tilde{C} with C_6H_6ZnBr at 0° yields (3) γ -chloro-nbutyl phenyl ketone [Beil. VII₁-(173)], b.p. 155-156° at 15 mm. (3) (semicarbazone, m.p. 123° (3)).]

 \tilde{C} on hydrolysis with aq. yields (1) γ -chloro-n-valeric acid (3:9270); for the amide, anilide, and other derivs, corresp. to C see the acid (3:9270).

3:9260 (1) Wohlgemuth, Compt. rend. 159, 80 (1914); Ann. chim. (9) 2, 301 (1914). (2) Wohlgemuth, Ann. chim. (9) 2, 405-406, 410-412 (1914). (3) Ref. 2, 417-419.

B.P. 75-80° at 5-8 mm. (1)

[For prepn. of C from δ-chloro-n-valeric acid (3:0075) with SOCl₂ see (1).]

3:9264 (1) Child, Pyman, J. Chem. Soc. 1931, 41.

3:9266 CHLOROPIVALYL CHLORIDE $(\beta$ -Chloro- α, α -dimethylpropionyl chloride)

B.P. 85-86° at 60 mm. (1)

$$n_{\rm D}^{20} = 1.4539 (1)$$

[For prepn. of C from pivalyl chloride (trimethylacetyl chloride) (3:7450) with SO₂Cl₂ + dibenzovl peroxide in CCl4 see (1).1

- Chloropivalamide: pl. from aq., m.p. 108-109° (1).
- 3:9266 (1) Kharasch, Brown, J. Am. Chem. Soc. 62, 925-929 (1940).

3:9267 5-CHLOROPENTANONE-2
$$C_{\delta}H_{\theta}OCl$$
 Beil. I — $(\gamma\text{-Chloro-}n\text{-propyl} CH_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$ I₁— I_{2} —(738) I_{2} —(738) B.P. 76° at 34 mm. (6) $D_{4}^{18} = 1.0571$ (1) $n_{F}^{18} = 1.4461$ (1) $n_{C}^{18} = 1.4371$ (1) $n_{C}^{18} = 1.4371$ (1)

B.P. 76° at 34 mm. (6)
$$D_4^{18} = 1.0571$$
 (1) $n_F^{18} = 1.4461$ (1) $71-72^\circ$ at 20 mm. (2) $n_C^{18} = 1.4371$ (1)

[For prepn. of C from 2,5-dichloropentene-2 (3:9202) by hydration with conc. H₂SO₄ (43% yield) see (1); from 2,5-epoxypentene-1 ("α-methylenetetrahydrofuran") (for whose prepn. + characteristics see (3)) by ring cleavage with conc. HCl see (4); from cyclopropyl methyl ketone cyanohydrin ("acetyltrimethylene cyanohydrin") with conc. HCl by ring cleavage and loss of HCN see (5); from α -acetobutyrolactone with HCl as directed see (6).

[C with 50% excess KOH on refluxing loses HCl and ring-closes giving (60% yield (2)) (5) cyclopropyl methyl ketone [Beil. VII-7, VII₁-(7)], b.p. 112-113° (5), $D_4^{20} = 0.8993$, $n_D^{20} = 1.4244$ (corresp. semicarbazone, m.p. 120-121° (5)).]

5-Chloropentanone semicarbazone: m.p. 92-93° (5), 91-92° (1).

3:9267 (1) D'yakonov, J. Gen. Chem. (U.S.S.R.) 10, 414-426 (1940); C.A. 34, 7861 (1940). (2) Zelinsky, Dengin, Ber. 55, 3360 (1922). (3) Paul, Bull. soc. chim. (4) 53, 425-426 (1933); (5) 2, 752-754 (1935). (4) Topchiev, Russ. 57,345, June 30, 1940; C.A. 36, 2509 (1942). (5) Khaletskii, J. Gen. Chem. (U.S.S.R.) 11, 319-323 (1941); Cent. 1942, I 1364; C.A. 35, 5853 (1941) (6) Boon (to Imperial Chem. Ind. Ltd.), U.S. 2,370,392, Feb. 27, 1945; Brit. 558,286, Dec. 30 1943; C.A. 39, 4090 (1945).

[For prepn. of \bar{C} from propionyl chloride (3:7170) with ethylene + AlCl₃ with or without diluent (50% yield (4)) (2), or over suitable cat. at 100-300° and at 20-200 atm. press. (3), see indic. refs.; from β -chloropropionyl chloride (3:5690) with ZnEt₂ in toluene (70% yield) see (1).]

 \tilde{C} with hot aq. alk. or alk. carbonates gives only resins, but \tilde{C} on boilg. with dry diethylaniline loses HCl yielding (1) ethyl vinyl ketone [Beil. I-731, I₂-(791)], b.p. 96°.

[\bar{C} with diethyl sodio-malonate in ether gives (5) diethyl α -(γ -keto-n-amyl)malonate, b.p. 166° at 14 mm. (5); \bar{C} with sodio-acetylacetone yields (5) the triketone 3-acetyloctane-dione-2,6, b.p. 154° at 16 mm. (5); \bar{C} with ethyl sodio-acetoacetate in ether yields (6) the expected ethyl octandione-2,6-carboxylate-3 (3-carbethoxyoctanedione-2,6), b.p. 150° at 8 mm. (6).]

[$\ddot{\mathbf{C}}$ with diethylamine in ether in cold, followed by treatment with dil. aq. alk., yields (7) 1-diethylaminopentanone-3, b.p. 84° at 13 mm., $n_{15}^{15} = 1.4368$ (7).]

[\bar{C} with aniline (2 moles) + a little water reacts vigorously on warming yielding (8) 1-anilinopentanone-3 [Beil. XII-214], tbls. from ether, m.p. 55.5° (8); note, however, that \bar{C} with aniline htd. in abs. alc. or C_6H_6 (8), or \bar{C} with aniline htd. with conc. HCl (or 40% H_2SO_4) + nitrobenzene (or H_3AsO_4), gives (9) (4) 4-ethylquinoline [Beil. XX-406, XX₁-(153)].]

[C̄ with hydrazine hydrate in MeOH gives (80% yield (10)) by ring closure 3-ethyl-Δ²-pyrazoline [Beil. XXIII-32], liq., b.p. 76° at 22 mm. (10) (corresp. picrate, B.PkOH, yel. ndls. from 95° alc., m.p. 117° (10)). — C̄ with phenylhydrazine in ether gives (10) by ring closure 3-ethyl-1-phenyl-Δ²-pyrazoline [Beil. XXIII-32], oil, b.p. 155° at 9 mm. (10).]

[\bar{C} with NH₂OH.H \bar{C} l + K₂CO₃ in aq. MeOH htd. for a few minutes gives (20% yield (10)) by ring closure 3-ethyl- Δ^2 -isoxazoline [Beil. XXVII-13], oil, b.p. 69° at 11 mm. (10).]

① 1-Carbamido-3-ethyl- Δ^2 -pyrazoline: cryst. from EtOAc or C_6H_6 , m.p. 96° (10). [Note that \bar{C} with 1 equiv. semicarbazide HCl + NaOAc in aq. immediately ppts. the corresp. semicarbazone; this on htg. with strong aq. NaOAc (or \bar{C} + semicarbazide HCl + strong NaOAc soln. htd. directly) loses HCl and ring-closes to the indic. deriv. (10).]

3:9268 (1) Blaise, Maire, Bull. soc. chim. (4) 3, 268-271 (1908); Compt. rend, 142, 216 (1906). (2) Schoeller, Zöllner (to I.G.), U.S. 1,737,203, Nov. 26, 1929; Cent. 1939, II 1133; Brit. 282,412, Feb. 15, 1928; Cent. 1929, I 143. (3) Frolich, Wiezevich (to Standard Oil Development Co.), U.S. 2,006,198, June 25, 1935; Cent. 1936, I 2827. (4) Kenner, Statham, Ber. 69, 16-17 (1936). (5) Blaise, Maire, Bull. soc. chim. (4) 3, 421, 423 (1908). (6) Blaise, Maire, Bull. soc. chim. (4) 3, 413-417 (1908). (7) Adamson, McQuillin, Robinson, Simonsen, J. Chem. Soc. 1937, 1578. (8) Blaise, Maire, Bull. soc. chim. (4) 3, 659-660, 662-665 (1908). (9) Schering-Kahlbaum, A.G., Brit. 283,577, March 7, 1928; Cent. 1929, I 3148. (10) Blaise, Maire, Bull. soc. chim. (4) 3, 272-279 (1908).

B.P. 60-62° at 16 mm. (1)

[For prepn. of \bar{C} from 2-methylbutanon-3-ol-1 (β -acetyl-n-propyl alc.) [Beil. I_1 -(422)] with 3 moles HCl (satd. at 0°), preferably in pres. of 5-10% AlCl₃ (50% yield, accompanied by some 2-methylbuten-1-one-3, b.p. 96-99°) see (1).]

3:9269 (1) Decombe, Compt. rend. 202, 1685-1687 (1936); Cent. 1936, II 1525.

M.P. 33°

—
$$d,l$$
- β -CHLORO- n -VALERIC ACID $C_{\delta}H_{9}O_{2}Cl$ Beil. S.N. 162 CH₃.CH₂.CH.CH₂COOH

Cl

B.P. 112° at 10 mm. M.P. 33° $D_{4}^{20} = 1.1484$ $n_{D}^{20} = 1.4462$

See 3:0270. Division A: Solids.

3:9270
$$d_i l_{-\gamma}$$
-CHLORO- n -VALERIC ACID $C_5 H_9 O_2 Cl$ Beil. II — CH₃.CH.CH₂.CH₂.COOH II_1 -(131) II_2 —

B.P. 117° at 10 mm. (1)
$$D_4^{20} = 1.1514$$
 (1) $n_D^{20} = 1.4458$ (1) 115-116° at 10 mm. (2) 1.1510 (1) 1.4456 (1)

[For prepn. of \tilde{C} from γ -n-valerolactone (1:5080) with conc. HCl at 150° see (2); from β-ethylidene-propionic acid (penten-3-oic acid-1) [Beil. II-426, II₁-(191), II₂-(400)] or from allyl-acetic acid (penten-4-oic acid-1) [Beil. II-425, II₁-(191), II₂-(399)] with dry HCl gas in ether or heptane at -15° see (1).] [For opt. act. isomers of \bar{C} see Beil. II₂-(268) and subsequent literature.]

C with SOCl₂ yields (2) γ-chloro-n-valeryl chloride (3:9260).

- ---- Methyl ~-chloro-n-valerate: unrecorded.
- Ethyl γ -chloro-n-valerate: b.p. 196° (see 3:8703).
- D γ-Chloro-n-valeramide: tbls. from ether, m.p. 79-79.5° (2). [From γ-chloro-nvaleryl chloride (3:9260) with conc. aq. NH₄OH (2).]
- (2), [From pet. eth. + a little AcOH, m.p. 104° (2). γ-chloro-n-valeryl chloride (3:9260) with aniline in ether soln. (2).
- Φ γ-Chloro-n-valero-phenylhydrazide: ndls. from EtOAc, m.p. 100° (2). [From γchloro-n-valeryl chloride (3:9260) with 2 moles phenylhydrazine in ether (2).

3:9276 (1) Schjanberg, Ber. 70, 2385-2391 (1937). (2) Wohlgemuth, Compt. rend. 158, 1577 (1914); Ann. chim. (9) 2, 298-304 (1914).

--- CHLOROPIVALIC ACID CH₈ C₅H₉O₂Cl Beil. S.N. 162

B.P. 126-129° at 30 mm.

M.P. 40-42°

See 3:0440. Division A: Solids.

1277 LIQUIDS (WITH B.P. REPTD, AT RED. PRESS.)

Beil. S.N. 199

3:9280-3:9287

("Cellosolve" chloroformate; β -ethoxyethyl chlorocarbonate)

3:9280 B-ETHOXYETHYL CHLOROFORMATE

C₂H₅.O.CH₂.CH₂.O.CO.Cl

C₆H₉O₈Cl

B.P. 67.2° at 14 mm. (1)

 $D_{\text{th}}^{25} = 1.1341 \ (1)$

 $n_{\rm D}^{25} = 1.4169 (1)$

Colorless liq. insol. aq.

[For prepn. (77% yield (1)) from β -ethoxyethanol ("Cellosolve") (1:6410) + phosgene (3:5000) see (1).]

 \bigcirc β -Ethoxyethyl carbamate: m.p. 62.2° (1). [From \ddot{C} + aq. NH₄OH in 39% yield; cryst. from propylene chloride (1).

3:9280 (1) Asburn, Collett, Lazzell, J. Am. Chem. Soc. 60, 2933-2934 (1938).

3:9285 β-METHOXYETHYL CHLOROACETATE C₅H₉O₂Cl Beil. S.N. 160 (Methyl "cellosolve" chloroacetate) CH₂.O.CH₃

CH2.O.CO.CH2Cl $D_4^{20} = 1.2015 (1)$ $n_D^{20} = 1.43821 (1)$ B.P. 85-86° at 9 mm. (1) 60° at 1.3 mm. (1)

Colorless oil.

[For prepn. (80% yield (1)) from ethylene glycol monomethyl ether (1:6405) + chloroacetyl chloride (3:5235) in CHCl₃ see (1).]

 \bar{C} on shaking with aq. saponifies to β -methoxyethanol (1:6405) + chloroacetic ac. (3:1370); titration of aq. soln. neutralizes 1 equiv. alk. (i.e., Sap. Eq. = 188.5).

3:9285 (1) Meerwein, Sönke, J. prakt. Chem. (2) 137, 319-320 (1933).

CH₂.CH₂—C—CH₃
OCI ter-AMYL HYPOCHLORITE C₅H₁₁OCl 3:9287 Beil. I — (Dimethyl-ethyl-carbinyl I_1 hypochlorite) I₂-(423) $D_4^{25} = 0.8547 (1)$ B.P. see text.

[See also ter-butyl hypochlorite (3:7165).]

Yellow mobile liquid with irritating odor and giving vapor which violently attacks eves and mucous membranes (1). — C boils with considerable decomposition; a thermometer in the vapor recorded 76° at 752 mm., but this cannot, of course, be regarded as a b.p. (1).

Č is relatively stable and even after 2 months (in dark) is practically unchanged (1); for study of stability of \bar{C} in aq. or in CCl4 see (2). — \bar{C} on exposure to bright sunlight dec. quietly with evolution of heat leaving a colorless liq. contg. acetone (1:5400) and other prods.

[For prepn. of C from ter-amyl alc. (1:6160) with Cl₂ in aq. alk. (1) (3) or alk. earth (4) or with aq. HOCl in pres. of CCl4 (90% yield (5)) (2) see indic. refs.]

 \bar{C} with KI + AcOH liberates I₂ quant. according to equation $C_5H_{11}OCl + 2HI \rightarrow$ $C_8H_{11}OH + HCl + I_2$ (use in quant. detn. of \bar{C} (1)).

[For reactn. of C with R₂C=NMgX cpds. to yield N-chloroimines see (3); for reactn. of C with Schiff's bases see (5) (6).]

3:9287 (1) Chattaway, Backeburg, J. Chem. Soc. **123**, 2999-3003 (1923). (2) Taylor, MacMullen, Gammal, J. Am. Chem. Soc. **47**, 397-398 (1925). (3) Hauser, Humble, Haus, J. Am. Chem. Soc. **54**, 2476-2480 (1932). (4) Deanesly (to Shell Development Co.), U.S. 1,938,175, Dec. 5, 1933; Cent. **1934**, I 1709; C.A. **28**, 1053 (1934). (5) Fusco, Musante, Gazz. chim. ital. **66**, 258-264 (1936); Cent. **1936**, II 2341; C.A. **31**, 1777 (1937). (6) Musante, Fusco, Gazz. chim. ital. **66**, 639-648 (1936); Cent. **1937**, I 1674; C.A. **31**, 3459 (1937).

No physical constants on C appear to be recorded.

[For prepn. of \bar{C} from 2,3-epoxy-2-methylbutane (trimethylethylene oxide) [Beil. XVII-18] by addn. of HCl see (1).]

Č passed over clay at 350° and 18 mm. pressure yields (2) 2-methylbutadiene-1,3 (isoprene) (1:8020).

3:9290 (1) Henry, Compt. rend. **144**, 311 (1907); Rec. trav. chim. **26**, 430-433 (1907). (2) Badische Anilin und Soda Fabrik, Ger. 255,519, Jan 3, 1913; Cent. **1913**, I 476.

3:9295 5-CHLOROPENTANOL-1 $CH_2.(CH_2)_3.CH_2OH$ $C_5H_{11}OCl$ Beil. S.N. 24 $(\omega$ -Chloro-n-amyl alcohol)

B.P. 114° at 16 mm. (1)

[For prepn. of \bar{C} from α, ω -pentamethylene glycol (1:6519) with SOCl₂ (35% yield (2)) or with S₂Cl₂ (35% yield (1)) see indic. refs.]

 \tilde{C} with aliphatic mercaptans has apparently not been studied. [However, 5-chloro-n-amyl acetate (see below) with MeSH in MeOH/KOH yields (1) 5-hydroxy-n-amyl methyl sulfide, b.p. 121° at 16 mm., $D_4^{20} = 0.9846$, $n_a^{20} = 1.488185$ (corresp. N-phenylcarbamate, m.p. 43.5°); this prod. with SOCl₂ gives (75% yield (3)) 5-chloro-n-amyl methyl sulfide, b.p. 94° at 15 mm., $D_4^{20} = 1.0300$, $n_D^{20} = 1.48597$. — Similarly 5-chloro-n-amyl acetate with EtSH in alc. KOH gives (68% yield (4)) 5-hydroxy-n-amyl ethyl sulfide, b.p. 135° at 20 mm.; this prod. with SOCl₂ + diethylamline in CCl₄ gives (64% yield (4)) 5-chloro-n-amyl ethyl sulfide b.p. 122° at 25 mm. (4).]

 \tilde{C} with aromatic mercaptans has apparently not been studied. [However, 5-chloro-namyl acetate (see below) with thiophenol in alc. KOH gives (1) 5-hydroxy-n-amyl sulfide, ndls. from lt. pet., m.p. 31.5° (corresp. N-phenylcarbamate, m.p. 59°); this prod. with SOCl₂ + dimethylaniline in CHCl₃ gives (3) 5-chloro-n-amyl phenyl sulfide, b.p. 174° at 14 mm., sl. dec., 140° at 1 mm., $D_4^{20} = 1.1065$, $n_D^{20} = 1.56040$.]

 \bar{C} with Et₂NH appears never to have been studied. [However, the prod. to be expected, viz., 5-(diethylamino)pentanol-1, b.p. 131° at 23-24 mm. (5), 125° at 18 mm. (6), $D_{20}^{20} = 0.8842$ (5), $n_D^{20} = 1.4642$ (5), has been reported by other means; this prod. with SOCl₂ in CHCl₃ would be expected to yield 5-(diethylamino)-n-amyl chloride, but this cannot be isolated in the free state owing to its isomerization (7) to N-ethyl 1-ethyl-2-methylpyrrolidinium chloride.]

Č with morpholine gives (8) alm. quant. 5-(4-morpholinyl)pentanol-1, b.p. 133.0-133.5° at 5 mm., $D_4^{25} = 1.005$, $n_D^{24} = 1.4755$ (corresp. N-phenylcarbamate, m.p. 55.5-57.0° cor.) (8). — Č (1 mole) with N-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (2) in alm. 100% yield (as salt) N-(5-hydroxy-n-amyl)-N'-phenylpiperazine, m.p. 74.0-75.0° cor. (corresp. N-phenylcarbamate, m.p. 100.0-101.5° cor.) (2).

- 5-Chloro-n-amyl acetate: b.p. 103° at 18 mm., $D_4^{20}=1.0648$, $n_{\alpha}^{20}=1.43791$ (1). 5-Chloro-n-amyl N-phenylcarbamate: m.p. 72° (1).
- 3:9295 (1) Bennett, Heathcoat, J. Chem. Soc. 1929, 273-274. (2) Anderson, Pollard, J. Am. Chem. Soc. 61, 3439-3440 (1939). (3) Bennett, Heathcoat, Mosses, J. Chem. Soc. 1929, 2569-2571. (4) Bennett, Turner, J. Chem. Soc. 1938, 814-815. (5) Magidson, Strukow, Arch. Pharm. 271, 575 (1933). (6) von Braun, Ber. 49, 974 (1916). (7) Clemo, Hook, J. Chem. Soc. 1936, 608-609. (8) Anderson, Pollard, J. Am. Chem. Soc. 61, 3440-3441 (1939).

CHAPTER XXI

DIVISION C. LIQUIDS WITH BOILING POINTS REPORTED ONLY UNDER REDUCED PRESSURE

3:9300-3:9599 (C₆-C₈ inclusive)

(Arranged in sequence of empirical formulas)

--- 1,2,4,4,6,6-HEXACHLOROCYCLOHEXEN- O C₆O₂Cl₆ Beil. VII - 272
1-DIONE-3,5 | VII₁--("Hexachlororesorcinol") | Cl

B.P. 159-160° at 13-15 mm.

M.P. 115°

See 3:3470. Division A: Solids.

3:9300 3,4-DICHLOROHEXATETRAENE-1,2,4,5 C₆H₄Cl₂ Beil. S.N. 14

$$\begin{array}{c} Cl & Cl \\ \downarrow & \downarrow \\ CH_2 \hspace{-0.1cm} = \hspace{-0.1cm} C \hspace{-0.1cm} = \hspace{-0.1cm} C \hspace{-0.1cm} = \hspace{-0.1cm} CH_2 \end{array}$$

$$D_4^{20} = 1.1819 (1) \quad n_D^{20} = 1.5456 (1)$$

[For prepn. of \bar{C} from 1,3,4,6-tetrachlorohexadiene-2,4 (3:9306) with 15% excess KOH in abs. MeOH at 10-15° (a much larger amt. of 1,3,4-trichlorohexatriene-2,4,5 (3:9302) is also formed) see (1).]

3:9300 (1) Coffman, Carothers, J. Am. Chem. Soc. 55, 2040-2047 (1933).

3:9302 3,4,6-TRICHLOROHEXATRIENE-1,2,4 C₆H₅Cl₃ Beil. S.N. 13

B.P. 50° at 1 mm. (1)
$$D_4^{20} = 1.3132$$
 (1) $n_D^{20} = 1.5517$ (1)

[For prepn. of \bar{C} from 1,3,4,6-tetrachlorohexadiene-2,4 (3:9306) with 15% excess KOH in abs. MeOH at 10-15° (a small amt. of 3,4-dichlorohexatetraene-1,2,4,5 (3:9300) is also formed) see (1).]

3:9362 (1) Coffman, Carothers, J. Am. Chem. Soc. 55, 2040-2047 (1933).

3:9304 3,6-DICHLOROHEXATRIENE-1,3,4 C₆H₆Cl₂ Beil. S.N. 13

B.P. 45-46° at 3 mm. (1)
$$D_4^{20} = 1.1807$$
 (1) $n_D^{20} = 1.5195$ (1) 38° at 1 mm. (1)

[For prepn. of \bar{C} from hexadien-2,5-yne-3 (divinylacetylene) (2) with Cl_2 in CCl_4 at -50° (20-25% yield together with other products) or in small yield with HOCl see (1).] \bar{C} slowly polymerizes, changing in 3 months to a viscous sirup (1).

C on cat. hydrogenation in EtOAc yields n-hexane (1:8530), b.p. 69-70° (1).

C on further treatment with Cl₂ in CCl₄ at 5-10° gives (1) 1,3,4,6-tetrachlorohexadiene-2,4 (3:9306), b.p. 85-92° at 3 mm., $D_4^{20} = 1.4902$, $n_D^{20} = 1.5458$ (1).

Č with conc. HCl contg. Cu₂Cl₂ shaken for 12 hrs. at 27° adds HCl yielding (1) 3,3,6-trichlorohexadiene-1,4 (3:9308) q.v.

 \bar{C} refluxed with stirring for 8 hrs. with 6 pts. aq. contg. 2 moles Na₂CO₃ gives (1) chloride ion corresp. to one of the two initial halogenations together with a soft sticky resin. — \bar{C} with MeOH/KOH at 10–15° or with NaOMe in dry MeOH loses 1 HCl giving excellent yield (1) of 3-chlorohexatetraene-1,3,4,5 (3:7735).

C on oxidn. with aq. KMnO4 yields (1) chloroacetic acid (3:1370).

3:9304 (1) Coffman, Carothers, J. Am. Chem. Soc. 55, 2040-2047 (1933). (2) Nieuwland, Calcott, Downing, Carter, J. Am. Chem. Soc. 53, 4200-4202 (1931).

B.P. 84-89° at 2 mm. (1)

$$D_4^{20} = 1.4013$$
 (1) $n_{D_4}^{20} = 1.5465$ (1)

[For prepn. of \tilde{C} from hexadien-2,5-yne-3 (divinylacetylene) (2) with Cl_2 at -40° to -50° (together with other products) see (1).]

 \bar{C} treated directly with Cl_2 for 8 hrs. at 60-70° gives (23% yield (1)) 1,2,3,4,5,6-hexachlorohexene-3 (3:1220), m.p. 57-58° (1).

 \bar{C} refluxed for 8 hrs. with stirring with aq. Na₂CO₃ soln. gives (1) chloride ion corresp. to two of the initial four chlorine atoms. — \bar{C} with abs. MeOH/KOH at 10-15° loses HCl in each of two ways yielding (1) both 1,3,4-trichlorohexatriene-2,4,5 (3:9302) and 3,4-dichlorohexatetraene-1,2,4,5 (3:9300).

C on oxidn. with aq. KMnO₄ for 5 hrs. at 35-40° gives (1) chloroacetic acid (3:1370).

3:9306 (1) Coffman, Carothers, J. Am. Chem. Soc. 55, 2040-2047 (1933). (2) Nieuwland, Calcott, Downing, Carter, J. Am. Chem. Soc. 53, 4200-4202 (1931).

B.P. 110-112° at 2 mm.

M.P. 58-59°

See 3:1220. Division A: Solids.

3: 9308 3,3,6-TRICHLOROHEXADIENE-1,4 C₆H₇Cl₃ Beil S.N. 12

Cl Cl

CH₂=CH-CH-CH-CH₂

Cl

B.P. 100-103° at 4 mm. (1) $D_4^{20} = 1.3036$ (1) $n_D^{20} = 1.5585$ (1)

[For prepn. of C from 3,6-dichlorohexatriene-1,3,4 (3:9304) with conc. HCl contg. Cu₂Cl₂ by shaking for 12 hrs. at 27° see {1}.]

 \bar{C} refluxed with stirring for 7 hrs. with aq. Na₂CO₃ gives (1) chloride ion corresp. to three halogen atoms but the org. product was not identified.

C on oxidn, with alk, KMnO₄ for 4 hrs. at 30-40° yields (1) chloroacetic acid (3:1370).

3:9308 (1) Coffman, Carothers, J. Am. Chem. Soc. 55, 2040-2047 (1933).

3:9310 1,3-DICHLOROHEXADIENE-2,4

C₆H₈Cl₂ Beil. S.N. 12

(Divinylacetylene dihydrochloride)

Cl Cl CH₃—CH—CH—C—CH—CH₂

$$D_4^{20} = 1.1456 (1) \quad n_D^{20} = 1.5271 (1)$$

[For prepn. of $\bar{\mathbf{C}}$ (53% yield (1)) from divinylacetylene by shaking with 12 N HCl contg. Cu₂Cl₂ see (1).]

 $\bar{\rm C}$ refluxed with NaOAc + AcOH yields (by reactn. of one chlorine atom) 1-acetoxy-3-chlorohexadiene-2,4, b p. 84-85° at 3 mm., $D_4^{20}=1.0915, n_D^{20}=1.4890$ (1). — Similarly $\bar{\rm C}$ on htg. with MeOH/KOH yields (1) 1-methoxy-3-chlorohexadiene-2,4, n.p. 88-92° at 30 mm., $D_4^{20}=1.0239, n_D^{20}=1.4928$ (1).

 \bar{C} on oxidn. with aq. KMnO₄ in K₂CO₃ soln. gives (1) chloroacetic acid (3:1370) + acetic acid (1:1010).

Č with naphthoquinone-1,4 (1:9040) or with maleic anhydride (1:0625) gives (1) only a small amt. of dark gummy material.

3:9310 (1) Coffman, Nieuwland, Carothers, J. Am. Chem. Soc. 55, 2048-2051 (1933).

3:9312 3-CHLOROHEXADIENE-1,3

C₆H₉Cl Beil. S.N. 12

B.P. 68.2-69° at 117 mm. (1)
$$D_4^{20} = 0.9390$$
 (1) $n_D^{20} = 1.4770$ (1)

[For prepn. of \bar{C} from α -ethyl- β -vinylacetylene by shaking with conc. HCl contg. $Cu_2Cl_2 + NH_4Cl$ see (1).]

[For polymerization of \bar{C} see (1) (2).]

C on htg. with 2 pts. naphthoquinone-1,4 (1:9040) for 2 hrs. at 100° then suspended in alc. NaOH and aerated gives (1) 2-chloro-1-ethylanthraquinone, yel. ndls. from alc., m.p. 151-152° (1).

[For study of another chlorohexadiene obtd. from allyl chloride (3:7035) by actn. of NaNH₂ in liq. NH₃ see $\{3\}$.]

3:9312 (1) Jacobson, Carothers, J. Am. Chem. Soc. 55, 1624-1627 (1933). (2) Carothers, Coffman (to du Pont), U.S. 1,950,441, March 13, 1934; Cent 1934, II 1037; C.A. 28, 3270 (1934). (3) Kharasch, Nudenberg, Sternfeld, J. Am. Chem. Soc. 62, 2034-2035 (1940).

3:9314 1-CHLORO-3-METHYLPENTADIENE-1,2 C₆H₉Cl Beil. S.N. 12

B.P. 68-70° at 100 mm. (1)
$$D_4^{20} = 0.9562$$
 (1) $n_\alpha^{20} = 1.46967$ (1)

[For formn. of C from 3-methylpentyn-1-ol-3 (ethyl-ethynyl-methyl-carbinol) by shaking

with conc. HCl contg. $Cu_2Cl_2 + NH_4Cl$ see (1) (considerable 3-chloro-3-methylpentyne-1 (3:9322) is also formed).

Č on stdg. 8 months with Cu₂Cl₂, NH₄Cl, plus a few drops conc. HCl isomerized to 1-chloro-3-methylbutadiene-1,3 (3:7355) (1).

3:9314 (1) Favorskaya, Zakharova, J. Gen. Chem. (U.S.S R.) 10, 446-450 (1940); C.A. 34, 7844 (1940).

B.P. 62-63° at 100 mm. (1)
$$D_4^{20} = 0.9574$$
 (1) $n_2^{20} = 1.47714$ (1)

[For prepn. of \bar{C} from 1-chloro-3-methylpentadiene-1,2 (3:9314) by stdg. 8 months with Cu₂Cl₂, NH₄Cl, plus a few drops conc. HCl see (1).]

Č reacts with maleic anhydride (1:0625) to give a mixt. from which after hydrolysis two acids, one m.p. 218-220°, the other, m.p. 350-351°, are obtd. (1).

3:9316 (1) Favorskaya, Zakharova, J. Gen. Chem. (U.S.S R), 16, 446-450 (1940); C.A. 34, 7844 (1940).

B.P. 57-60° at 96 mm. (1)
$$D_4^{20} = 0.9437$$
 (1) $n_D^{20} = 1.4671$ (1)

[For prepn. of \bar{C} from 3-methylpenten-2-yne-4 in 22% yield (1) by shaking for 5½ hrs. at 20° with conc. HCl contg. Cu₂Cl₂ + NH₄Cl see (1).]

C on htg. with 2 pts. naphthoquinone-1,4 (1:9040) for 1 hr. at 100° gives (1) on cooling 2-chloro-3,4-dimethyltetrahydroanthraquinone, colorless ndls. from aq. acetone, m.p. 107° (1); suspension of this intermediate in dil. alc. NaOH and aeration until the purple solution becomes yellow gives (1) 2-chloro-3,4-dimethylanthraquinone, yel. cryst. from AcOH, m.p. 171.5° (1).

[For polymerization of C see (1) (2).]

3:3318 (1) Carothers, Coffman, J. Am. Chem. Soc. 54, 4075–4076 (1932). (2) Carothers, Coffman (to du Pont), U.S. 1,950,441, March 13, 1934; Cent. 1934, II 1038; C.A. 28, 3270 (1934).

3:9320 1-CHLOROHEXYNE-1
$$C_6H_9Cl$$
 Beil. S.N. 12 $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.Cl$

B.P. 47° at 55 mm. (1)
$$n_D^- = 1.43350$$
 (1)

[For prepn. of \bar{C} from hexyne-1 (1:8055) by conversion in liq. NH₃ to C₄H₉.C \equiv C \rightarrow K and treatment of this prod. in ether suspension with Cl₂ at -32° see (2) (3); for prepn. of \bar{C} from C₄H₉.C \equiv C.Na with benzenesulfonyl chloride in ether see (1) (4).]

Č in MeOH + HgO + BF₃ as specified (2) adds 2 MeOH giving in 83% yield 1-chloro-2.2-dimethoxyhexane, b.p. 77-80° at 14 mm., $D_{-}^{25} = 0.9873$, $n_{\rm D}^{25} = 1.4305$ (2).

3:9326 (1) Pflaum, Wenzke, J. Am. Chem. Soc. 56, 1106-1107 (1934). (2) Verbanc, Hennion, J. Am. Chem. Soc. 66, 1711-1713 (1938). (3) McCusker, Vogt, J. Am. Chem. Soc. 59, 1308-1309 (1937). (4) Truchet, Ann. chim. (10) 16, 309-416 (1931).

B.P. 55° at 130 mm. (1)
$$D_4^{20} = 0.9163$$
 (1) $n_D^{20} = 1.4330$ (1) (2) $51-52^\circ$ at 135 mm. (2) 0.9140 (2) $48-50^\circ$ at 100 mm. (3) 0.9141 (3) $n_\alpha^{20} = 1.42963$ (3)

[For prepn. of \bar{C} from 3-methylpentyn-1-ol-3 (ethyl-ethynyl-methyl-carbinol) by shaking with conc. HCl (40% yield (2)) best overnight (60% yield (1)); if the acid also contains $Cu_2Cl_2 + NH_4Cl$, \bar{C} is accompanied (3) by 1-chloro-3-methylpentadiene-1,2 (3:9314).] [Note that dry HCl at 0° reacts with the alc. only slightly while PCl₃ + pyridine gave a product difficult to purify (1).]

 $\bar{\mathbf{C}}$ with CH₃MgBr gives (66% yield (1)) 3,3-dimethylpentyne-1, b.p. 69° at 100 mm., $D_4^{20}=0.7610,\ n_D^{20}=1.4360;\ \bar{\mathbf{C}}$ with C₂H₅MgBr gives (61% yield (1)) 3-ethyl-3-methylpentyne-1, b.p. 88° at 100 mm., $D_4^{20}=0.7714,\ n_D^{20}=1.4386$. [In orig. paper these products are incorrectly numbered and named.]

3:8322 (1) Campbell, Eby, J. Am. Chem. Soc. **62**, 1798–1800 (1940). (2) K. N. Campbell, B. K. Campbell, Eby, J. Am. Chem. Soc. **60**, 2882–2884 (1938). (3) Favorskaya, Zakharova, J. Gen. Chem. (U.S.S.R.) **10**, 446–450 (1940); C.A. **34**, 7844 (1940).

B.P. 57-61° at 47 mm. (1)
$$n_{\rm D}^{20} = 1.4143$$
 (1)

[For prepn. of C (33% yield (1)) from 2-methylpropyn-3-ol-2 (trimethylpropargyl alcohol) with PCl₃ in dry ether see (1).]

 \ddot{C} in acetone refluxed 4 hrs. with K_2CO_3 and phenol gives (69% yield (1)) phenyl trimethylpropargyl ether, $n_D^{2D} = 1.3408$, but undistillable without decomposition (1).

3:9324 (1) Hurd, Cohen, J. Am. Chem. Soc. 53, 1074 (1931).

B.P. 90-93° at 10 mm. (1) (2)
$$D_{-}^{25} = 1.225$$
 (1) (2) $n_{D}^{25} = 1.4760$ (1) (2)

This compound was at first (2) thought to be 1,2,2-trichlorohexane but later (1) was established as C.

[For formn. of C from hexyne-1 (n-butylacetylene) (1:8055) with Cl₂ in aq. ter-BuOH, MeOAc, AcOH, or Ac₂O at 45° (2) or in 35% aq. HCl, 30% aq. H₂SO₄, 30% H₃PO₄, or 22% MeOH/HCl (1) see indic. refs.]

3:3326 (1) Norris, Hennion, J. Am. Chem. Soc. 62, 449-450 (1940). (2) Norris, Vogt, Hennion, J. Am. Chem. Soc. 61, 1460-1461 (1939).

Beil. S.N. 11

3:9330 1,2-DICHLOROHEXENE-1

55-57° at 25 mm. (2)

B.P. 129-131° at 10 mm. (1)
$$D_{-}^{25} = 1.370$$
 (1) $n_{D}^{25} = 1.4980$ (1)

[For formn. of C from hexyne-1 (n-butylacetylene) (1:8055) with Cl₂ in MeOAc at 45° (1) or in 35% aq. HCl, 30% aq. H₂SO₄, 30% aq. H₃PO₄, or 22% MeOH/HCl (2) (together with other products) see indic. refs.

3:9328 (1) Norris, Vogt, Hennion, J. Am. Chem. Soc. 61, 1460-1461 (1939). (2) Norris, Hennion, J. Am. Chem. Soc. 62, 449-450 (1940).

C6H10Cl2

[For prepn. of C (cis form) from 2-chlorohexene-1 (3:7530) with Cl₂ in CCl₄ at 35-40° (1) (yield 26.7% together with 25.4% of 1,1,2,2-tetrachlorohexane (3:9332)) (1) or in Ac₂O, or AcOH (2), see indic. refs.; for prepn. of C (trans form) from hexyne-1 (1:8055) with Cl2 in CCl4 or heptane in pres. of trace of SbCl5 (yield 19.6% together with 30.6% yield of 1,1,2,2-tetrachlorohexane (3:9332)) (1) or in aq. or ter-BuOH (2) see indic. refs.; for prepn. of C (both forms) from hexyne-1 (1:8055) + Cl₂ in conc. HCl, 30% H₂SO₄. 30% H₃PO₄, or MeOH satd. with HCl (together with other prods.) see (3) (4) or in MeOAc see (2).1

Neither cis nor trans forms of C will add HCl even in pres. of BiCl₂ (1) (3).

3:9330 (1) Hennion, Welsh, J. Am. Chem. Soc. 62, 1367-1368 (1940). (2) Norris, Vogt, Hennion, J. Am. Chem. Soc. 61, 1460-1461 (1939). (3) Norris, Hennion, J. Am. Chem. Soc. 62, 449-450 (1940). (4) Verbanc, Hennion, J. Am. Chem. Soc. 60, 1711-1713 (1938).

B.P. 99-101° at 14 mm. (1)
$$D_4^{25} = 1.3096$$
 (1) $n_D^{25} = 1.4888$ (1) $108-110^\circ$ at 10 mm. (1) $D_-^{25} = 1.320$ (2) 1.4890 (2)

[For formn. of C from hexyne-1 (n-butylacetylene) (1:8055) with Cl₂ in aq., MeOAc, Ac₂O, or AcOH at 45° (1), or in 35% aq. HCl, 30% aq. H₂SO₄, 30% aq. H₃PO₄, or 22% MeOH/HCl (3), or in CCl₄ + SbCl₅ (30.6% yield (1)) (together with other products) see indic. refs.; for formn. of C from 2-chlorohexene-1 (3:7530) with Cl2 in C6H6 + BiCl3 at 35-40° (25.4% yield $\ddot{C} + 26.7\%$ yield cis 1,2-dichlorohexene-1 (3:9330)) see (1).

3:9332 (1) Hennion, Welsh, J. Am. Chem. Soc. 62, 1367-1368 (1940). (2) Norris, Vogt, Hennion, J. Am. Chem. Soc. 61, 1460-1461 (1939). (3) Norris, Hennion, J. Am. Chem. Soc. 62, 449-450 (1940).

[This compound is as yet unrecorded: a dextrorotatory isomeride has been prepared (1) from levorotatory hexen-1-ol-3 with PCl₃ in pyridine. Although distd. at 20 mm., no b.p. was reported (1).]

3:9334 (1) Levene, Haller, J. Biol. Chem. 83, 595 (1929):

B.P. 59-61° at 60 mm. (1)
$$D_4^{24} = 0.900$$
 (1) $n_D^{24} = 1.435$ (1)

Two geometrical stereoisomers of this structure are theoretically possible, but only that with the cis configuration (\bar{C}) has as yet been recognized.

[For prepn. of \overline{C} from cis-hexen-3-ol-1 [Beil. I_1 -(229), I_2 -(486)] (1) (2) (b.p. 156.1° at 760 mm. (3), 63.3° at 14 mm. (3), $D_1^{21.6} = 0.8478$ (2), $n_D^{24.6} = 1.4373$ (2); 3,5-dinitrobenzoate, m.p. 44.5-46°, N-(α -naphthyl)carbamate, m.p. 80° (4)) with $SOCl_2$ + pyridine in CHCl₃ (72% yield (1)) see (1).]

 \bar{C} with NaI htd. 12 hrs. in acetone yields (1) 1-iodohexene-3, b.p. 62-63° at 12 mm., $D_4^{21} = 1.469$ (1).

C fails to react with activated Mg in dry ether, but the corresponding iodo cpd. (see above) yields the corresp. RMgI (1), and a mixt. of both can be used (5).

3:9336 (1) Ruzicka, Schinz, Helv. Chim. Acta 17, 1606 (1934). (2) Stoll, Rouvé, Helv. Chim. Acta 21, 1542-1547 (1938). (3) von Rechenberg, J. prakt. Chem. (2) 101, 120 (1920). (4) van Romburgh, Proc. Acad. Sci. Amsterdam 22, 758-761 (1920); C.A. 14, 2780 (1920). (5) Stoll, Bolle, Helv. Chim. Acta 21, 1551 (1938).

3:9338
$$d,l$$
4-CHLORO-3-METHYLPENTENE-2 Cl CH₃ C₆H₁₁Cl Beil I — (α,β,γ -Trimethylallyl chloride) CH₃—C—C—CH—CH₃ I₁-(90) I₂—

B.P. 41-43° at 31 mm. (1)

Note: although the product is as yet unrecognized, \vec{C} by virtue of allylic transposition may conceivably be in equilibrium with its synionic isomer 2-chloro-3-methylbutene-3.

[For prepn. of \bar{C} (75-80% yield (1)) from 3-methylpenten-2-ol-4 [Beil. I-445] by distn. with 6 N HCl see (1).]

 \bar{C} with quinoline at 170° loses HCl giving (66% yield {1}) 3-methylpentadiene-1,3 [Beil. I₁-(118), I₂-(231)], b.p. 76°.

3:9338 (1) Abelmann, Ber. 43, 1579, 1583 (1910).

B.P. 74-78° at 10 mm. (1)

Heavy oil with agreeable odor. — Insol. aq.

[For prepn. of C (50% yield (1)) from N-benzoyl-2-methylpiperidine (N-benzoyl-α-pipecoline) [Beil. XX-97] with PCl₅ (1), from hexanediol-1,5 [Beil. I-484] or the corresponding internal ether, 2-methyltetrahydropyran [Beil. XVII-13], by repeated treatment with HCl (2), or from hexamethylenediamine [Beil. IV-269] with NOCl (3) see indic. refs.]

3:9340 (1) von Braun, Sobecki, Ber. 44, 1042-1043 (1911). (2) Lipp, Ber. 18, 3283-3286 (1885). (3) Ssolonina, J. Russ. Phys.-Chem. Soc. 30, 606-632 (1898); Cent. 1899, I 25.

3: 9342 2,2-DICHLOROHEXANE Cl
$$C_0H_{12}Cl_2$$
 Beil. S.N. 10
$$CH_3.CH_2.CH_2.CH_2.CH_2$$

$$D_4^{25} = 1.0150 (1) \quad n_D^{25} = 1.4353 (1)$$

[For formn. of \bar{C} (40% yield (1) together with 20% yield (1) of 2-chlorohexene-1 (3:7530)) from hexyne-1 (1:8055) with HCl gas + BiCl₃ see (1).]

 \bar{C} htd. at 95° with soln. of solid KOH in *n*-propyl alc. gives (60.5% yield (1)) 2-chlorohexene-1 (3:7530).

3:9342 (1) Hennion, Welsh, J. Am. Chem. Soc. 62, 1367-1368 (1940).

$$D_{-}^{20} = 1.055 (1) \quad n_{\rm D}^{20} = 1.4490 (1)$$

Colorless liq. with sweetish odor.

[For prepn. of \bar{C} from hexene-3 (1:8270) with Cl₂ in CHCl₃ at -30° to -40° (67% yield (1)), or with SO₂Cl₂ at 40-50° (1), or with PCl₅ in CCl₄ (1) see (1).]

3:9344 (1) Spiegler, Tinker, J. Am. Chem. Soc. 61, 941-942 (1939).

3: 9346
$$d$$
, l -2,3-DICHLORO-2-METHYLPENTANE $C_6H_{12}Cl_2$ Beil. 1 — H CH₃ I_1 — CH₈.CH₂—C—C—CH₈ I_2 —(111)

B.P. 82-84° at 42 mm. (1)

[For formn. of Č from 2-methylpentene-2 (1:8275) with Cl₂ in CHCl₃ (some 2-(or 3)-chloro-2-methylpentane (3:7490) is also formed) see (1).]

3:9346 (1) van Risseghem, Bull. soc. chim. Belg. 32, 149-150 (1923).

3:9348 d,l-1-CHLORO-3-METHYLPENTANE

Beil, S.N. 10

Č itself seems to be unreported.

[The dextrorotatory isomer of C has, however, been studied (1) (2) (3). For prepn. of it from dextrorotatory 3-methylpentanol-1 with SOCl₂ see (1); b.p. 73° at 100 mm. (1), $D_4^{27} = 0.892, n_D^{25} = 1.4210$ (1). — With Mg in dry ether this isomer yields (2) (3) RMgCl which with CO2 gives (2) (3) dextrorotatory 3-methylhexanoic acid-6, b.p. 115° at 16 mm. (2) (3), $D_4^{22} = 0.923$ (3).]

3:9348 (1) Levene, Marker, J. Biol. Chem. 91, 86 (1931). (2) Levene, Marker, J. Biol. Chem. 95, 11 (1932). (3) Levene, Marker, J. Biol. Chem. 95, 161 (1932).

3:9350 d.l-2-CHLORO-3-METHYLPENTANE

C₆H₁₃Cl CH₃ H

Beil. S.N. 10

(sec.-Butyl-methyl-carbinyl chloride)

CaH5O2Cl

B.P. 71.1-73.3° at 160 mm. (1)

[For formn. of C (together with other products) in reaction of 2-ethylbutanol-1(1:6223) with $HCl + ZnCl_2$ see (1)].

 \bar{C} with Mg + dry ether yields (1) RMgCl which with O₂ yields (1) 3-methylpentanol-2 (1:6202); this alc. upon oxidn. with CrO₃/H₂SO₄ yields (1) 3-methylpentanone-2 (2,4dinitrophenylhydrazone, m.p. 71.2° (2), 70.5-72.5° (1)).

3:9350 (1) Whitmore, Karnatz, J. Am. Chem. Soc. 60, 2535 (1938). (2) Drake, Veitch, J. Am. Chem. Soc. 57, 2624 (1935).

3-CHLOROCATECHOL

VI₁-(388)

B.P. 110-111° at 11 mm.

M.P. 47°

See 3:0745. Division A: Solids.

4-CHLOROCATECHOL

Beil. VI - 783 VI₁-(389)

VI₂-(787)

B.P. 139° at 10 mm.

M.P. 90-91°

See 3:2470. Division A: Solids.

3:9351 DIMETHYL CHLOROMALEATE
$$C_6H_7O_4Cl$$
 Beil. II — $II_{1-}(305)$ $II_{2-}(646)$

B.P. 106.5° cor. at 18 mm. (1)
$$D_{4\text{vac.}}^{25} = 1.2775$$
 (1) $D_{4}^{20} = 1.276$ (2) $n_{\text{He}}^{20} = 1.461$ (2) $D_{4}^{18 9} = 1.2775$ (2) $n_{\text{He}}^{18 9} = 1.46170$ (2)

[For prepn. of C from chloromaleic anhydride (3:0280) with abs. MeOH + conc. H₂SO₄ in cold see (2).]

3:9351 (1) Walden, Swinne, Z. physik. Chem. 79, 741 (1912). (2) von Auwers, Harres, Ber. 62, 1681, 1686-1687 (1929).

3:9352 ADIPYL (DI)CHLORIDE
$$C_6H_8O_2Cl_2$$
 Beil. II - 653 II_{1^-} (277) C_1 C_1 C_1 C_1 C_2 C_3 C_4 C_5 C_6 C_7 C_8 C

[For prepn. of \tilde{C} from adipic acid (1:0775) with PCl₅ (5) (yield: 79% (4), 50% (1)), with PCl₃ (5) (82% yield (6)), with PCl₃ + $ZnCl_2$ (76% yield (4)), or with SOCl₂ (yield: 100% (2), 90% (3), 81% (4), 60% (7)) (8) (9) (10) (19) see indic. refs.]

[For study of reactn. of \tilde{C} with Cl_2 see (11); of \tilde{C} with Br_2 see (11) (12) (13) (19); with diethyl sodio-malonate see (14); with MeZnI or EtZnI see (7); with triethylamine or with pyridine in C_6H_6 see (15).]

[\bar{C} with AlCl₃ + C₆II₆ gives (75–81% yield (9)) (8) (1) (6) (16) 1,6-diphenylhexanedione-1,6 (dibenzoylbutane) [Beil. VII-777, VII₁-(404)], cryst. from alc., m.p. 106–107° (9), 107° (6) (16) (note that some \$\delta\$-benzoyl-n-valeric acid [Beil. X₁-(339)], m.p. 78° (16) 77–78° (17) (p-nitrophenylhydrazone, m.p. 187° (17), semicarbazone, m.p. 187° (17)), is, also formed). — For reactn. of \bar{C} with AlCl₃ + toluene, m-xylene, p-xylene, mesitylene, (18) or chlorobenzene (8) see indic. refs]

Č on hydrolysis yields adipic acid (1:0775) (for the diamide, dianilide, di-p-toluidide, and other derivs. corresp. to Č see 1:0775).

3:9352 (1) Etaix, Ann. chim. (7) 9, 369-377 (1896). (2) Fröschl, Maier, Monatsh. 59, 271-272 (1932). (3) Lieser, Macura, Ann. 548, 226-254 (1941); C.A. 37, 4699 (1943). (4) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (5) Ruggli, Ann. 399, 179-180 (1913). (6) Borsche, Wollemann, Ber. 45, 3715-3716 (1912). (7) Blaise, Koehler, Bull. soc. chim. (4) 5, 683 (1909). (8) Skraup, Guggenheimer, Ber. 58, 2495 (1925). (9) Fuson, Walker, Org. Syntheses, Coll. Vol. 2 (1st ed.), 169-171 (1943); 13, 32-34 (1933). (10) Meyer, Jäger, Ann. 347, 49 (1906). (11) Ingold, J. Chem. Soc. 119, 961 (1921). (12) Bernton, Ing, Perkin, J. Chem. Soc. 125, 1500 (1924). (13) Holmberg, Müller, Ber. 58, 1602 (1925). (14) Scheiber, Lungwitz, Ber. 42, 1323 (1909). (15) Wedekind, Miller, Weinand, J. prakt. Chem. (2) 109, 161-174 (1925). (16) Bauer, Ann. chim. (9) 1, 343-344, 394 (1914). (17) von Auwers, Trippmann, Ber. 48, 1217 (1915). (18) Borsche, Ber. 53, 2079-2080 (1919). (19) Guha, Sankaran, Org. Syntheses 26, 57-80 (1946).

1290

II₂-(557)

DIMETHYL d,l-α,α'-DICHLORO-

l,l-α,α'-DICHLORO-COOCH₃

C₆H₈O₄Cl₂ Beil. II — II₁-(267)

COOCH8

B.P. 116.5-120.5° cor. at 12.5 mm.

M.P. 43° '

See 3:0485. Division A: Solids.

SUCCINATE

2-CHLOROCYCLOHEXANONE

 $\mathrm{C}_{\mathrm{H_2}}$

B.P. 88-90° at 16 mm.

M.P. 23-24°

 $D_{15}^{20} = 1.161$

 $n_{\rm D}^{20} = 1.4825$

Beil. VII- 10

See 3:0120. Division A: Solids.

3:9360 3-CHLOROCYCLOHEXANONE

 $\begin{array}{c} O & C_6H_9OCl \\ \parallel & \\ C & \\ H_2C & CH_2 \\ H_2C & CH_2 \\ \end{array}$

B.P. 91-92° at 14 mm. (1).

Colorless oil. — \bar{C} does not fume in air or attack skin (1).

[For prepn. from cyclohexen-1-one-3 + dry HCl in dry ether see (1).]

3:9360 (1) Kötz, Grethe, J. prakt. Chem. (2) 80, 503-504 (1909).

3:9364 4-CHLOROCYCLOHEXANONE

 C_6H_9OCl

Beil. S.N. 612

H₂C CH₂ H₂C CH₂

B.P. 95° at 17 mm. (1)

 $n_{\rm D}^{20} = 1.4867 \, (1)$

Liq. with penetrating odor (1).

[For prepn. from 4-chlorocyclohexanol-1 (3:9376) by oxidn. with CrO₂ see (1) (3).]

1291

4-Chlorocyclohexanone-1 semicarbazone: from \bar{C} + semicarbazide HCl + KOAc (1); cryst. from aq., m.p. 191° (block) (1); 196° (2).

3:9364 (1) Sabetay, Palfray, Bull. soc. chim. (4) 43, 909 (1928). (2) Palfray, Rothstein, Compt. rend. 190, 944 (1930). (3) Backer, Tamsma, Rec. trav. chim. 57, 1205-1206 (1938).

3:9368 ETHYL
$$\alpha$$
-CHLOROISOCROTONATE $C_6H_9O_2Cl$ Beil. II — CH_8 — C — H II₁— II_2 —(396)

B.P. 75° at 30 mm. (1)
$$D_4^{20} = 1.100$$
 (1) $n_{\text{He}}^{20} = 1.4530$ (1) $D_4^{18} = 1.1021$ (1)

[See also ethyl α -chlorocrotonate (3:8523).]

[For prepn. of \tilde{C} from Ag salt of α -chloroisocrotonic acid (3:1615) with C_2H_5I see (1); note that attempts to prepare \tilde{C} from α -chloro-isocrotonic acid (3:1615) in EtOH with conc. H_2SO_4 at 100° give only (1) the stereoisomeric ethyl α -chlorocrotonate (3:8523).]

 \bar{C} with alc. KOH at room temp. gives upon acidification α -chloroisocrotonic acid (3:1615), m.p. 66°.

3:9368 (1) von Auwers, Ann. 432, 61-62 (1923).

3:9372 sec.-BUTYL TRICHLOROACETATE
$$C_0H_9O_2Cl_3$$
 Beil. S.N. 160 $CH_3CH_2CH.O.CO.CCl_3$ CH_3

B.P. 88-89° at 19 mm. (1)
$$D_4^{25} = 1.252$$
 (1) $n_D^{25} = 1.4440$ (1)

[For prepn. (82-89% yield) from butanol-2 (1:6155) + trichloroacetic ac. (3:1150) see (1).]

[For study of chlorination of C see (1).]

3:9372 (1) Waddle, Adkins. J. Am. Chem. Soc. 61, 3361-3364 (1939).

— ter-BUTYL TRICHLOROACETATE C₆H₉O₂Cl₃ Beil. S.N. 160 Cl₂C.CO.O.C₄H₉

B.P. 37° at 1 mm. M.P. 25.5°
$$D_4^{25} = 1.2363$$
 $n_-^{25} = 1.4398$

See 3:0138. Division A: Solids.

3:9373 METHYL γ -(CHLOROFORMYL)-n-BUTYRATE $C_6H_9O_3Cl$ Beil. S.N. 172 (γ -(Carbomethoxy)-n-butyryl chloride) CH_2 — CH_2 — $COOCH_8$ CH_2 —C1

Note that C is both an acid chloride and an ester.

[For prepn. of C from methyl hydrogen glutarate [Beil. II₂-(565)] (b.p. 158° at 27 mm. (1), 153° at 20 mm. (2), 150-151° at 10 mm. (3), $D_{-}^{18} = 1.164$ (3), $n_{D}^{18} = 1.4392$ (3), itself obtd. from glutaric anhydride with MeOH (2) (1)) with SOCl2 at 20° for 12 hrs., then at 30° for 3 hrs. (yield 93% (1), 87% (5)) (2), see indic. refs.]

1292

[For behavior of \tilde{C} with EtMgI in toluene followed by hydrolysis giving δ -keto-n-heptanoic acid, m.p. 50° see (2); for reaction of C with atoxyl see (1).]

[For use of C in Friedel-Crafts type of reaction see (4).]

[\bar{C} on catalytic hydrogenation as directed gives (70–85% yield (5)) methyl γ -formyl n-butyrate, b.p. 100-103° at 23 mm. (corresp. 2,4-dinitrophenylhydrazone, m.p. 105-106°) (5).1

3:9373 (1) Morgan, Walton, J. Chem. Soc 1932, 277. (2) Clutterbuck, Raper, Biochem. J. 19, 393-394 (1925). (3) Fourneau, Sabetay, Bull. soc. chim. (4) 45, 838-839 (1929). (4) Robinson, Walker, J. Chem. Soc. 1937, 62, 66-67. (5) Harris, Wolf, Mozingo, Arth, Anderson, Easton, Folkers, J. Am. Chem. Soc. 67, 2098 (1945).

TRICHLOROPARALDEHYDE O
$$C_6H_9O_3Cl_3$$
 Beil. XIX - 386 XIX₁-(807)
$$ClCH_2-CH HC-CH_2Cl$$

$$U$$

$$ClCH_2-CH HC-CH_2Cl$$

$$CH_2Cl$$

B.P. 142° at 10 mm.

M.P. 87-87.5° cor.

See 3:2300. Division A. Solids.

B.P. 93-94° at 26 mm. (1)

76°

3: 9374
$$cis$$
-2-CHLOROCYCLOHEXANOL-1 OH C_6H_{11} OCl Beil. S.N. 502 $(cis$ -Cyclohexene chlorohydrin)

H₂C H₂C CH₂

CH₂

B.P. 93-94° at 26 mm. (1)

 $D_0^{25} = 1.1261$ (1) $n_D^{25} = 1.4860$ (1)

 $D_0^{16} = 1.150$ (2) $n_D^{16} = 1.4860$ (2)

at 15 mm. (2) [See also trans-2-chlorocyclohexanol-1 (3:0175).]

[For prepn. of C from 2-chlorocyclohexanone-1 (3:0120) by reductn, with isopropyl MgCl, ter-butyl MgX, or cyclohexanyl MgX (the prod. is actually a mixt. of C (72-73%) with the trans isomer (27-28%) see (1); for formn. of C from cyclohexene (1:8070) with HOCl see (2) cf. (5) (this method is claimed by (2) to yield some C, but according to (1) gives solely the trans isomer).

Č with aq. NaOH gives on refluxing (76% yield (1)) cyclohexanone (1:5465) (note difference from the trans isomer which gives cyclohexene oxide). — C with conc. HCl or with ZnCl₂ in ether shows no tendency to convert to the trans isomer (1).

(Note: the following derivatives are listed as trans on the assumption of inversion during formation.)

- ----trans-2-Chlorocyclohexanyl acetate: consts. not reported (4).
- -----trans-2-Chlorocyclohexanyl N-phenylurethane: m.p. 56-59° (3). [From Č + phenyl isocyamate in lt. pet. (3).]
- ——trans-2-Chlorocyclohexanyl N-(α-naphthyl)carbamate: m.p. 165° (1). [From C with α-naphthyl isocyanate htd. 4 hrs. at 100° (1).]

3:9374 (1) Bartlett, J. Am. Chem. Soc. 57, 224-227 (1935). (2) Godchot, Mousseron, Granger, Compt. rend. 200, 748-749 (1935). (3) Cook, Hewitt, Lawrence, J. Chem. Soc. 1936, 75. (4) Winstein, Buckles, J. Am. Chem. Soc. 65, 616 (1943). (5) Newman, Van der Werf, J. Am. Chem. Soc. 67, 235 (1945).

B.P. 104-106° at 45 mm.

M.P. 29°

 $D_{-}^{16} = 1.146 \quad n_{\rm D}^{16} = 1.4850$

See 3:0175. Division A: Solids.

B.P. 106° at 14 mm. (1) 105° at 12 mm. (2) $D_4^{17} = 1.1435 (2) \quad n_D^{17} = 1.4930 (2)$

Colorless oil.

[For prepn. from quinitol (cyclohexanediol-1,4) [Beil. VI-74] by htg. with conc. HCl see (1) (2); for formn. from resorcitol (cyclohexanediol-1,3) [Beil. VI-740] with conc. HCl see (3).]

[$\bar{\mathbf{C}}$ on refluxing 2 days in dry ether with Na yields (3) (by loss of HCl and rearr.) cyclohexen-3-ol-1, b.p. 67-68° at 14 mm., $D_{20}^{20}=0.9425$, $n_{\mathrm{D}}^{20}=1.4627$; N-phenylcarbamate, m.p. 82° (block) (1).] — [$\bar{\mathbf{C}}$ with powd. KOH in ether is only partially transformed to cyclohexen-3-ol-1, even on boiling (1).]

C on oxidn. with CrO₃ yields (1) (3) 4-chlorocyclohexanone-1 (3:9364).

[The acetyl deriv. of \bar{C} is an oil, b.p. 111–112° cor. at 18 mm., $D_4^{18.5} = 1.1282$, $n_D^{18.5} = 1.4659$ (2).]

1 4-Chlorocyclohexyl N-phenylcarbamate: m.p. 99° (2).

3:9376 (1) Sabetay, Palfray, Bull. soc. chim. (4) 43, 908-909 (1928). (2) Palfray, Rothstein, Compt. rend. 189, 701-703 (1929). (3) Palfray, Rothstein, Compt. rend. 199, 942-945 (1930).

3: 9380 n-AMYL CHLOROFORMATE C₆H₁₁O₂Cl Beil. S.N. 199 (n-Amyl chlorocarbonate) n-C₈H₁₁O.CO.Cl

B.P.
$$60-62^{\circ}$$
 at 15 mm. (1) $n_{\rm D}^{18}=1.4181$ (2) $53.4-54.5^{\circ}$ at 11 mm. (2)

 \tilde{C} on htg. with quinoline dec. at 72° (3) into *n*-amyl chloride (3:7460) + CO_2 ; \tilde{C} on htg. with $ZnCl_2$ gives these + amylene (and its polymers) + HCl (4).

3:9380 (1) Eastman Organic Chemicals, List No. 36 (1946). (2) Kohlrausch, Sabathy, Monatsh. 72, 307 (1939). (3) Carré, Bull. soc. chim. (5) 3, 1069 (1936). (4) Underwood, Baril, J. Am. Chem. Soc. 57, 2729 (1935).

3: 9384 n-PROPYL d,l- α -CHLOROPROPIONATE $C_6H_{11}O_2Cl$ Beil. S.N. 162 H n- C_3H_7 .O CO.C.CH₃ Cl

B.P. —
$$D_4^{20} = 1.0478 \, (1) \quad n_D^{20} = 1.4218 \, (1)$$

3:9384 (1) Schjanberg, Z. physik. Chem. A-172, 230 (1935).

3:9388 ISOPROPYL β -CHLOROPROPIONATE $C_6H_{11}O_2C_1$ Beil. S.N. 162 $(CH_3)_2CH.O.CO \ CH_2 \ CH_2C_1$

B.P. –
$$D_4^{20} = 1.0503 (1) \quad n_D^{20} = 1.4230 (1)$$

3:9388 (1) Schianberg, Z. physik. Chem. A-172, 231 (1935).

3:9390 β-(β-HYDROXYETHOXY)ETHYL CHLOROACETATE Beil. S.N. 160
(Diethylene glycol mono (chloroacetate)) C₆H₁₁O₄Cl

HOCH₂.CH₂.O.CH₂.CO.CO.CH₂Cl

B.P. 130-142° at 0.2 mm. (1)

Viscous oil, insol. in aq. but slowly dissolving when shaken with aq. because of hydrolysis to diethylene glycol (1:6525) + chloroacetic ac. (3:1370) (1).

3:9390 (1) Meerwein, Sönke, J. prakt. Chem. (2) 137, 317 (1933).

3:9394 FORMALDEHYDE $\beta_1\beta'$ -DICHLORO- $C_6H_{12}O_2Cl_2$ Beil. I — ISOPROPYL-ETHYL-ACETAL (ClCH₂)₂CH.O.CH₂.O.C₂H₆ I₁— ($\beta_1\beta'$ -Dichloroisopropyl-ethyl-formal) I₂-(640)

B.P. 96-98° at 16 mm. (1)
$$D_{17}^{17} = 1.182$$
 (2) $n_{\rm D}^{17} = 1.44912$ (2) 90-91° at 12 mm. (2)

Colorless liq. with ethereal odor.

[For prepn. of \tilde{C} from epichlorohydrin (3-chloro-1,2-epoxypropane) (3:5358) + chloromethyl ethyl ether (3:7195) see (1) (2).]

3:9394 (1) Blanchard, Bull. soc. chim. (4) 39, 1265 (1926). (2) Blanchard, Bull. soc. chim. (4) 49, 285 (1931).

3:9395 6-CHLOROHEXANOL-1 CH₂.(CH₂)₄.CH₂OH C₆H₁₃OCl Beil. S.N. 24 (ω-Chloro-n-hexyl alcohol)

B.P. 116-117° at 19 mm. (1) 112° at 17 mm. (1)

[For prepn. of \bar{C} from α,ω -hexamethylene glycol [Beil. I-484, I₁-(251), I₂-(551)] (b.p. 145-149° at 18 mm. (2)) with conc. HCl as directed (1) cf. (2) (yields: 65% (3)) see indic. refs.]

[C with KSEt in alc. htd. ½ hr. gives (1) ethyl 6-hydroxy-n-hexyl sulfide, colorless oil, b.p. 134-136° at 17 mm.; this prod. with SOCl₂ + diethylaniline in CCl₄ at 55° gives (1) 6-chloro-n-hexyl ethyl sulfide, b.p. 128-131° at 26 mm.]

Č with thiophenol has not been studied [however, 6-chloro-n-hexyl acetate with excess thiophenol in aq. NaOH htd. 3 hrs. gives (85% yield (2)) 6-hydroxy-n-hexyl phenyl sulfide, pl. from lt. pet., m.p. 43°; this prod. with SOCl₂ + diethylaniline in CCl₄ yields (2) 6-chloro-n-hexyl phenyl sulfide, m.p. 7-8° (undistillable)].

[C (1 mole) with Et₂NH (2 moles) in s.t. at 100° for 16 hrs. gives (58% yield (4)) 6-(diethylamino)hexanol-1, b.p. 96-99° at 2 mm. (4); this prod. with SOCl₂ in CHCl₃ gives (39% yield (4)) 6-(diethylamino)-n-hexyl chloride, b.p. 118-120° at 19 mm

 $\bar{\rm C}$ with morpholine gives (5) alm. quant. 6-(4-morpholinyl)hexanol-1, b.p. 146.0-147.0° at 5 mm., $D_{\rm A}^{25}=0.9884$, $n_{\rm D}^{25}=1.4750$ (corresp. N-(α -naphthyl)carbamate, m.p. 71.0-72.0° cor.) (5). — $\bar{\rm C}$ (1 mole) with N-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (3) in alm. 100% yield (as salt) N-(6-hydroxy-n-hexyl)-N-phenylpiperazine, m.p. 65.5-67.0° cor. (corresp. N-phenylcarbamate, m.p. 91.5-93.0° cor.) (3).

——6-Chloro-n-hexyl acetate: oil, b.p. 113-116° at 17 mm. [Prepd. indirectly (2).] © 6-Chloro-n-hexyl N-phenylcarbamate: m.p. 49-50° (3).

3:9395 (1) Bennett, Turner, J. Chem. Soc. 1938, 813-815. (2) Bennett, Mosses, J. Chem. Soc. 1931, 1698-1699. (3) Anderson, Pollard, J. Am Chem. Soc. 61, 3439-3440 (1939). (4) Work. J. Chem. Soc. 1942, 428. (5) Anderson, Pollard, J. Am. Chem. Soc. 61, 3440-3441 (1939).

3: 9396 *n*-BUTYL α -CHLOROETHYL ETHER H C_8H_{13} OCl Beil. S.N. 78 (α -Chloroethyl *n*-butyl ether) CH₃ C.O.*n*-C₄H₉

B.P. $48.9-50.3^{\circ}$ cor. at 11 mm. (1) $D_4^{20} = 0.9335$ (1) $n_D^{20} = 1.4155$ (1)

C decomposes considerably if distd. at ord. press. (2).

[For prepn. (95% yield (1)) from paraldehyde (1:0170) + n-butyl alc. (1:6180) + dry HCl see (1).]

C on stdg. polymerizes to dark tarry residue (1).

 $[\bar{C} \text{ on bromination yields } \alpha, \beta\text{-dibromoethyl } n\text{-butyl ether (2).}]$

 \bar{C} on shaking with aq. yields acetaldehyde (1:0100), n-butyl alc. (1:6180), + HCl.

3:9396 (1) Henze, Murchison, J. Am. Chem. Soc. 53, 4077-4079 (1931). (2) Dykstra, Lewis, Boord, J. Am. Chem. Soc. 52, 3399-3400 (1930).

2,5-DICHLOROBENZAL (DI)CHLORIDE C₇H₄Cl₄ Beil. V - 302 V₁— CHCl₂ V₂-(234)

B.P. 118-120° at 14 mm.

M.P. 43°

See 3:0490. Division A: Solids.

3:9397 2,3,4,5-TETRACHLOROBENZAL (DI)CHLORIDE C7H2Cl6 Beil. S.N. 466

No physical constants on C are available.

[For prepn. of \bar{C} from 2,3,4,5-tetrachlorotoluene (3:2710) with Cl_2 see (1).]

 \bar{C} on hydrolysis (presumably with strong H_2SO_4) gives (1) 2,3,4,5-tetrachlorobenzal-dehyde (3:3140).

3:337 (1) Chem. Fabrik Griesheim-Elektron, Brit. 251,511, May 27, 1926; Cent. 1926, II 2355; C.A. 21, 1361 (1927); French 603,650, April 26, 1926; Cent. 1926, II 2355; not in C.A.

3:9398 2,6-DICHLOROBENZAL (DI)CHLORIDE . C₇H₄Cl₄ Beil. V-302 V₁— V₂—

B.P. 124-126° at 16 mm. (1)

Oil with penetrating odor.

[For prepn. of \bar{C} from 2,6-dichlorobenzaldehyde (3:1690) with PCl₅ (90% yield (1)) (2) (note the intermediate form. of bis-(α ,2,6-trichlorobenzyl) ether (2)) or from 2,6-dichlorotoluene (3:6270) with Cl₂ (4) see indic. refs.]

 \bar{C} is extremely resistant to hydrolysis with either acid or alkali or conc. H₂SO₄; for details see (3) (5).

[For condens. of \bar{C} with various phenols (e.g., 2,4-dichlorophenol (3:0560)) in prepn. of mothproofing agts. see (6).]

3:9398 (1) Lock, Asinger, Monatsh. 59, 157-160 (1932). (2) Olivier, Weber, Rec. trav. chim. 52, 169-174 (1933). (3) Olivier, Weber, Rec. trav. chim. 53, 875, 882, 889 (1934). (4) Geigy, Ger. 213,503, Oct. 14, 1909; Cent. 1909, II 1515. (5) Asinger, Lock, Monatsh. 62, 326, 328, 337 (1933). (6) Weiler, Wenk, Stotter (to I.G.), Ger. 540,208, Dec. 12, 1931; Brit. 337,832, Dec. 4, 1930; French 39,334, Oct. 12, 1931; Cent. 1932, I 3013.

3: 9399 2,4-DICHLOROBENZAL (DI)CHLORIDE C7H4Cl4 Beil. S.N. 466
Cl CHCl2

This compound appears to be unreported. However, for many isomeric compounds see the Formula Index.

B.P. 48-49° at 28 mm. (1)
$$n_{\rm D}^{15}=1.4812$$
 (1) $31-32^{\circ}$ at 10 mm. (1)

[For prepn. of \bar{C} from dimethyl-vinylethynyl-carbinol (b.p. 58-59° at 13 mm., $D_4^{15}=0.8925, n_D^{15}=1.4786$ (2), see (1).]

[$\bar{\mathbf{C}}$ with phenol + KOH in acetone refluxed 3 hrs. yields (3) about equal amts. of 2-methylhexadien-1,5-yne-3 (α -isopropenyl- β -vinyl-acetylene) + the phenyl ether of $\bar{\mathbf{C}}$ (dimethyl-phenoxy-vinylethynyl-methane), b.p. 105.5° at 7 mm., $D_4^{16} = 0.9714$, $n_D^{16} = 1.5350$ (3).]

3:9492 (1) Nazarov, Bull. acad. sci. U.R.S.S., Classe sci. math. nat., Ser. chim. 1938, 695-705; Cent. 1939, II 3403; C.A. 33, 5682 (1939). (2) Nazarov, Bull. acad. sci. U.R.S.S., Classe sci. math. nat., Ser. chim. 1938, 683-694; Cent. 1939, II 3402; C.A. 33, 5682 (1939). (3) Nazarov, Elizarova, Bull. acad. sci. U.R.S.S., Classe sci. chim. 1941, 423-430; C.A. 36, 1298 (1942).

3:9406 1-CHLORO-3-ETHYLPENTADIENE-1,2 Cl C7H11Cl Beil. S.N. 12

B.P. 85-88° at 100 mm. (1)
$$D_4^{18.5} = 0.9297 \text{ (1)} \quad n_{\alpha}^{18.5} = 1.47036 \text{ (1)} \\ D_4^{16.5} = 0.9329 \text{ (1)} \quad n_{\beta}^{18.5} = 1.48431 \text{ (1)}$$

[For prepn. of \bar{C} from 3-ethylpentyn-1-ol-3 (diethyl-ethynyl-carbinol) [Beil. I₁-(236), I₂-(506)] (1) directly, or from the intermediate 1-chloro-3-ethylpentyne-1 (3:9410) by rearr., on shaking either with aq. HCl contg. Cu₂Cl₂ + NH₄Cl (some 3-ethylpenten-3-yne-1 also being formed in the latter case) see (1).]

 \bar{C} with aq. + CaCO₃ first isomerizes to 1-chloro-3-ethylpentyne-1 (3:9410) which then yields 3-ethylpentyn-1-ol-3 (b.p. 136-137°, $D_4^{17} = 0.8748$; N-phenylcarbamate, m.p. 52-53° (1); allophanate, m.p. 130-131° (2)) and 3-ethylpenten-3-yne-1, b.p. 41-43° at 100 mm., $D_4^{13} = 0.7733$, $n_a^{13} = 1.43962$, $n_B^{13} = 1.45224$ (1).

3:9406 (1) T. A. Favorskaya, I. A. Favorskaya, J. Gen. Chem. (U.S.S.R.) 10, 451-460 (1940); C.A. 34, 7844 (1940). (2) Locquin, Sung, Bull. soc. chim. (4) 35, 601 (1924).

3: 9410 1-CHLORO-3-ETHYLPENTYNE-1 Cl
$$C_7H_{11}Cl$$
 Beil. S.N. 12
$$CH_3.CH_2-CH-C \stackrel{|}{=} C$$

$$C_2H_5$$

B.P. 73-76° at 100 mm. (1)
$$D_4^{18.5} = 0.9230$$
 (1) $n_a^{18.5} = 1.44372$ (1) $D_4^{0} = 0.9330$ (1) $n_{\beta}^{18.5} = 1.45364$ (1)

[For prepn. of \bar{C} from 3-ethylpentyn-1-ol-3 (diethyl-ethynyl-carbinol) [Beil. I₁-(236), I₂-(506)] (1) on shaking with HCl alone, or with HCl + Cu₂Cl₂ + NH₄Cl (70% yield together in the latter case with a maximum of 25-30% 1-chloro-3-ethylpentadiene-1,2 (3:9406)) see (1).]

 \bar{C} on shaking with HCl + Cu₂Cl₂ + NH₄Cl is partly converted to 1-chloro-3-ethylpentadiene-1.2 (3:9406) (some 3-ethylpenten-3-yne-1 also being formed), but without the HCl no action occurs (1).

C easily loses HCl yielding 3-ethylpenten-3-yne-1, b.p. 41-43° at 100 mm., $D_4^{13} = 0.7733$, $n_4^{13} = 1.43962$, $n_8^{13} = 1.45224$ (1).

C upon hydrolysis (1) with aq. + CaCO₃ gives a mixt. of 3-ethylpentyn-1-ol-3 (b.p. 136-137°, $D_4^{17} = 0.8748$, $n_{\alpha}^{14} = 1.4385$, $n_{\beta}^{14} = 1.44697$ (1) [N-phenylcarbamate, m.p. 52-53° (1), allophanate, m.p. 130-131° (2)]) and 3-ethylpenten-3-yne-1 (see above).

3:9410 (1) T. A. Favorskaya, I. A. Favorskaya, J. Gen. Chem. (U.S.S.R.) **10**, 451-460 (1940); C.A. **34**, 7844 (1940). (2) Locquin, Sung, Bull. soc. chm. (4) **35**, 601 (1924).

3:9412 d,l-3-CHLOROHEPTENE-1 C₇H₁₃Cl Beil. S.N. 11 (n-Butyl-vinyl-carbinyl chloride) H CH₃ CH₂ CH₂.CH₂—C—CH—CH₂

 $\bar{\mathbf{C}}$ as such is as yet unreported, but both of the opt. active stereoisomerides have been prepared.

[The dextrorotatory isomer, b.p. $92-94^{\circ}$ at 125 mm. (1), $87-88^{\circ}$ at 90 mm. (1), $D_4^{25} = 0.8857$ (1), has been obtd. from levorotatory hepten-1-ol-3 (*n*-butyl-vinyl-carbinol) [Beil. I₂-(488)] with PCl₅ in dry ether (1), with PCl₃ + pyridine (2), or from levorotatory 3-bromoheptene-1 (1) with LiCl in MeOH (1).

[Upon ozonolysis in CHCl₃ followed by Br_2/aq , oxidn, of the resultant aldehyde, levorotatory α -chlorocaproic acid, b.p. 80-95° at 1 mm., was obtd. (2).]

[The levorotatory isomer, b.p. 87-90° at 92 mm. (3), $D_4^{25} = 0.8883$ (4), $n_D^{25} = 1.4380$ (4), has been obtd. from dextrorotatory hepten-1-ol-3 (n-butyl-vinyl-carbinol) [Beil. I₂-(488)] with PCl₅ (3); upon catalytic hydrogenation it yields (3) dextrorotatory 3-chloroheptane, b.p. 87-90° at 113 mm., $n_D^{25} = 1.4221$ (3); cf. d,t-isomer (3:8080).]

3:9412 (1) Levene, Rothen, Kuna, J. Biol. Chem. 120, 787-790 (1937). (2) Levene, Haller, J. Biol. Chem. 83, 597 (1929). (3) Levene, Rothen, J. Biol. Chem. 119, 191-192 (1937). (4) Levene, Rothen, J. Chem. Phys. 5, 981 (1937).

3:9414 4-CHLORO-3-METHYLHEXENE-2 Cl CH₃ C₇H₁₃Cl Beil. I — CH₃.CH₂—C—CH.CH₃
$$I_{1}$$
-(91)

B.P. 51° at 11.5 mm. (1)

[For prepn. of \bar{C} from 3-methylhexen-2-ol-4 [Beil. I-447, I_1 -(229)] with 6 N HCl see (1)]. **3:9414** (1) Abelmann, Ber. 43, 1581 (1910).

3:9418 4-CHLORO-2,4-DIMETHYLPENTENE-2 C₇H₁₃Cl Beil. S.N. 11

(2-Chloro-2,4-dimethylpentene-3; Cl
trimethylcrotyl chloride)

CH₃—C=CH—C—CH₃

CH₃

[Č is too unstable for purification by distillation; however, it can be prepared in solution from 2,4-dimethylpenten-3-ol-2 (1) with PCl₃ in dry ether.]

C on attempted distillation gave (1) almost quantitative yields of 2,4-dimethylpentadiene-1,3 [Beil. I-257, I₁-(121), I₂-(235)], b.p. 92-93° (1).

[For reactn. of \ddot{C} with phenol + K_2CO_3 in acctone see (1).]

3:9418 (1) Hurd, Cohen, J. Am. Chem. Soc. 53, 1920-1922 (1931).

B.P. 68-72° at 7 mm. (1)
$$D_4^{20} = 1.064$$
 (1) $n_D^{20} = 1.4490$ (1)

[For prepn. of \tilde{C} from heptene-1 (1:8324) with Cl_2 in CCl_4 at -15° (13% yield (1)) or with $SOCl_2$ (30-40% yield (1)) see (1).]

 \bar{C} passed over soda-lime at 420° (3% yield) or htd. to 250° with powdered KOH in mineral oil (33% yield) loses 2 HCl giving (1) n-amylacetylene (1.8085) accompanied by other prods.

3:9420 (1) Bachmann, Hill, J. Am. Chem. Soc. 56, 2730-2731 (1934).

B.P. 120° at 28 mm. (1)

[For prepn. of \bar{C} (60% yield (1)) from N,N'-bis-benzoylheptamethylenediamine [Beil. IX-264] via conversion with PCl₅ to the corresp bis-imidechloride and distillation of the latter see (1); for formn. of \bar{C} (together with other prods) from heptamethylenediamine [Beil. IV-271] + NOCl see (2).]

① 1,7-Diphenoxyheptane (heptanediol-1,7 bis-phenyl ether) [Beil. VI-148]: colorless cyrst. from hot alc., m.p. 53° (1), 54.5-55° (2). [From C on htg. with excess NaOC₆H₅ in alc. (1) (2).]

3:9422 (1) von Braun, Muller, Ber. 38, 2347 (1905). (2) Ssolonina, J. Russ. Phys.-Chem. Soc. 30, 606-632 (1898); Cent. 1898, I 26.

B.P. 77° at 25 mm. (1)

[For prepn. of \bar{C} from heptanone-2 (n-amyl methyl ketone) (1:5460) with PCl₅ (23% yield accompanied by 40% yield of 2-chloroheptene-1 (3:7988)) see (1).]

3:9424 (1) Bachmann, Hill, J. Am. Chem. Soc. 56, 2730 (1934).

3: 9426 4,4-DICHLOROHEPŢANE Cl
$$C_7H_{14}Cl_2$$
 Beil. I - 154 I_1 — I_2 —CH₂.CH₂.CH₂.CH₂.CH₃ I_1 — I_2 —(117) Cl B.P. 86° at 27 mm. (1) $D_-^{17} = 1.008$ (1) $n_D^{17} = 1.448$ (1) (2) 60.5° at 11 mm. (2) 1.006 (2)

[For prepn. of \tilde{C} from heptanone-4 (butyrone) (1:5447) with PCl₅ see (1); note that heptyne-3 (1:8095), b.p. 105-106°, and 4-chloroheptene-3 (3:8023) are also formed (1). The earlier prepns. are regarded as impure.]

3:9426 (1) Bourgeul, Bull. soc. chim. (4) **35**, 1636–1637 (1924). (2) Bourgeul, Ann. chim. (10) **3**, 372 (1925).

3: 9428 2,4-DICHLORO-2,4-DIMETHYLPENTANE
$$C_7H_{14}Cl_2$$
 Beil. S.N. 10 Cl Cl $CH_3-C-CH_2-C-CH_3$ CH_3 CH_3 CH_3

B.P. 51.5°, at 8 mm. (1)

[For study of behavior of \ddot{C} with aq. alc. N/10 NaOH see (1).]

3:9428 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 9, 1380-1388 (1939); C.A. 34, 1611 (1940).

3:9430 1,5-DICHLORO-3,3-DIMETHYLPENTANE
$$C_7H_{14}Cl_2$$
 Beil. I — Cl CH_3 Cl I_1 — I_2 -(121) CH_2 . CH_2 CH_3

B.P. 135° at 80 mm. (1)
$$D_4^{15} = 1.0917$$
 (2) $n_D^{15} = 1.48990$ (2) $58-59$ ° at 8 mm. (2)

[For prepn. of \bar{C} from 3,3-dimethylpentanediol-1,5 (1) with SOCl₂ refluxed for 4 hrs. (yield 80% (1)); from N-benzoyl-4,4-dimethylpiperidine (2) with PCl₅ see (2).]

[For reactn. of \bar{C} with alc. NaCN giving (yield: 80% (2), 40% (1)) 3,3-dimethylpimelonitrile, cryst. from $C_6H_6/lgr.$, m.p. 123° (2), b.p. 155–157° at 7 mm. (1), $D_{20}^{20}=1.0936$ (1), $n_{20}^{20}=1.4404$ (1), see indic. refs.] [This dinitrile upon htg. with conc. HCl in s.t. 4 hrs. at 120° gives (85% yield (2)) γ,γ -dimethylpimelic acid; ndls. from $C_6H_6/lgr.$, m.p. 83° (2) (diamide, m.p. 176° (2); dianilide, m.p. 165° (2)).]

3:9430 (1) Miller, Adams, J. Am. Chem. Soc. 58, 789 (1936). (2) Komppa, Ber. 62, 1371-1372 (1929).

B.P. 46.0° at 19.5 mm. (1)
$$D_4^{20} = 0.8672$$
 (1) $n_D^{20} = 1.4221$ (1) $D_4^{15} = 0.8725$ (1)

[For prepn. from heptanol-2 (1:6235) with conc. $HCl + ZnCl_2$ at 0° for 6-8 hrs. (60-64% yield (1)) see (1).]

 \tilde{C} converted to corresp. acetate by 7-hr. reflux with KOAc + AcOH, then hydrolyzed by 6-hr. boilg. with 20% alc. KOH, and the resultant heptanol-2 oxidized with CrO₃/H₂SO₄, gives (1) heptanone-2 (1:5460), pptd. as the semicarbazone, m.p. 123° (1).

3:9432 (1) Sherrill, J. Am. Chem. Soc. 52, 1985-1988 (1930).

B.P. 53-58° at 36 mm. (1)

[For prepn. of \tilde{C} (80% yield (1)) from 3-methylhexanol-2 [Beil. I₁-(206), I₂-(445)] with PCl₅ see (1).]

3:9434 (1) Bielouss, Ber. 45, 627-628 (1912).

Only a levorotatory isomer of C has been reported; this resulted from treatment (1) of levorotatory 3-methylhexanol-4 (1) with SOCl₂ in pet. ether; b.p. 37° at 15 mm. (1).

3:9436 (1) Duveen, Kenyon, Bull. soc. chim. (5) 5, 1120-1126 (1938).

3:9438 2-CHLORO-3-ETHYLPENTANE Cl
$$C_7H_{16}Cl$$
 Beil. I — $I_1-I_{1-1}CH_{3}$ CH₃.CH₂—CH— $I_{1-1}CH_{3}$ CH₃.CH₂—CH₃ H

B.P. 62-62.5° cor. at 50 mm. (1)
$$D_{25}^{25} = 0.8911$$
 (1) $n_{20}^{25} = 1.4295$ (1) $n_{20}^{20} = 1.4318$ (1)

[For prepn. of \tilde{C} from 3-ethylpentanol-2 [Beil. I 416, I_1 -(207), I_2 -(445)] (1) with conc. $HCl + ZnCl_2$ at room temp. in 35% yield see (1).]

3:9438 (1) Lucas, J. Am. Chem. Soc. 51, 252 (1929).

B.P. 93° at 250 mm. (1)
$$D_4^{20} = 0.855$$
 (1) $n_D^{20} = 1.4180$ (1) 63-65° at 85 mm. (2) 1.4183 (2)

[For prepn. of \bar{C} from 2,2-dimethylpentanol-4 (methyl-neopentyl-carbinol) satd. with dry HCl and stood 8 weeks (90% yield (1)) or treated with dry HCl under press. for 22 weeks (2) see indic. refs.]

 \bar{C} with Mg in dry ether gives RMgCl; this on oxidn. with O_2 yields (1) 2,2-dimethylpentanol-4, b.p. 136-136.5° at 730 mm. (2), $n_D^{20} = 1.4183$ (2) (N-(\alpha-naphthyl)carbamate, m.p. 84° (1)).

 \tilde{C} converted to RMgCl, treated with CO₂, gives (50% yield (2)) methyl-neopentyl-acetic acid, b.p. 109° at 14 mm., $n_D^{2D} = 1.4233$ (2) (amide, m.p. 123° (2); anilide, m.p. 117.5° (2)).

3:9440 (1) Whitmore, Johnston, J. Am. Chem. Soc. 60, 2267 (1938). (2) Whitmore, Noll, Heyd, Surmatis, J. Am. Chem. Soc. 63, 2028 (1941).

3: 9442 d.l-2-CHLORO-2,3-DIMETHYLPENTANE Beil. S.N. 10 C₇H₁₅Cl (sec.-Butyl-dimethyl-carbinyl

chloride)

B.P. 38-39° at 20 mm. (1)

 $n_{\rm D}^{20} = 1.4264 (1)$

C has been obtd. (1) only as a by-product (10% yield) from the reactn. of 2,3-dimethylpentanol-2 with AlCl₃ and C₆H₆; the structure assigned above should be accepted with reserve.

3:9442 (1) Huston, Fox, Binder, J. Org. Chem. 3, 253 (1939).

C7H5O2Cl Beil. VIII -53 5-CHLORO-2-HYDROXYBENZALDEHYDE VIII₁— CHO ΉO

B.P. 105° at 12 mm.

M.P. 100°

See 3:2800. Division A: Solids.

Beil. VIII-81 3-CHLORO-4-HYDROXYBENZALDEHYDE C₇H₅O₂Cl VIII₁---CHO

B.P. 149-150° at 14 mm.

M.P. 139° cor.

See 3:4065. Division A: Solids.

2-HYDROXYBENZOYL CHLORIDE C7H5O2Cl Beil. X ---

 X_{1} -(43)

 $D_{-}^{20} = 1.3112$ B.P. 92° at 15 mm. M.P. 19° See 3:0085. Division A: Solids.

3:9446 3-HYDROXYBENZOYL CHLORIDE C7H5O2Cl Beil. X ---X1-(66)

B.P. 110-113° at 0.5 mm. (1)

Pale yel. oil, not solidifying at -15° (2). — \bar{C} has odor and lachrymatory props. similar to benzoyl chloride; on stdg. even in s.t. turns brown and decomposes (1).

[For prepn. of C from Na or K salts of m-hydroxybenxoic acid (1:0825) with SOCl₂ (2) or with COCl₂ in toluene (3) see indic. refs.]

Č with MeOH yields (1) methyl m-hydroxybenzoate (1:1468), m.p. 70°, b.p. 178° at 17 mm. (1); Č with EtOH yields (1) ethyl m-hydroxybenzoate (1:1471), m.p. 73.8°, b.p. 180° at 17 mm. (1); Č with dry NH3 gas in CHCl3 yields (1) m-hydroxybenzamide, lfts.

from hot aq., m.p. 167° (1); Č with aniline in CHCl₃ yields (1) *m*-hydroxybenzanilide [Beil. XII-502, XII₁-(269)], ndls. from hot aq. or dil. alc., m.p. 156° (4), 154-155° (1) (5), Č with *p*-toluidine in CHCl₃ yields (1) *m*-hydroxybenzo-*p*-toluidide, ndls. from dil. alc., m.p. 163° (1).

3:9446 (1) Anschütz, Krone, Ann. 442, 41-42 (1925). (2) Kopetschni, Karczag, Ger. 262,783, July 25, 1913; Cent. 1913, II 728. (3) Kopetschni, Karczag, Ger. 266,351, Oct. 21, 1913; Cent. 1913, II 1715. (4) Klemenc, Ber. 49, 1373 (1916). (5) Kupferberg, J. prakt. Chem. (2) 16, 445 (1877).

The precise physical props. of \tilde{C} have never been reported; it appears to be a yellow oil still liquid at -15° (1) which cannot be distilled with decompn. even in high vac. (2); \tilde{C} has odor and lachrymatory character of benzoyl chloride (2).

[For prepn. of \bar{C} from Na or K salt of p-hydroxybenzoic acid (1:0840) with SOCl₂ (1) (4) or with COCl₂ (3:5000) in toluene (3) see indic. refs.; from p-hydroxybenzoic acid (1:0840) with 4 pts. SOCl₂ at b.p. in pres. of AlCl₃, SnCl₄, or SbCl₅ see (5).]

 \tilde{C} with MeOH yields methyl p-hydroxybenzoate (1:1549), m.p. 131°; \tilde{C} with EtOH yields (2) ethyl p-hydroxybenzoate (1:1534), m.p. 116°, 112.5° (2); \tilde{C} with dry NH₃ gas in CHCl₃ yields p-hydroxybenzamide, ndls. with 1 H₂O from aq., m.p. 162° (2); \tilde{C} with aniline in CHCl₃ yields p-hydroxybenzamilide [Beil. XII-502, XII₁-(269)], lfts. from hot aq., m.p. 196-197° (2); \tilde{C} with p-toluidine in CHCl₃ yields p-hydroxybenzo-p-toluidide, ndls. from alc., n.p. 203-204° (2).

3:9447 (1) Kopetschni, Karczag, Ger. 262,883, July 25, 1913; Cent. 1913, II 728. (2) Anschütz, Zerbe, Ann. 442, 38 (1925). (3) Kopetschni, Karczag, Ger. 266,351, Oct 21, 1913, Cent. 1913, II 1715. (4) Kopetschni, Karczag, Ber. 47, 237 (1914). (5) Kissling (to I.G.), Ger. 701,953, Jan. 2, 1940; C.A. 36, 99 (1942).

3:9448 PHENOXYMETHYL CHLORIDE C₇H₇OCl Beil. S.N. 514 (Chloromethyl phenyl ether; α -chloroanisole; ω -chloroanisole)

Authentic physical constants for this compound are unreported.

[For attempts to prepare \bar{C} from methylene (di)chloride (3:5020) (1) or from chloromethyl acetate (3:5356) (2) by reaction with sodium phenolate, from formaldehyde diphenylacetal (diphenoxymethane) [Beil. VI-150] by partial cleavage to phenoxymethyl alcohol followed by conversion to \bar{C} (1), or from anisole (1:7445) by chlorination (3) see indic. refs.]

[For claim on use of \bar{C} in refining of mineral oils see (4).]

3:9448 (1) Bentley, Haworth, Perkin, J. Chem. Soc. 69, 166-167 (1896). (2) Kirner, J. Am. Chem. Soc. 48, 2747-2748 (1926). (3) Weygand, Vogel, J. prakt. Chem. (2) 155, 342-346 (1940). (4) Clarke, Towne (to Texas Co.), U.S. 2,075,269, March 30, 1937; Cent. 1937, II 330; C.A. 31, 3686 (1937).

2,6-DICHLORO-4-METHYLPHENOL C7H6OCl2 Beil. VI - 403 OH VI₁-(204) VI₂---

B.P. 138-139° at 28 mm.

M.P. 38-39°

See 3:0400. Division A: Solids.

Beil. II-671 3:9450 PIMELYL (DI)CHLORIDE II1-

B.P. 137° at 15 mm. (1)

[For prepn. of C from pimelic acid (1:0456) with excess SOCl₂ (1) (2) see indic. refs.] [C with 1 mole MeOH should give 6-carbomethoxyhexanovl chloride-1, b.p. 135-136° at 17 mm. (3), usually prepd. (3) from methyl hydrogen pimelate + SOCl₂.

 $\ddot{C} + AlCl_3 + C_6H_6$ yields (2) 1,5-diphenylpentanedione-1,5.

C on hydrolysis yields pimelic acid (1:0456) (for the dianilide, di-p-toluidide, and other derivs. corresp. to C see 1:0456).

3:9450 (1) Blaise, Koehler, Bull. soc. chim. (4) 5, 687 (1909). (2) Skraup, Guggenheimer, Ber. 58, 2498 (1925). (3) Morgan, Walton, J. Chem. Soc. 1935, 291.

3:9452 $d_i l - \alpha$ -METHYL-n-CAPROYL CHLORIDE C7H18OCl Beil. II - 342 (n-Butyl-methyl-acetyl CH3.CH2.CH2.CH2.CH-C=O II1--chloride) II_{2} -(296)

Physical constants for C appear to be as yet unrecorded. [The dextrorotatory stereoisomer of C, b.p. 45-48° at 9 mm. (1) (amide, m.p. 66° (1)), has been obtd. from the dextrorotatory acid with SOCl₂ (1).]

[For prepn. of C from n-butyl-methyl-acetic acid (1:1134) with PCl₃ (2) or with SOCl₂ (3) see indic. refs.l

Č on hydrolysis yields 2-methylhexanoic acid-1 (n-butyl-methyl-acetic acid) (1:1134) (for the amide, anilide, p-toluidide, and other derivs, corresp. to \bar{C} see 1:1134).

3:9452 (1) Levene, Mikesa, J. Biol. Chem. 84, 581-582 (1929). (2) Rasetti, Bull. soc. chim. (3) 33, 690 (1905). (3) Reichstein, Trivelli, Helv. Chim. Acta 15, 258-259 (1932).

3:9456 α,α-DIMETHYL-n-VALERYL CHLORIDE C7H13OCl Beil. S.N. 162 (Dimethyl-n-propyl-acetyl CH₂ chloride)

B.P. 45° at 10 mm. (1)

[For prepn. of \ddot{C} from α,α -dimethyl-n-valeric acid [Beil. II-345] see (1).] \bar{C} on hydrolysis yields α, α -dimethyl-n-valeric acid (see above), b.p. 199-200°, 101-102° at 11 mm. (2), 98-99° at 9 mm. (1).

Dimethyl-n-propyl-acet-amide: m.p. 95-96° (1) (2).

3:9456 (1) Locquin, Leers, Compt. rend. 178, 2097 (1924). (2) Haller, Bauer, Compt. rend. 148, 129 (1909).

3:9458 α,β-DIMETHYL-n-VALERYL CHLORIDE C₇H₁₃OCl (sec.-Butyl-methyl-acetyl CH₃.CH₂.CH—CH—C=O chloride CH₃.CH₂.CH CH₃.CH₂.CH CH₃.CH₃

B.P. 110-113° at 193 mm. (1)

[For prepn. of \bar{C} from α,β -dimethyl-n-valeric acid (1) see (1).]

 \ddot{C} on hydrolysis yields α,β -dimethyl-n-valeric acid, b.p. 210.5-210.8° at 750 mm. (1), $D_{18}^{18} = 0.9316$ (methyl ester, b.p. 155-158° at 743 mm. (1)).

- \bigcirc α,β -Dimethyl-n-valeramide: m.p. 101-103° (1)
- $\bigcirc \alpha_n \beta$ -Dimethyl-n-valeranilide: m.p. 71-72° (1).
- D αβ-Dimethyl-n-valero-p-bromognilide; m.p. 115-117° (1).

3:9458 (1) Chichibabin, Katznelson, Bull. acad. sci. U.R.S.S., Classe sci. math. nat. 1933, 267-271; Cent. 1933, II 3409; C.A. 27, 3698 (1933).

3:9460 γ,γ -DIMETHYL-n-VALERYL CHLORIDE $C_7H_{13}OCl$ Beil. S.N. 162 (Neopentylacetyl chloride) CH_3 CH_3 CH_4 C CH_2 CH_2 CH_5 CH_6 CH_7 CH_8 CH_8

B.P. 94° at 100 mm. (1) .

 $n_{\rm D}^{20} = 1.4294 \, (1)$

[For prepn. of \bar{C} from neopentylacetic acid (1) with SOCl₂ see (1).]

[$\ddot{\mathbf{C}}$ with a large excess of ter-BuMgCl (4 moles) gives (1) 67% yield 2,2,6,6-tetramethylheptanol-3, m.p. 58–59° (1) (3,5-dinitrobenzoate, m.p. 99.5° (1); $N-(\alpha-\text{naphthyl})$ carbamate, m.p. 92° (1)), and 13.5% 2,2-dimethylpentanol-5, b.p. 160° at 728 mm. (1), 158° at 737 mm. (2), 96° at 62 mm. (2), $D_4^{20} = 0.815$ (2), $D_D^{20} = 1.4202$ (2) ($N-(\alpha-\text{naphthyl})$ carbamate, m.p. 80.5–81° (2)).]

 \tilde{C} on hydrolysis presumably yields neopentylacetic acid, b.p. 159° at 150 mm. (1), $n_{D}^{20} = 1.4215$ (1).

3:9460 (1) Whitmore, Whitaker, Mosher, Breivik, Wheeler, Miner, Sutherland, Wagner, Clapper, Lewis, Lux, Popkin, J. Am. Chem. Soc. 63, 647 (1941). (2) Whitmore, Homeyer, J. Am. Chem. Soc. 55, 4558 (1933).

3:9462 α-ETHYL-β-METHYL-n-BUTYRYL CHLORIDE C₇H₁₈OCl Beil. S.N. 162 (α-Ethyl-isovaleryl chloride; CH₃—CH—CH—C=O ethyl-isopropyl-acetyl chloride)

B.P. 63-65° at 12 mm. (1)

[For prepn. of \tilde{C} from ethyl-isopropyl-acetic acid [Beil. II-345, II₁-(147)] see (1).] \tilde{C} on hydrolysis yields α -ethyl-isovaleric acid (see above), b.p. 202–203° (1), 202–204° (2).

- Ethyl-isopropyl-acet-amide: ndls. from aq., m.p. 136° cor. (3), 134-135.5° (2), 134° (2). [From C + NH₃ at 180° (2).]
- (1). Ethyl-isopropyl-acet-anilide: ndls. from lgr., m.p. 114-115° (1).
- DEthyl-isopropyl-acet-p-toluidide: ndls. from lt. pet. m.p. 122.5-123° (2).

3:9462 (1) Nenitzescu, Chicos, Ber. 68, 1587 (1935). (2) Crossley, Le Sueur, J. Chem. Soc. 77, 94 (1900). (3) Fischer, Rohde, Brauns, Ann. 492, 375-376 (1914).

3:9470 ISOBUTYL d,l-a-CHLOROPROPIONATE C7H13O2Cl Bell. S.N. 162 (CH₃)₂CH.CH₂.O.CO.C.CH₃

 $D_4^{20} = 1.0175$ (1) $n_D^{20} = 1.4230$ (1) B.P. --

3:9479 (1) Schjanberg, Z. physik. Chem. A-172, 230 (1935).

3:9474 n-BUTYL β-CHLOROPROPIONATE $C_7H_{13}O_2Cl$ Beil. II — Π_1 n-C₄H₉O.CO.CH₂.CH₂Cl II₂-(227)

 $D_4^{20} = 1.0394$ (2) $n_D^{20} = 1.4321$ (2) $D_4^{15} = 1.0708$ (1) $n_D^{10} = 1.4385$ (1) B.P. 104° at 22 mm. (1) 97° at 15 mm. (1)

[For prepn. from n-butyl alc. (1:6180) + β -chloropropionic ac. (3:0460) see (1).]

Č htd. at 200° with diethylaniline loses HCl and gives (90-100% yield (1)) in distillate n-butyl acrylate, b.p. 138-140° at 756 mm. (1).

3:9474 (1) Moureu, Murat, Tampier, Ann. chim. (9) 15, 246, 251 (1921). (2) Schjanberg, Z. physik. Chem. A-172, 231 (1935).

R H $C_7H_{15}OCl$ Beil. S.N. 78 $CH_3.C.O.n-C_5H_{11}$ Cl $D_4^{20} = 0.9200 (1)$ $n_D^{20} = 1.4218 (1)$ 3:9480 n-AMYL α-CHLOROETHYL ETHER (α -Chloroethyl n-amyl ether)

B.P. 63.3-66.3° cor. at 8 mm. (1)

[For prepn. (99% yield (1)) from paraldehyde (1:0170) + n-amyl alc. (1:6205) + dry HCl see (1).

C on stdg. polymerizes to dark tarry residue (1).

 \overline{C} on shaking with aq. yields acetaldehyde (1:0100), n-amyl alc. (1:6205), + HCl.

3:9480 (1) Henze, Murchison, J. Am. Chem. Soc. 53, 4077-4079 (1931).

3:9490 \(\beta\)-CHLOROPROPIONALDEHYDE DIETHYLACETAL Beil. I - 632 $ClCH_2.CH_2.CH(OC_2H_5)_2$ $C_7H_{15}O_2Cl$ I₁-(335) I₂-(690)

 $D_4^{22\ 3} = 0.9845\ (2)$ $n_D^{22.3} = 1.4203\ (2)$ $D_4^{18\ 7} = 0.9951\ (2)$ $n_D^{18\ 1} = 1.4206\ (2)$ B.P. 84° at 25 mm. (1) at 20 mm. (2) (10) 74° 56-66° at 8 mm. (3) 47-50° at 3-4 mm. (4)

Oil, insol. in aq. but sol. in org. solvents. — C may be preserved only if completely free from acid (11) and should be kept over moist K₂CO₃ (3). — C on htg. dec. at abt. 145° yielding (1) HCl and acrolein (1:0115).

[For prepn. from acrolein (1:0115) in abs. alc. at 0° with HCl gas (34% yield (5)) (6) (7) (11) (12) in the presence of CaCl₂ (90% yield (8), 56% yield (8)) see indic. refs.; for prepn. from α, γ-dichloro-n-propyl ethyl ether (9) by reactn. in the cold with EtOH (83% yield (9)) (1) or with NaOEt (1) see indic. refs.]

Č readily hydrolyzes in the presence of dil. acid yielding β -chloropropionaldehyde (3:5576) q.v. and EtOH (1:6130) q.v.

 \tilde{C} on refluxing with 2 moles aq. soon undergoes spontaneous reactn., the initial two layers becoming miscible, and after rapid cooling and shaking with conc. KHSO₃ or NaHSO₃ soln. gives (2) upon addn. of alcohol a ppt. of the corresp. bisulfite cpd. of β -chloropropionaldehyde (3:5576).

[$\bar{\mathbf{C}}$ shaken with a large excess (6 moles) of powdered KOH, then htd. at 210-220°, gives (yields: 75% (13), 70% (8)) (10) (3) (12) acrolein diethylacetal (1:0169) q.v., b.p. 123°. — $\bar{\mathbf{C}}$ on shaking with dil. aq. NaOH at 115° yields (11) β -hydroxypropionaldehyde diethylacetal [Beil. I-820, I₁-(418)].]

[For reactn. of \bar{C} with aniline (14) (15), with hydrazine hydrate (16), with alcoholates or phenolates (17), with diethyl sodiomalonate (18), with MeNH₂ (19), or with sodium methyl mercaptide (20) see indic. refs.]

3:9490 (1) Brabant, Z. physiol. Chem. 86, 208-209 (1913). (2) Crawford, Kenyon, J. Chem. Soc. 1927, 399. (3) Witzemann, J. Am. Chem. Soc. 36, 1909-1912 (1914). (4) Hartung, Adkins, J. Am. Chem. Soc. 49, 2521 (1927). (5) Witzemann, Evans, Hass, Schroeder, Org. Syntheses, Coll. Vol. 2 (1st ed.), 137-138 (1943). (6) Neuberg, Wendisch, Biochem. Z. 166, 480 (1925). (7) Evans, Hass, J. Am. Chem. Soc. 48, 2705-2706 (1926). (8) Reeves, J. Chem. Soc. 1927, 2481. (9) Dulière, Bull. soc. chim. (4) 33, 1651-1652 (1923). (10) Wohl, Ber. 31, 1797-1798 (1898).

(11) Wohl, Emmerich, Ber. 33, 7051-7052 (1822). (10) Wohl, Emmerich, Ber. 33, 7051-7052 (1822). (1928). (11) Wohl, Emmerich, Ber. 33, 2761 (1900). (12) Spoehr, Young, Carnegie Inst. Wash. Yearbook 25, 175-177 (1925/6); Expt. Sta. Record, 57, 817; C.A. 22, 2368 (1928). (13) Witzemann, Evans, Hass, Schroeder, Org. Syntheses, Coll. Vol. 2 (1st ed.), 17-18 (1943). (14) Barr, J. Am. Chem. Soc 52, 2422-2425 (1930). (15) Rath, Ber. 57, 717 (1924). (16) Wohl, Ber. 64, 1384 (1931). (17) Schorigin, Korschak, Ber. 68, 841-844 (1935). (18) Ellinger, Ber. 38, 2886 (1905). (19) Wohl, Johnson, Ber. 40, 4714 (1907). (20) Barger, Coyne, Buchem. J. 22, 1420 (1928).

3:9494 α -CHLORO- β -PHENYLACETYLENE C_8H_5Cl Beil. V - 513 (Chloroethynylbenzene; phenylethynyl chloride; ω -chlorophenylacetylene)

B.P.
$$74^{\circ}$$
 at 15 mm. (1) $D_{-}^{18} = 1.126$ (5) (6) $n_{D}^{18} = 1.576$ (5) (6) $n_{D}^{14} = 1.576$ (7) (6) $n_{D}^{14} = 1.5798$ (7) at 16 mm. (3) $n_{D}^{14} = 1.5798$ (6) $n_{D}^{14} = 1.5798$ (7) at 15 mm. (4) $n_{D}^{14} = 1.5798$ (8) $n_{D}^{14} = 1.5798$ (9) $n_{D}^{14} = 1.5798$ (9) $n_{D}^{14} = 1.5798$ (9) $n_{D}^{14} = 1.5798$ (9) $n_{D}^{14} = 1.5798$ (10) $n_{D}^{14} = 1.5798$ (11) $n_{D}^{14} = 1.5798$ (11) $n_{D}^{14} = 1.5798$ (12) $n_{D}^{14} = 1.5798$ (13) $n_{D}^{14} = 1.5798$ (13) $n_{D}^{14} = 1.5798$ (13) $n_{D}^{14} = 1.5798$ (13) $n_{D}^{14} = 1.5798$ (14) $n_{D}^{14} = 1.5798$ (15) $n_{D}^{14} = 1.5798$ (17) $n_{D}^{14} = 1.5798$ (17) $n_{D}^{14} = 1.5798$ (17) $n_{D}^{14} = 1.5798$ (18) $n_{D}^{14} = 1.5798$

Colorless mobile liq. with strong and characteristic odor. — Polymerizes rapidly on stdg. with sepn. of crystals (never identified) (7).

[For prepn. of \bar{C} from sodium deriv. of phenylacetylene (1:7425) in dry ether with p-toluenesulfonyl chloride (65% yield (6)) (3) (7) or benzenesulfonyl chloride (yield 54% (6)) (8) see indic. refs.; from phenylethynyl MgBr in dry ether with benzenesulfonyl chloride (yields: 35% (6), 13.7% (9)) or p-toluenesulfonyl chloride (33% yield (6)) see indic. refs.; from dichloroacetylene (3:5010) with C_6H_5MgX (70% yield) see (4); from sodium or silver salts of phenylacetylene (1:7425) with SO_2Cl_2 in dry ether (small yield) see (2); from ω , ω -dichlorostyrene (α , α -dichloro- β -phenylethylene) [Beil. V-477, V_2 -(367)] by elimination of 1 HCl with alc. KOH (1 mole) at 100° for 1 hr. see (2).]

Č on protracted boilg, with excess alc. KOH followed by acidification yields (2) (6) phenylacetic acid (1:0665).

[For reactn. of C with diethyl sodiomalonate see (2) (6).]

Č does not react with KI in acetone (7).

3:9494 (1) Bergmann, J. Chem. Soc. 1936, 404. (2) Nef, Ann. 368, 316-328 (1898). (3) Cleveland, Murray, J. Am. Chem. Soc. 61, 3547 (1939). (4) Ott, Bossaller, Ber. 76, 89-90 (1943); C.A. 37, 5015 (1943). (5) Bourgeul, Truchet, Compt. rend. 190, 753-755 (1930). (6) Truchet, Ann. chim. (10) 16, 320-327, 335-337, 340-358 (1931). (7) Murray, J. Am. Chem. Soc. 60, 2663 (1938). (8) Wilson, Wenzke, J. Am. Chem. Soc. 56, 2026 (1934). (9) Gilman, Fothergill, J. Am. Chem. Soc. 51, 3506 (1929).

3:9497 o-CHLOROPHENYLACETYLENE

C₈H₅Cl Beil. S.N. 474

B.P. 71° at 18 mm. (1) (2)

$$D_{-}^{25} = 1.1249 (2) \quad n_{\rm D}^{25} = 1.5690 (2)$$

[For prepn. of \tilde{C} from o-chlorophenylpropiolic acid (3:3956) by elimination of CO₂ with NaHCO₃ + CuCl₂ (66% yield (1)) or Cu(OAc)₂ (yield not stated (2)) see indic. refs.] [For study of dipole moment see (3).]

 $\overset{\circ}{C}$ with PCl₅ (3 wt. pts.) in C₆H₆ stood 24 hrs. then poured into aq. gives (54% yield (1)) α-chloro-α-(o-chlorophenyl)ethylene-β-phosphinic acid (C₈H₇O₅Cl₂P), lfts. from dil. HCl, m.p. 187° (1). — [This prod. with 5% aq. KOH boiled for 6 hrs. loses HCl, giving (1) upon acidification o-chlorophenylacetylenephosphinic acid (C₈H₆O₃ClP), lfts. from C₆H₆/AcOH, m.p. 134° (1).]

[\overline{C} with I₂ in liq. NH₃ at -34° readily gives (95% yield (4)) o-chlorophenyl-iodo-acetylene, cryst. from MeOH, m.p. 37.7–38.0° (4).]

Di-(o-chlorophenylethynyl)mercury: m.p. 213-214° (2). [From C in alc. with alk. K₂HgI₄ according to (5); note, however, that m.p. of this prod. is only slightly lower than that (221-222°) of the corresp. prod. from p-chlorophenylacetylene (3:0590).]

3:9497 (1) Bergmann, Bondi, Ber. 66, 282-283 (1933). (2) Otto, J. Am. Chem. Soc. 56, 1393-1394 (1934). (3) Otto, Wenzke, J. Am. Chem. Soc. 56, 1314-1315 (1934). (4) Vaughn, Nieuwland, J. Am. Chem. Soc. 56, 1207-1209 (1934). (5) Johnson, McEwen, J. Am. Chem. Soc. 48, 471 (1926).

3:9500 m-CHLOROPHENYLACETYLENE

C₈H₅Cl Beil. S.N. 474

B.P. 64-65° at 12 mm. (1)

[See also o-chlorophenylacetylene (3:9497).]

[For prepn. of \bar{C} from m-chlorophenylpropiolic acid (3:4102) by elimination of CO_2 with $Cu(OAc)_2$ (yield not stated) see (1); for formn. of \bar{C} from m-chlorocumene by pyrolysis see (5).]

[For study of dipole moment see (2).]

[\bar{C} with I_2 in liq. NH₃ at -34° readily gives (91% yield (3)) m-chlorophenyl-iodo-acetylene, m.p. 11.1°, $D_2^{25} = 1.818$, $n_1^{25} = 1.6638$ (3).]

Di-(m-chlorophenylethynyl)mercury: m.p. 138-139° (2), 138.0-138.5° (3). [From C in alc. with alk. K₂HgL₄ according to (4).]

3:9500 (1) Otto, J. Am. Chem. Soc. 56, 1393-1394 (1934). (2) Otto, Wenzke, J. Am. Chem. Soc. 56, 1314-1315 (1934). (3) Vaughn, Nieuwland, J. Am. Chem. Soc. 56, 1207-1209 (1934). (4) Johnson, McEwen, J. Am. Chem. Soc. 48, 471 (1926). (5) Dreisbach (to Dow Chem. Co.), U.S. 2,110,830, March 8, 1938; Cent. 1938, I 4110; C.A. 52, 3426 (1938).

1309 LIQUIDS (WITH B.P. REPTD. AT RED. PRESS.) 3:9504-3:9514

3:9504 2,5-DICHLORO-2,5-DIMETHYLHEXYNE-3
$$C_8H_{12}Cl_2$$
 Beil. I — Cl Cl I_{1} -(121) CH_3 — C—C—C—CH₃ CH_3

B.P. 62-63° at 15 mm. (1) M.P. 29° (1)

[From 2,5-dimethylhexyn-3-diol-2,5 [Beil. I-501, I₁-(263)] with HCl at 0° see (1).]

3:9504 (1) Dupont, Compt. rend. 152, 198 (1911).

B.P. 64-65° at 18 mm. (1) (3)
$$D_4^{20} = 0.9366$$
 (1) $n_D^{20} = 1.4794$ (1)

[For prepn. of \bar{C} from 1-n-butyl-2-vinylacetylene (2) by shaking with conc. HCl contg. $Cu_2Cl_2 + NH_4Cl$ see (1).]

Č htd. ½ pt. naphthoquinone-1,4 (1:9040) at 100° for 2 hrs., prod. suspended in alc. NaOH and aerated, yields (1) 1-n-butyl-2-chloroanthraquinone, yel. ndls. from MeOH, m.p. 129-130° (1).

[For polymerization of \bar{C} see (1) (3).]

3:9506 (1) Jacobson, Carothers, J. Am. Chem. Soc. **55**, 1624–1627 (1933). (2) Jacobson, Carothers, J. Am. Chem. Soc. **55**, 1622–1624 (1933). (3) Carothers, Coffman, U.S. 1,950,441, March 13, 1934; Cent. **1934**, II 1037; C.A. **28**, 3270 (1934).

B.P. 61-62° at 17 mm. (1)
$$D_{-}^{20} = 0.912$$
 (1) $n_{D}^{20} = 1.445$ (1)

[For prepn. of \bar{C} from octyne-1 (n-hexylacetylene) (1:8105) via conversion with NaNH₂ to $C_6H_{18}.C = C$ —Na and reaction in ether with bezenesulfonyl chloride (65% yield (1)) see (1).]

[Refractive indices via Pulfrich instrument: $n_{\rm C}^{12.7} = 1.4447$, $n_{\rm D}^{12.7} = 1.4472$, $n_{\rm F}^{12.7} = 1.4536$, $n_{\rm C}^{12}$ = 1.4589 (1).]

Č on refluxing for 12 hrs. with alc. KOH gives (70% yield (1)) n-caprylic acid (1:1145).

3:9510 (1) Truchet, Ann. chim. (10) 16, 334, 337, 351 (1931).

B.P. 80.5-81° at 15 mm. (1)

[For prepn. of C from octyn-2-ol-1 [Beil I-456, I₁-(236), I₂-(506)] with PCl₃ see (1).] **3:9514** (1) Toussaint, Wenzke, J. Am. Chem. Soc. **57**, 668-669 (1935).

B.P. 55° at 130 mm. (1)
$$D_4^{20} = 0.9163$$
 (1) $n_D^{20} = 1.4330$ (1)

[For prepn. of C from 3-methylheptyn-4-ol-3 (1) by saturation with HCl gas (60% yield) see (1).1

[\bar{C} with MeMgBr gives (66% yield) 3,3-dimethylheptyne-4, b.p. 69° at 100 mm., D_4^{20} = 0.7610, $n_D^{20} = 1.4360$ (1); \bar{C} with EtMgBr gives (61% yield) 3-ethyl-3-methyl-heptyne-4, b.p. 88° at 100 mm., $D_4^{20} = 0.7714$, $n_D^{20} = 1.4386$ (1).]

3:9516 (1) Campbell, Eby. J. Am. Chem. Soc. 62, 1799-1800 (1940).

3:9518
$$d$$
, l -3-CHLORO-OCTENE-1 $C_8H_{16}Cl$ Beil. S.N. 11 CH_3 — CH — CH — CH = CH_2

No record of this compound can be found in the literature.

[Note, however, that the levorotatory enantiomorph has been reported (1).]

3:9518 (1) Levene, Rothen, J. Chem. Phys. 5, 982 (1937).

B.P. 60-61° at 15 mm. (1)
$$D_4^{18} = 0.8931$$
 (1) $n_D^{18} = 1.4458$ (1 59-61° at 15 mm. (2)

Colorless mobile liq., insol. aq., sol. in usual org. solvents

[For prepn. from 2-methylhepten-2-ol-6 [Beil. I-448, I_1 -(230), I_2 -(490)] with SOCl₂ + pyridine (39% yield (1)) see (1) (2).]

Č could not be induced to yield an R.MgCl cpd. (2).

Č in AcOH treated with O₃ and the soln. subsequently shaken with Zn dust gives (61% yield (1)) γ -chloro-n-valeraldehyde, b.p. 70-71° at 16 mm. (1).

3:9520 (1) Helferich. Dommer. Ber. 53, 2008-2009 (1920). (2) Doeuvre. Bull. soc. chim. (4) 45, 359-360 (1929).

[For prepn. of C from 3-methylhepten-2-ol-4 (1) with 6 N HCl see (1).]

3:9524 (1) Abelmann, Ber. 43, 1581 (1910).

B.P. 57° at 13 mm. (1)

[For prepn. of C from 6-methylhepten-2-ol-4 with HCl see (1).]

3:9525 (1) Knorr (to I.G.), Ger. 553,279, June 24, 1932; Cent. 1932, II 2370; C.A. 26, 4611 (1932).

B.P. 75-78° at 53 mm. (1)

Two geom. stereoisomers of C are possible, but only this one is as yet recorded.

[For prepn. of \bar{C} from 4-methylhepten-3-ol-5 [Beil. I₁-(201), I₂-(491)] by distn. with conc. HCl (1) (3) or by saturation with dry HCl gas at 0° (2) see indic. refs.]

 \bar{C} is very reactive toward aq.; at 15° \bar{C} is 93% hydrolyzed in 48 hrs., at 45-50° 90% hydrolyzed in 75 min. (2).

 \bar{C} on oxidn. with Na₂Cr₂O₇ + H₂SO₄ at 45–50° yields (2) 4-methylhepten-3-one-5 [Beil. I₂-(799)], b.p. 170–172° at 735 mm., 96–98° at 70 mm., $D_4^{15} = 0.8773$, $n_D^{15} = 1.4510$ (2,4-dinitrophenylhydrazone, m.p. 147°, semicarbazone, m.p. 167° (2)).

3:9526 (1) Bjelouss, Ber. 43, 2331 (1910). (2) Courtot, Pierron, Bull. soc. chim. (4) 45, 292 (1929). (3) Knorr (to I.G.), Ger. 553,279, June 24, 1932; Cent. 1932, II 2370.

Č has never been reported in pure form; note that, in addition to the possibility of existence of two geometrical stereoisomers, Č by virtue of allylic rearrangement can yield 4-chloro-2,5-dimethylhexene-2 (3:9529) q.v.

[For prepn. of $\bar{\rm C}$ (as a mixt. with some or all of these other compds.) from 2,5-dimethylhexadiene-2,4 ("di-isocrotyl") [Beil. I-259, I₁-(122), I₂-(237)] by addn. of dry HCl gas see (1); note that the reaction prod. has b p. 45-60° at 15 mm., $n_{\rm D}^{20}=1.45$ to 1.46, and although stable in the cold decomposes on attempts to effect fractional distn.]

[\bar{C} with MeMgCl yields (1) mainly 2,4,5-trimethylhexene-2 [Beil. I₁-(95)], b.p. 128.4° at 760 mm. (1), $D_4^{20}=0.7403$ (1), $n_D^{20}=1.4268$ (1), accompanied by some 2,2,5-trimethylhexene-3, b.p. 114° at 760 mm. (1), $n_D^{20}=1.416$ (1).]

3:9527 (1) Henne, Chanan, Turk, J. Am. Chem. Soc. 63, 3474-3476 (1941).

[For prepn. of Č from 2,4-dimethylhexen-4-ol-3 (1) with 6 N HCl (80% yield) see (1).] **3:3528** (1) Abelmann, Ber. 43, 1581-1582 (1910).

Č, the allylic rearr. prod. of 2-chloro-2,5-dimethylhexene-3 (3:9527) q.v., has never been reported in pure form (1).

3:9529 (1) Henne, Chanan, Turk, J. Am. Chem. Soc. 63, 3474-3476 (1941).

B.P. 105-107° at 16 mm. (1)

[For prepn. of \tilde{C} from N-benzoyl-2-n-propylpiperidine (N-benzoylconiine) [Beil. XX-116] by conversion with PCl₅ to the amide-chloride $C_8H_{16}N.C(Cl)_2.C_6H_5$ followed by rapid distn. of the latter see (1).] [This prod. was originally (1) thought to be 1,5-dichloroctane [Beil. I-160] but is now regarded (2) as \tilde{C} .]

3:9530 (1) von Braun, Schmits, Ber. **39**, 4366 (1906). (2) von Braun, Pohl, Ber. **57**, 482–483 (1924).

B.P. 132-138° at 20-25 mm. (1)

[For prepn. of C from octamethylenediamine [Beil. IV-271] with NOCl see (1). The prod. is admittedly impure and contains also 8-chloro-octene-2 and 1,8-dichloro-octane (3:8805).]

Č on htg. with sodium phenolate yields (1) 1,7-diphenoxyoctane [Beil. VI-148], b.p. 240-250° at 20-25 mm., not volatile with steam.

3:9532 (1) Ssolonina, J. Russ. Phys.-Chem. Soc. 30, 620-621 (1898); Cent. 1898, I 26.

1313

[For prepn. of C from 2-ethylhexanediol-1,2 with conc. HCl at 120° see (1).]

3:9534 (1) von Braun, Mans, Ber. 67, 1704-1705 (1934).

B.P. 122-125° at 19 mm. (1)

[For prepn. of \tilde{C} from 2,2,4-trimethylpentanone-3 (pentamethylacetone) [Beil. I-708, I₁-(364), I₂-(760)] with PCl₅ in s.t. for 60 hrs. at 140° (1) (together with other products) see (1).]

3:9536'(1) Favorskii, Fritzman, J. Russ. Phys.-Chem. Soc. 44, 1353 (1912); Cent. 1913, I 1007; C.A. 7, 985 (1913); J. prakt. Chem. (2) 88, 654 (1913).

C as such is as yet unreported; however, the dextrorotatory isomer of C has been obtd. (1) from the metathesis of levorotatory 4-iodooctane with LiCl in MeOH; b.p. 92° at 50 mm.

3:9538 (1) Levene, Rothen, Kuna, J. Biol. Chem. 120, 786 (1937).

[For prepn. of \tilde{C} from 2-methylheptanol-6 [Beil. I-421, I₁-(209), I₂-(453)] with SOCl₃ in cold CHCl₃ + dimethylaniline, then refluxed 2 hrs., see (1).]

Č with activated Mg in dry ether gives with difficulty not over 41% of RMgCl (by carbonation and titration of the resultant acid (1)).

3:9540 (1) Peak, Robinson, J. Chem. Soc. 1937, 1589-1590.

1.4205 (2)

[For prepn. of \tilde{C} from 3-methylheptanol-3 (n-butyl-ethyl-methylcarbinol) [Beil. I-421, I₂-(453)] (1) (2) with dry HCl gas at -10° (2) or at $10-15^{\circ}$ (92% yield (1)) see indic. refs.] \tilde{C} with Mg in dry ether as specified (1) gives 70% yield corresp. RMgCl.

1314

 \bar{C} converted as above to RMgCl, treated with formaldehyde gas, gives (31% yield (1)) 2-ethyl-2-methylhexanol-1, b.p. 85.5-86° at 11 mm., $n_D^{20} = 1.4401$ (1).

3:9544 (1) Whitmore, Badertscher, J. Am. Chem. Soc. **55**, 1560-1562, 1565 (1933). (2) Whitmore, Woodburn, J. Am. Chem. Soc. **55**, 361-365 (1933). (3) Smart, Quayle, J. Am. Chem. Soc. **67**, 21 (1945).

B.P. 83-86° at 79 mm. (1)

[For prepn. of C from 4-methylheptanol-3 with PCl₅ see (1).]

3:9548 (1) Bjelouss, Ber. 45, 628 (1912).

B.P. 50-51° at 12 mm. (1) (3)
$$D_4^{20} = 0.8690$$
 (1) $n_D^{15} = 1.43098$ (1)

[For prepn. of \bar{C} from 4-methylheptanol-4 (methyl-di-n-propyl-carbinol (1)) by saturation with HCl gas see (1).]

[For data on density of \ddot{C} at 15°, 25°, 50°, and 65° and value of parachor at 0°, 25°, 50°, and 75° see (2).]

[\tilde{C} with C_6H_6 + AlCl₃ gives (64% yield (1)) 4-methyl-4-phenyl-heptane, b.p. 120-121° at 12 mm., D_4^{20} = 0.8708, n_D^{16} = 1.49326 (1); for behavior with naphthalene + AlCl₃ in CS₂ see (3).]

3:9550 (1) Halse, J. prakt. Chem. (2) 89, 453-454 (1914). (2) Quayle, Owen, Beavers, J. Am. Chem. Soc. 61, 3108 (1939). (3) Petrov, Kurbskii, J. Gen. Chem. (U.S.S.R.) 14, 492-494 (1944); C.A. 39, 4600 (1945).

 \tilde{C} as such is as yet unreported; however, the dextrorotatory isomer of \tilde{C} has been prepared from dextrorotatory 3-ethylhexanol-1 (1) with SOCl₂; b.p. 85° at 40 mm., $D_4^{27} = 0.879$, $n_D^{25} = 1.4335$ (1).

3:9552 (1) Levene, Marker, J. Biol. Chem. 91, 699-700 (1931).

B.P. 41-43° at 12 mm. (1)
$$n_{\rm D}^{25} = 1.4333 \ (2) \\ D_4^{20} = 0.8869 \ (1) \quad n_{\rm D}^{20} = 1.4353 \ (2) \\ 1.4350 \ (1)$$

[For prepn. from 2,3-dimethylhexanol-3 [Beil. I_1 -(210), I_2 -(454)] (2) (1) with dry HCl gas at 0° (81% yield (1)) see (1) (2).]

3:9554 (1) Whitmore, Evers, J. Am. Chem. Soc. 55, 813-814 (1933). (2) Stevens, Greenwood, J. Am. Chem. Soc. 65, 2152-2153 (1943).

3:9556 2-CHLORO-2,5-DIMETHYLHEXANE
$$C_8H_{17}Cl$$
 Beil. I — (Isoamyl-dimethyl-carbinyl chloride) Cl I_1 -(62) I_2 — CH_3 — CH_3 — CH_2 — CH_2 — CH_3 $CH_$

[For prepn. of \tilde{C} from 2,5-dimethylhexanol-2 (isoamyl-dimethyl-carbinol) (2) by saturation with HCl gas (79% yield (2)) see (1) (2); for formn. of \tilde{C} (together with other prods.) during hydrolysis of 2-nitroso-2,5-dimethylhexane see (1).]

[\bar{C} with C_6H_6 + AlCl₃ gives 2,5-dimethyl-2-phenylhexane, b.p. 116-117° at 14 mm., $D_4^{18} = 0.8844$, $n_D^{15} = 1.50233$ (2).]

3:9556 (1) Aston, Ailman, J. Am. Chem. Soc. 60, 1931 (1938). (2) Halse, J. prakt. Chem. (2) 89, 455 (1914).

3:9558 2-CHLORO-3,4-DIMETHYLHEXANE

C₈H₁₇Cl Beil. S.N. 10

No physical constants on this compound are recorded; for its formation, however, as a by-product of the addition of HCl to butene-2 see (1).

3:9558 (1) Coffin, Sutherland, Masss, Can. J. Research 2, 275-278 (1930).

3:9560 4-(CHLOROMETHYL)-3-METHYLHEXANE C₈H₁₇Cl Beil. S.N. 10

No physical constants on this compound are recorded; for its formation, however, as a by-product of the addition of HCl to butene-1 see (1).

3:3560 (1) Coffin, Sutherland, Mass, Can. J. Research 2, 277 (1930).

1-CHLORO-2,2,3,3-TETRAMETHYLBUTANE C₈H₁₇Cl Beil. S.N. 10

B.P. 80-81° at 40 mm.

M.P. 52-53°

See 3:0945. Division A: Solids.

— PIPERONYLOYL CHLORIDE $C_8H_5O_3Cl$ Beil. XIX-270 $C_8H_5O_3Cl$ Beil. XIX-270 $C_8H_5O_3Cl$ Cl

B.P. 155° at 25 mm.

M.P. 80°

See 3:1960. Division A: Solids.

3:9565 BENZYL CHLOROFORMATE C₈H₇O₂Cl Beil. VI- 437 (Benzyl chlorocarbonate, "carbobenzoxychloride") CH₂.O.CO.Cl VI₁— VI₂—

B.P. 103° at 20 mm. (1)

Colorless oil with penetrating odor. — \bar{C} is a valuable common reagent for characterization of amino acids and related compounds.

[For prepn. of \bar{C} from benzyl alc. (1:6480) by treatment with phospene (3:5000) directly at -8° (1) or in toluene (2) (91-95% yield (3)) see (1) (2) (3).]

Č on htg. loses CO₂ (1) (2), slowly at 100°, rapidly at 155°, leaving benzyl chloride (3:8535), b.p. 179°. Even vac. distd. Č may contain benzyl chloride.

Č with hydroquinone (1:1590) in aq. Na₂CO₃ under N₂ yields according to conditions (4) mono (carbobenzoxy)hydroquinone, pr. from 50% alc., m.p. 120-120.5° cor. (4), or di (carbobenzoxy)hydroquinone, ndls. from alc., m.p. 142-143° cor. (4).

- Benzyl carbamate [Beil. VI-437]: cryst. from aq. (1) or toluene (3), m.p. 87° (3) (5), 86° (1). [From C by addn. to 5 vols. conc. aq. NH₄OH; yield 95% (5), 91-94% (3).]
 Benzyl-N-phenylcarbamate [Beil. XII-328]: ndls. from pet. other. m. p. 78-77° (cf. 100).
- —— Benzyl-N-phenylcarbamate [Beil. XII-328]: ndls. from pet. ether, m.p. 76-77° (cf. under benzyl alc. (1:6480)). [From Č + aniline + aq. NaOH (6).]
- —— Benzyl N-(o-tolyl)carbamate: m.p. 83.5° (6). [From Č o-toluidine + aq. NaOH (6).]
- Benzyl N-(p-tolyl)carbamate: m.p. 83° (6). [From $\tilde{C} + p$ -toluidine + aq. NaOH (6).]

S:9565 (1) Thiele, Dent, Ann. 362, 257-258 (1898). (2) Bergmann, Zervas, Ber. 65, 1194-1195 (1932). (3) Carter, Frank, Johnston, Org. Syntheses 23, 13-16 (1943). (4) Olcott, J. Am. Chem. Soc. 59, 392 (1937). (5) Martell, Herbst, J. Org. Chem. 6, 882 (1941). (6) Bergstrom, Martell, J. Am. Chem. Soc. 67, 494-495 (1945).

3:9567 PHENYLACETYL CHLORIDE
$$C_8H_7OCl$$
 Beil. IX - 436 $(\alpha\text{-Toluyl chloride})$ CH_2 $C=0$ Cl Cl

B.P.		B.P. (contd.)	
170° cor.	at 250 mm. (1)	100-101° at 16 mm. (9) (10)	$D_4^{20} = 1.1685 (3)$
108-110°	at 25 mm. (2)	96° at 14 mm. (11)	1.16817 (7)
105.1°	at 23 mm. (3)	95.4-95.8° at 12 mm. (7)	
104-105°	at 23 mm. (4)	95.4-95.5° at 12 mm. (12)	$n_{\rm D}^{20} = 1.5333 (3)$
106°	at 22 mm. (5)	95° at 12 mm. (13)	
109-110°	at 20 mm. (6)	[100° at 12 mm. (14)]	
102.5°	at 17 mm. (7)		
102.3°	at 17 mm. (5)		
102°	at 17 mm. (8)		

Colorless liq.

[For prepn. of \tilde{C} from phenylacetic acid (α -toluic acid) (1:0665) with PCl₅ (63% yield (13)) (15) (16) (33) in CHCl₃ (yields: 80–90% (17), 80% (4)) (18) (19) (7); with PCl₅ in C₆H₆ (yield: 97% (5)) (20) (10); with PCl₃ + ZnCl₂ (73% yield (13)); with SOCl₂ (yields: 86% (5), 79% (11), 54% (13)) (21) (9) (22) in CCl₄ (79–80% yield (8)); with SiCl₄ in C₆H₆ (61% yield (23)); or with oxalyl (di)chloride (3:5060) (74% yield (14)) see indic. refs.; for formn. of \tilde{C} from sodium salt of phenylacetic acid (1:0665) with SO₂Cl₂ (phenylacetic acid anhydride (see below) also being formed) see (26).]

[\tilde{C} with Ag \bar{A} in ether (7) or with Pb \bar{A}_2 in ether in s.t. at 100° (24), or \tilde{C} treated with strong tertiary bases such as Et₃N or pyridine (25), or \tilde{C} with anhyd. FeCl₃ yields phenylacetic acid anhydride, pr. from ether, m.p. 72.5° (7), 72° (24); note that with tertiary bases (25) some α,α' -diphenylacetone (dibenzyl ketone) (1:5135), m.p. 34°, together with 6-benzyl-3,5-diphenyl-2-hydroxypyrone-4 (phenylketene trimer) [Beil. XVII-547, XVII₁-(278)], cryst. from C₆H₆, m.p. 173–174° (27), are also formed and that under favorable conds. (27) latter may amount to 50% yield.]—[Note also that phenylacetic acid anhydride, m.p. 72.5°, and phenylacetic acid, m.p. 76.5°, have m.p.'s in close proximity.]

[\overline{C} with Br₂ at 120-125° gives (84% yield (5)) α -bromo- α -phenylacetyl bromide, b.p. 150° at 26 mm. (5).]

[\bar{C} on cat. reductn. with H₂ + Pd/BaSO₄ in toluene as directed (28) gives (80% yield) phenylacetaldehyde (1:0200); however, cat. reductn. in vapor phase using Pd cat. (29) yields only ethylbenzene (1:7410) and β-phenylethyl alcohol (1:6505), while with H₂ + PtO at 200° \bar{C} , although giving traces of phenylacetaldehyde and β-phenylethyl alcohol, yields as the principal prod. (30) benzyl-β-phenylethyl-carbinol, m.p. 41-42° (30), 41° (31).] — [\bar{C} with KCN + quinoline yields 1-phenylacetyl-2-cyano-1,2-dihydroquinoline which on acid hydrolysis gives (32) phenylacetaldehyde (1:0200).]

[Č with C₆H₆ + AlCl₃ gives (82–83% yield (20)) (33) (36) benzyl phenyl ketone (desoxybenzoin) (1:5165), m.p. 60°; similarly Č with other hydrocarbons + AlCl₃ gives substituted desoxybenzoins: e.g., Č with toluene gives (81% yield (18)) (34) (35) 4-methyldesoxybenzoin [Beil. VII-47, VII₁-(239)], m.p. 109° (18); Č with o-xylene gives (37) 3,4-dimethyldesoxybenzoin [Beil. VII-454, VII₁-(244)], m.p. 95° (37); Č with m-xylene gives (37) cf. (38) 2,4-dimethyldesoxybenzoin [Beil. VII-454], oil, b.p. 202–205° at 13 mm. (38); Č with p-xylene gives (37) cf. (38) 2,5-dimethyldesoxybenzoin [Beil. VII-454], oil, b.p. 220–230° at 26 mm. (37); Č + naphthalene (in CS₂) gives (77% yield (39)) a mixt. of benzyl α-naphthyl ketone, m.p. 66–67° (39), and benzyl β-naphthyl ketone, m.p. 99.0–99.5° (39); Č + biphenyl (in CS₂ (40)) gives (40) (41) (42) 4-phenyldesoxybenzoin, m.p.

150° (42) (40), 149° (41); Č with acenaphthene gives (65–68% yield (43)) 5-(phenylacetyl)acenaphthene (4-acenaphthyl benzyl ketone), m.p. 114° (43); Č with bromobenzene (in CS₂) gives (44) 4-bromodesoxybenzoin, m.p. 114-115°, b.p. 165° at 3 mm. (44).] — [For oxidn. of many of these with SeO2 to corresp. benzils see (38).]

[Č with phenols + AlCl₃ (often in nitrobenzene) similarly yields hydroxy-substituted desoxybenzoins: e.g., C with phenol as directed gives (60-70% yield (45)) 4-hydroxydesoxybenzoin [Beil. VIII-165], m.p. 142° cor. (45); C with o-cresol gives (60-70% yield (46) 4-hydroxy-3-methyldesoxybenzoin [Beil, VIII-183], m.p. 152° (46); C with salicylic acid (1:0780) gives (47) 4-hydroxy-3-carboxy-desoxybenzoin; for similar reactn. with catechol resorcinol, and hydroquinone (48) or with phloroglucinol (49) see indic. refs.]

[C with phenol ethers + AlCl₃ (often in nitrobenzene) similarly yields substituted desoxybenzoins: e.g., C with anisole (1:7445) + SnCl4 (51) or AlCl3 (34) (50) gives 4methoxydesoxybenzoin [Beil. VIII-166, VIII₁-(571)], m.p. 77°; C with methyl m-tolyl ether (1:7510) + SnCl₄ (not AlCl₃) gives (60-70% yield (51)) (50) 4-methoxy-2-methyldesoxybenzoin, m.p. 76.5° (51); C with methyl p-tolyl ether (1:7495) + AlCl₃ in CS₂ gives (11) 2-methoxy-5-methyldesoxybenzoin, m.p. 75°, b.p. 205-207° at 14 mm. (11).]

C with phenols on htg. gives corresp. esters: e.g., C with phenol at 150° for 8 hrs. (6) (or C with phenol + aq. alk. (52)) yields phenyl phenylacetate [Beil. IX-435], ndls. from lt. pet., m.p. 50° (6), 42° (52); \bar{C} with β -naphthol at 150° for 6 hrs. yields (6) β -naphthyl phenylacetate, pl. from lt. pet., m.p. 87° (6); C with o-cresol at 90° yields (9) o-tolyl phenylacetate, m.p. 44-45° (9); \ddot{C} with m-cresol at 90° yields (9) m-tolyl phenylacetate, m.p. 51-52° (9); C with p-cresol at 90° yields (9) p-tolyl phenylacetate, m.p. 74-75° (9).

[C with MeZnI (53) in toluene + FtOAc or with Me₂Zn (54) gives (72% yield (53)) benzyl methyl ketone (phenylacetone) (1:5118); C with EtZnI (53) or with EtzZn (54) gives (78% yield (53)) benzyl ethyl ketone [Beil. VII-314, VII₁-(167)].]

(C + o-hydroxyacetophenone (1:1746) + NaĀ at 180° for 6 hrs. followed by hydrol.with alc. KOH gives (6) 4-methyl-3-phenylcoumarin, m.p. 153° (6); C with 2-hydroxy-5methylbenzophenone + Na \overline{A} at 180° gives (80–90% yield (55)) 3,4-diphenyl-6-methylcoumarin, cryst. from AcOH, m.p. 208-209° (55).]

[C with diazomethane in ether gives acc. to cond. (56) (57) (58) (62) either (yield: 84%) (56), 83% (62)) α-chloro-γ-phenylacetone [Beil. VII₁-(162)], m.p. 72-73° (56), b.p. 133-135° at 19 mm. (62), $n_D^{20} = 1.5379$ (62), or α -diazo- γ -phenylacetone (identified by reactn. with p-nitrobenzoic acid yielding (58) α -(p-nitrobenzoyloxy)- α -phenylacetone, pl. from alc., m.p. 120° (58)); note, however, that work of (56) could not be duplicated by later investigators (58) (62).1

 $[\bar{C}]$ with biuret yields (59) N_1 -(phenylacetyl)biuret, cryst. from alc., m.p. 199-200° u.c. dec. (59).1

[C with ethyl carbamate (urethane) at 60-70° gives (70% yield (60)) ethyl N-(phenylacetyl)carbamate, m.p. 113° (60).]

[C with MeOH yields methyl phenylacetate (1:3771), b.p. 220°; C with EtOH yields ethyl phenylacetate (1:3872), b.p. 227.5°.] [For use in prepn. of cellulose esters see (61).] C on hydrolysis yields phenylacetic acid (1:0665), m.p. 76.5°; for the amide, anilide, p-toluidide, and other derivs. corresp. to C see phenylacetic acid (1:0665)

3:9567 (1) Perkin, J. Chem. Soc. 69, 1205 (1896). (2) Bardan, Bull. soc. chim. (4) 49, 1428-1429 (3) Martin, Partington, J. Chem. Soc. 1936, 1177. (4) Schott, Ber. 29, 1985-1989 (5) Fourneau, Nicolitch, Bull. soc. chim (4) 43, 1239 (1928). (6) Chadha, Mahal, Venkatarman, J. Chem. Soc. 1933, 1461-1462. (7) Anschütz, Berns, Ber. 20, 1389-1392 (1887). (8) Bergs, Ber. 67, 240-241 (1934). (9) Raiford, Hildebrand, Am. J. Pharm. 101, 481-484 (1929); Cent. 1936, I 209. (10) Rupe, Ann. 369, 330 (1909). (11) von Auwers, Ber. 63, 2277, 2282-2283 (1920). (12) Kohlrausch, Pongrats, Monatsh. 64,

382 (1934). (13) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (14) Adams,

Ulich, J. Am. Chem. Soc. 42, 604 (1920). (15) Möller, Strecker, Ann. 113, 68 (1860). (16) Vanino, Thiele, Ber. 29, 1727, Note (1896). (17) Ivanov, Nicolov, Bull. soc. chim. (4) 51, 1333 (1932). (18) Weiss, Monatsh. 40, 394-395 (1919). (19) Metzner, Ann. 298, 375-376 (1897). (20) Allen, Barker, Org. Syntheses 12, 16-18 (1932); Coll. Vol. 2 (1st ed.), 156-158 (1943).

(21) Aeschliman, J. Chem. Soc. 1926, 2909. (22) Meyer, Monatsh. 22, 427-428 (1901). (23) Montonna, J. Am. Chem. Soc. 49, 2114-2116 (1927). (24) Rupe, Fiedler, J. prakt. Chem. (2) 84, 814 (1911). (25) Wedekind, Ber. 34, 2074-2077 (1901). (26) Durrans, J. Chem. Soc. 121, 49 (1922). (27) Wedekind, Ann. 378, 262-268, 275-283 (1910). (28) Rosenmund, Zetsche, Ber. 34, 337 (1921). (29) Fröschl, Danoff, J. prakt. Chem. (2) 144, 223-224 (1936). (30) Grignard, Mingasson, Compt. rend. 185, 1176 (1927).

(31) von Braun, Kochendorfer, Ber. 56, 2176 (1923). (32) Sugasawa, Tsuda, J. Pharm. Soc. Japan 56, 103-105 (1936); Cent. 1936, II 3670. (33) Graebe, Bungener, Ber. 12, 1079-1080 (1879). (34) Tiffeneau, Levy, Ditz, Bull. soc. chim. (5) 2, 1873-1874, 1875 (1935). (35) Mann, Ber. 14, 1646 (1881). (36) Kayser, Ann. chim. (11) 6, 187-188 (1936). (37) Wege, Ber. 24, 3540-3542 (1891). (38) Hatt, Pilgrim, Hurran, J. Chem. Soc. 1936, 94-95. (39) Ruggli, Reinert, Helv. Chim. Acta 9, 71-74 (1926). (40) Ferris, Turner, J. Chem. Soc. 117, 1148-1149 (1920).

(41) Delaville, Compt. rend. 184, 463 (1927). (42) Päpcke, Ber. 21, 1339 (1888). (43) Ruggli, Jenney, Helv. Chim. Acta 10, 231–232 (1927). (44) Speer, Hıll, J. Org. Chem. 2, 142 (1937). (45) Weisl, Monatsh. 26, 986–987 (1905). (46) Blau, Monatsh. 26, 1115–1153 (1905). (47) Glassner, Monatsh. 28, 282–285 (1907). (48) Finzi, Monatsh. 26, 1119–1138 (1905). (49) K. Rosenmund, M. Rosenmund, Ber. 61, 2610 (1928). (50) Ney, Ber. 21, 2450–2451 (1888).

(51) Hill, Short, J. Chem. Soc. 1935, 1125. (52) Stoermer, Biesenbach, Ber. 38, 1962 (1905). (53) Morgan, Drew, Porter, Ber. 58, 339-341 (1925). (54) Popov, J. Russ. Phys.-Chem. Soc. 4, 214 (1872); Ber. 5, 500-502 (1872). (55) Ziegler, Fries, Salzer, Ann. 448, 261 (1926). (56) Clibbens, Nierenstein, J. Chem. Soc. 107, 1492 (1915). (57) Lewis, Nierenstein, Rich, J. Am. Chem. Soc. 47, 1729 (1925). (58) Bradley, Schwarzenbach, J. Chem. Soc. 1928, 2906. (59) Ostrogovich, Tanislau, Gazz. chim. ital 64, 825-828 (1934); Cent. 1935, I 2820. (60) Basterfield, Woods, Wright, J. Am. Chem. Soc. 48, 2371-2372 (1926).

(61) I.G., Brit. 305,947, April 10, 1929; Cent. 1929, II 112. (62) McPhee, Klingsberg, J. Am. Chem. Soc. 66, 1134-1135 (1944).

3:9570
$$d$$
, l -CHLOROMETHYL-PHENYL-CARBINOL C_8H_9OCl Beil. VI — $(\beta$ -Hydroxy- β -phenylethyl chloride; H VI₁-(236) α -(chloromethyl)benzyl alcohol; C_8H_9OCl M -CH₂ M -CH

B.P.
$$128^{\circ}$$
 at 17 mm. (1) $n_{\rm D}^{25} = 1.5538$ (2) $1.8-126^{\circ}$ at 14 mm. (2) 1.5520 (2) $1.2-114^{\circ}$ at 10 mm. (3) $D_4^{20.5} = 1.1646$ (4) $n_{\rm D}^{20.5} = 1.5400$ (4) $1.0-112^{\circ}$ at 5 mm. (5) $D_-^0 = 1.225$ (1) $n_-^{17} = 1.55405$ (1)

[For prepn. of \bar{C} from phenylethylene (styrene) (1:7435) by addition of HOCl generated from Ca(OCl)₂ + CO₂ (76% yield (2)), from NaOCl + CO₂ (6), from N-chlorourea + AcOH (yield: 70% (1), 52% (4)), or from ter-butyl hypochlorite (3:7165) in dil. AcOH (60-70% yield (4)) see indic. refs. (note that omission of AcOH in ter-BuOCl method leads to formn. by direct addn. (4) of chloromethyl-phenyl-carbinyl ter-butyl ether, b.p. 87-88° at 1.5 mm., $D_4^{14} = 1.0549$, $n_D^{15} = 1.5102$ (4)).]

[For prepn. of \bar{C} from chloroacetaldehyde (3:7212) with C_6H_5MgBr in ether (71% yield (3)) or from α,β -dichloro- α -phenylethane (styrene dichloride) (3:6685) with a mild dehydrochlorinating agent such as Na₂CO₃, NaOAc, CaO, or CaCO₃ (but not an alkali hydroxide) as directed (5) see indic. refs.]

[C with alc. KOH (1) or with an alk. or alk.-earth metal oxide or hydroxide as directed (7) (8) loses HCl with ring closure to phenylepoxyethane (styrene oxide) [Beil. XVII-49 cf. (2), b.p. 191-192°, but no phenylacetaldehyde (1:0200) is formed (1) (for use of this

conversion to remove \tilde{C} from mixtures with styrene dichloride (3:6685) see (7) (8)). — However, \tilde{C} with NaOEt gives (yield not reported (1)) cf. (3) ethyl β -hydroxy- β -phenylethyl ether [Beil. VI-907], b.p. 242-243°.]

[\tilde{C} on dehydration by passing over HPO₃ on silica gel at 370–400° and 95–115 mm. press. gives (63% yield (9)) β -chlorostyrene (3:8717).]

[Č on passing over activated Al₂O₃ at 360-390° and 115-125 mm. press. gives (67% yield (9)) acetophenone (1:5515), but Č on passing over CaCO₃ on silica gel at 325-350° and 105-125 mm. press. gives (51% yield (9)) phenylacetaldehyde (1:0200).]

Č with pyridine at 120° for 6 hrs. gives in quant. yield (10) the corresp. quaternary pyridinium salt; m.p. 210-212° dec., sol. in aq., MeOH, EtOH, but spar. sol. in other org. solvents.

 \ddot{C} on oxidn. with $K_2Cr_2O_7/H_2SO_4/AcOH$ at low temp. (1) cf. (4) gives (84% yield (4)) ω -chloroacetophenone (phenacyl chloride) (3:1212).

- ——Chloromethyl-phenyl-carbinyl acetate: b.p. $101-104^{\circ}$ at 3 mm., $n_D^{12}=1.5182$ (4). [From \bar{C} with Ac_2O + pyridine (66% yield (4)).]
- ---- Chloromethyl-phenyl-carbinyl benzoate: unreported.
- ① Chloromethyl-phenyl-carbinyl p-nitrobenzoate: m.p. 81° (4). [From C with p-nitrobenzoyl chloride in pyridine (4).]
- --- Chloromethyl-phenyl-carbinyl 3,5-dinitrobenzoate: unreported.

3:9570 (1) Detoeuf, Bull. soc. chim. (4) 31, 176-177 (1922). (2) Emerson, J. Am. Chem. Soc. 67, 516-518 (1945). (3) Späth, Monatsh. 36, 6-7 (1915). (4) Hanby, Rydon, J. Chem. Soc. 1946, 114-115. (5) I.G., French 735,108, Nov. 3, 1932; Cent. 1933, II 1093; C.A. 27, 1011 (1933). (6) Essex, Ward (to du Pont Co.), U.S. 1,594,608, Aug. 3, 1926; Cent. 1926, II 1693; C.A. 20, 3170 (1926). (7) I.G., Brit. 381,459, Oct. 27, 1932; Cent. 1933, I 506; C.A. 27, 3950 (1933). (8) Knorr (to I.G.) Ger. 559,551, Sept. 21, 1932; Cent. 1933, I 1843; C.A. 27, 736 (1933): French 735,000, Oct. 31, 1932; Cent. 1933, I 1843; C.A. 27, 1011 (1933). (9) Emerson, Agnew, J. Am. Chem. Soc. 67, 518-520 (1945). (10) Gautier, Compt. rend. 198, 1430-1431 (1934).

3:9576 SUBERYL (DI)CHLORIDE
$$C_8H_{12}O_2Cl_2$$
 Beil. II - 694 O=C-(CH₂)₆-C=O II₁-(287) C₁ C₁ C₁ C₁

B.P.
$$162-163^{\circ}$$
 at 15 mm., sl. dec. (1) $D_4^{20.8} = 1.1718$ (3) $n_D^{20.6} = 1.46847$ (3) $159-160^{\circ}$ at 12 mm. (2) $149-150^{\circ}$ at 12 mm. (3) 147° at 12 mm. (4) $143-147^{\circ}$ at 12 mm. (5)

[For prepn. of \bar{C} from suberic acid (1:0755) with PCl₅ (1), with PCl₃ (4), or with SOCl₂ (yield: 100% (2)) (3) (5) (6) (8) (10) see indic. refs.]

[\bar{C} with excess MeOH yields (6) dimethyl suberate (1:4186), b.p. 268°. \bar{C} with 1 mole MeOH should yield 7-carbomethoxyheptanoyl chloride-1, b.p. 163-165° at 34 mm. (7), usually prepd. from methyl hydrogen suberate with SOCl₂ (7).]

C with excess phenol htd. at 100° yields (8) diphenyl suberate, m.p. 70-71° (8).

Č htd. with dry disodium subcrate yields (1) subcric anhydride, m.p. 65-66° (1), presumably the linear polymeric subcric α-anhydride (cf. 1:0755).

 \tilde{C} with AlCl₃ + C₆H₆ yields (1) (4) 1,8-diphenyloctanedione-1,8, m.p. 85° (4), 83-85° (1) (dioxime, m.p. 192-193° (1)).

[Č on cat. hydrogenation over Pd/diatomaceous earth as directed (9) yields suberic dialdehyde (octanedial-1,8), (bis-oxime, m.p. 152° (9), bis-phenylhydrazone, m.p. 84-86° u.c. (9), bis-semicarbazone, m.p. 183-185° (9)) cf. (2).]

1321

 \bar{C} treated with Br₂, then poured into abs. formic acid and boiled until evolution of CO ceases, yields (10) α,α' -dibromosuberic acid, m.p. 172-173° (10). [From the mother liq. a small amt. of another form, m.p. 120-121° (10), can be obtd.]

C on hydrolysis yields suberic acid (1:0755), m.p. 141° (for the diamide, dianilide, di-z-toluidide, and other derivs. corresp. to C see 1:0755).

3:9576 (1) Etaix, Ann. chim. (7) 9, 386-391 (1896). (2) Fröschl, Maier, Monatsh. 59, 273-274 (1932). (3) von Auwers, Schmidt, Ber. 46, 479 (1913). (4) Borsche, Wolleman, Ber. 45, 3717 (1912). (5) Blaise, Koehler, Bull. soc. chim. (4) 5, 690 (1909). (6) Meyer, Monatsh. 22, 421 (1901). (7) Morgan, Walton, J. Chem. Soc. 1935, 292. (8) Marangoni, Atti ist. Veneto sci. Pt. 2. Sci. math. nat. 97, 209-218 (1937-1938); Cent. 1939, I 96; C.A. 34, 6934-6935 (1940). (9) Rosenmund, Zetsche, Ber. 54, 2889-2890 (1921). (10) Goss, Ingold, J. Chem. Soc. 1926, 1473.

3:9578 DIETHYL d_1l - $\alpha_1\alpha'$ -DICHLOROSUCCINATE $C_8H_{12}O_4Cl_2$ Beil. II - 620 (Diethyl allo-dichlorosuccinate; COOC₂H₅ II₁— diethyl isodichlorosuccinate) H-C-Cl H-C-Cl H-C-Cl COOC₂H₅

B.P. 132° cor. at 15 mm. (1)
$$D_4^{90} = 1.1636$$
 (1) $n_D^{61.5} = 1.4296$ (1) 129.5° at 12.5 mm. (1) $D_4^{77} = 1.1963$ (1) $n_D^{10} = 1.4512$ (1) $n_D^{17.5} = 1.4521$ (1)

Stable oil (1), contrary to earlier (2) report.

[For prepn. of \bar{C} from $d,l-\alpha,\alpha'$ -dichlorosuccinic acid (3:4711) in EtOH with HCl gas see (1) cf. (2).]

 \overline{C} with 30% H_2SO_4 on boilg. not only hydrolyzes but also loses HCl yielding (3) chlorofumaric acid (3:4853).

3:9578 (1) Kuhn, Wagner-Jauregg, Ber. **61**, 485–486, 504 (1928). (2) van der Riet, Ann. **286**, 221 (1894). (3) Patterson, Todd, J. Chem. Soc. **1929**, 1769–1770.

3:9580 ISOAMYL d,l- α -CHLOROPROPIONATE H $C_8H_{15}O_2Cl$ Beil. S.N. 162

B.P.—
$$D_4^{20} = 1.0050 (1) \quad n_D^{20} = 1.4289 (1)$$

3:9580 (1) Schjanberg, Z. physik. Chem. A-172, 231 (1935).

B.P. 180-195° at 0.5 mm. (1)

Viscous oil, insol. in aq. but slowly dissolving when shaken with aq. because of hydrolysis to triethylene glycol (1:6538) + chloroacetic ac. (3:1370) (1).

3:9588 (1) Meerwein, Sönke, J. prakt. Chem. (2) 137, 317 (1933).

3:9590 8-CHLORO-OCTANOL-1 CH₂.(CH₂)₆.CH₂OH C₈H₁₇OCl Beil. S.N. 24 (ω-Chloro-n-octyl alcohol)

B.P. 139° at 18.5 mm. (1) 125-140° at 18 mm. (2)

[For prepn. of \bar{C} from α, ω -octamethylene glycol (m.p. 63°, b.p. 167–168° at 18 mm. (2)) with conc. HCl as directed (yields: 81% (2), 75% (1), 65% (3)) see indic. refs.]

Č with thiophenol in aq. NaOH htd. 3 hrs. gives (2) 8-hydroxy-n-octyl phenyl sulfide, pl. from lt. pet., m.p. 55° [this prod. with SOCl₂ gives (2) 8-chloro-n-octyl phenyl sulfide, cryst. from aq. alc. at low temp., m.p. 16°].

[$\bar{\mathbf{C}}$ (1 mole) with Et₂NH (3-4 moles) in s.t. at 120-160° for 12-15 hrs. gives (88% yield (1)) 8-(diethylamino)octanol-1, b.p. 151° at 12 mm., $D_4^{15.5} = 0.8610$, $n_D^{19} = 1.4570$ (1) cf. (5) (corresp. *p*-nitrobenzoate, m.p. 74° (1)); this prod. with SOCl₂ in C₆H₆ yields (1) (5) 8-(diethylamino)-*n*-octyl chloride, b.p. 130.5° at 11 mm., $n_D^{18} = 1.4535$ (1) cf. (5) (corresp. $\bar{\mathbf{B}}$.HCl, m.p. 73° (5)).]

 \bar{C} with morpholine gives (4) alm. quant. 8-(4-morpholinyl)octanol-1, b.p. 164.0-164.2° at 5 mm., $D_4^{25} = 0.9675$, $n_D^{27} = 1.4735$ (corresp. $N-(\alpha-\text{naphthyl})$ carbamate, m.p. 73.0-74.0° cor.) — \bar{C} (1 mole) with N-phenylpiperazine (2 moles) at 100° for 5 hrs gives (3) in alm. 100% yield (as salt) N-(8-hydroxy-n-octyl)-N'-phenylpiperazine, m.p. 57.0-58.5° cor. (corresp. N-phenylcarbamate, m.p. 99.5-100.5° cor.); note that this free base readily absorbs an from air to form a monohydrate, m.p. 80-82° (3).

- **8-Chloro-n-octyl N-phenylcarbamate:** ndls from aq. alc, m.p. 77° (2).
- **© 8-Chloro-n-octyl** N-(m-nitrophenyl)carbamate: m p. 62° (1)

3:9590 (1) Altman, Rec. trav. chim **57**, 951-952 (1938). (2) Bennett, Mosses, J. Chem. Soc. **1931**, 1698-1701. (3) Anderson, Pollard, J. Am. Chem. Soc. **61**, 3439-3440 (1939). (4) Anderson, Pollard, J. Am. Chem. Soc. **61**, 3440-3441 (1939). (5) Pyman, Levene (to Boot's Pure Drug Co.), Brit. **402**,159, Dec. 21, 1933; Cent. **1934**, I 2005, C.A. **28**, 3081 (1934).

3:9594
$$\beta$$
-CHLORO- n -BUTYRALDEHYDE $C_8H_{17}O_2Cl$ Beil. I - 663 DIETHYLACETAL $CH_3.CH$ $CH_2.CH(OC_2H_5)_2$ I_1 — I_2 -(724)

B.P. 70-71° at 12 mm. (1)
$$D_4^{20} = 0.9677$$
 (2) $n_D^{20} = 1.42103$ (2)

Oil insol. aq.; misc. with alc., C6H6, AcOH, or CHCl3 or pet. ether.

[For prepn. of \tilde{C} from crotonaldehyde (1:0150) with abs. EtOH + dry HCl (yield: 66% (1), 50% (3)) (2) see indic. refs.]

Č on distn. with dry KOH gives (70-80% yield) crotonaldehyde diethylacetal [Beil. I-730, I₁-(380), I₂-(789)], b.p. 146-148°.

[For reactn. of \tilde{C} with alc. NH₃ in s.t. at 120-130° giving (20% yield (4)) β -amino-n-butyraldehyde diethylacetal see (4); for analogous behavior of \tilde{C} with other amines see (4) (3).]

3:3594 (1) Wohl, Frank, Ber. 35, 1905–1906 (1902). (2) Wichterle, Vavrecka, Collection Czechoslov. Chem. Commun. 10, 494 (1938). (3) Mason, J. Chem. Soc. 127, 1033 (1925). (4) Mannich, Horkheimer, Arch. Pharm. 264, 171–172 (1926).

CHAPTER XXII

DIVISION C. LIQUIDS WITH BOILING POINTS REPORTED ONLY UNDER REDUCED PRESSURE

3:9600-3:9999 (C₉-C₁₈ inclusive) (Arranged in sequence of empirical formulas)

3:9604 1-CHLORO-1-PHENYLPROPENE-1
$$C_8H_9Cl$$
 Beil. V — $C=CH-CH_3$ $V_1-(232)$ $V_2-(372)$

B.P.
$$90.5^{\circ}$$
 at 9 mm. (1) $D_4^{20} = 1.085$ (1) $D_D^{14.6} = 1.0890$ (1) $n_D^{14.6} = 1.56352$ (1)

[For prepn. of C from ethyl phenyl ketone (propiophenone) (1:5525) by treatment with PCl₅ followed by alc. KOH see (1).]

[\bar{C} with NaNH₂ in toluene at 110° gives traces (2) of methyl-phenyl-acetylene [Beil. V-514, V₂-(408)].]

3:9604 (1) von Auwers, Ber. 45, 2799-2801 (1912). (2) Bourgeul, Ann. chim. (10) 3, 351 (1925).

B.P. 118-123° at 28 mm. (1)
$$D_4^{19} = 1.0738$$
 (3) $n_D^{19} = 1.5565$ (3) $120-124$ ° at 26 mm. (2) $D_4^{0} = 1.0912$ (3) $0.5-62.5$ ° at 2 mm. (3)

[For prepn. of \bar{C} from benzyl methyl ketone (phenylacetone) (1:5118) with PCl₅ in C₆H₆ (26.3% yield accompanied by 45.9% of the mesomeric 2-chloro-3-phenylpropene-1 (3:9608)) see (2); from 2,3-dichloro-1-phenylpropene-1 (3) by partial reduction with Zn dust in EtOH under N₂ (70% yield accompanied by 16-20% 1-phenylpropadiene-1,2 (phenylallene)) see (3); for formn. as by-prod. during addn. of HOCl to α -methylcinnamic acid see (1).

Note that \ddot{C} on stdg. isomerizes in part (2) to the mesomeric 2-chloro-3-phenylpropene-1 (3:9608).

 \bar{C} (freshly distilled) with O₃ in CHCl₃ gives (2) benzoic acid (1:0715); \bar{C} on oxidn. with KMnO₄ yields (3) benzoic acid (1:0715) + AcOH (1:1010) (note difference from the mesomer).

3:9606 (1) Hose, Farmer, J. Chem. Soc. 1933, 965. (2) Zaki, Iskander, J. Chem. Soc. 1943, 68-69. (3) Ginzburg, J. Gen. Chem. (U.S.S.R.) 8, 1029-1041 (1938); Cent. 1939, I 2183; C.A. 33, 3776 (1939).

1324

B.P. 140° at 37 mm.

M.P. 8-9°

 $D_4^{25} = 1.08815$

 $n_{\rm D}^{25} = 1.58065$

See 3:0010. Division A: Solids.

3:9608 2-CHLORO-3-PHENYLPROPENE-1

B.P. 105-107° at 26 mm. (1)

[For prepn. of \bar{C} from benzyl methyl ketone (phenylacetone) (1:5118) with PCl₅ in C_6H_6 (yield 45.9% accompanied by 26.3% of the mesomeric 2-chloro-1-phenylpropene-1 (3:9606)) see (1).]

C on stdg. isomerizes in part to the mesomeric 2-chloro-1-phenylpropene-1 (3:9606)(1).

Č (freshly distilled) with O₃ in CHCl₃ contg. some EtOH yields (1) ethyl phenylacetate (1:3872) (note difference from the mesomer).

3:9698 (1) Zaki, Iskander, J. Chem. Soc. 1943, 68-69.

3:9610 α-CHLORO-ISOPROPYLBENZENE
(Dimethyl-phenyl-carbinyl

chloride; 2-chloro-2-phenylpropane)

No physical constants for C appear to have been reported, presumably because of its ease of decomposition.

[For prepn. of \bar{C} from dimethyl-phenyl-carbinol [Beil. VI-506] by saturation with dry HCl gas at 0° see (1) (2).]

 \tilde{C} on htg. evolves HCl (1). — \tilde{C} in C_6H_6 + SnCl₄ stood for several hours below 10° gives (88% yield) the "saturated dimer of α -methylstyrene," i.e., 1,1,3-trimethyl-3-phenyl-hydrindene, cryst. from alc., m.p. 52° (3).

 \bar{C} on slow addn. to boilg. alc. KOH (4) or on warming with pyridine (1) (4) loses HCl smoothly giving (70% yield (5)) α -methylstyrene (β -phenylpropylene) [Beil. V-484, V₁-(233)], b.p. 161-162° (5).

 $\ddot{\mathbf{C}}$ dislvd. in MeOH and merely stood overnight gives (6) the corresponding ether, viz., 2-methoxy-2-phenylpropane, b.p. 78° at 13 mm., $D_4^{20} = 0.945$, $n_D^{20} = 1.4981$ (6).

3:9610 (1) Klages, Ber. **35**, 2638 (1902). (2) Hoffman, J. Am. Chem. Soc. **51**, 2546 (1929). (3) Schoepffle, Ryan, J. Am. Chem. Soc. **52**, 4028 (1930). (4) Tiffeneau, Ann. chim. (8) **10**, 156-157 (1907). (5) Harries, Ann. **390**, 265 (1912). (6) Ziegler, Schnell, Ann. **437**, 254-255 (1924).

3:9614 2-CHLORO-6-METHYL-5-METHYLENEHEPTENE-2 CoHisCl Beil. S.N. 10

B.P. 95-96° at 18 mm. (1) $D_4^{25} = 0.9310$ (1) $n_D^{25} = 1.4730$ (1)

[For prepn. of C from 2-methyl-3-methyleneheptanone-6 (thujaketone) [Beil. I-745, I₁-(386)] with PCl₅ in the cold, then htd. at 100° for 2½ hrs. (40% yield), see (1).]

 \bar{C} on oxidn. with KMnO₄ yields (1) 2-methylbutanone-3 (isopropyl methyl ketone) (1:5410) q.v.

3:9614 (1) Werner, Bogert, J. Org. Chem. 3, 585 (1939).

B.P. 75-77° at 15 mm. (1)
$$D_{-}^{20} = 0.906$$
 (1) $n_{D}^{20} = 1.450$ (1)

[For prepn. of \bar{C} from nonyne-1 (1:8125) by conversion with NaNH₂ to C_7H_{15} —C=C—Na and subsequent reactn. with benzenesulfonyl chloride in dry ether (55% yield (1)) see (1).] [Refractive indices of \bar{C} by Pulfrich instrument: $n_C^{13} = 1.4492$, $n_D^{13} = 1.4519$, $n_F^{13} = 1.4582$, $n_D^{13} = 1.4634$ (1).]

3:9618 (1) Truchet, Ann. chim. (10) 16, 335, 337 (1931).

3:9622
$$d$$
, l -2-CHLORO-2-METHYLOCTYNE-3 Cl C₉H₁₆Cl Beil. S.N. 12 CH₃.CH₂.CH₂.CH₂.CH₂.CH₂.CH₃

B.P. 68° at 15 mm. (1)
$$D_4^{20} = 0.8929$$
 (1) $n_D^{20} = 1.4480$ (1)

[For prepn. of \bar{C} from 2-methyloctyn-3-ol-2 (1) by saturation with HCl gas (85% yield) see (1).]

[C with MeMgBr gives 74% yield 2,2-dimethyloctyne-3, b.p. 79° at 70 mm., $D_4^{20} = 0.7491$, $n_2^{20} = 1.4270$ (1); C with EtMgBr gives 60% yield 3,3-dimethylnonyne-4, b.p. 82° at 40 mm., $D_4^{20} = 0.7650$, $n_2^{20} = 1.4312$ (1).]

3:9622 (1) Campbell, Eby, J. Am. Chem. Soc. 62, 1799-1800 (1940).

B.P. 59-62° at 11 mm. (1)

[For prepn. of \bar{C} from 4-methylocten-3-ol-5 [Beil. I₁-(230), I₂-(492)] with conc. HCl see (1).]

3:9624 (1) Bjelouss, Ber. 45, 626 (1912).

B.P. 124-126° at 108 mm. (1)

[For prepn. of \bar{C} from 2-methylocten-6-ol-5 (isoamyl-propenyl-carbinol) [Beil. I-449, I_1 -(230), I_2 -(492)] with PCl₅ see {1}.]

3:9628 (1) Reif, Ber. 41, 2740, 2743, Note 1 (1908).

3:9630 4-CHLORO-3,6-DIMETHYLHEPTENE-2 Cl
$$C_0H_{17}Cl$$
 Beil. I — CH₃.CH=C-CH.CH₂—CH.CH₃ I_1 - (95) I_2 — CH₃ CH_3

B.P. 59-63° at 9 mm. (1)

[For prepn. of \tilde{C} from 2,5-dimethylhepten-5-ol-4 [Beil. I₁-(231)] with 6 N HCl (78% yield) see (1).]

3:9630 (1) Abelmann, Ber. 43, 1582 (1910).

3:9632
$$d$$
, l -1,2-DICHLORONONANE Cl Cl C $_9$ H $_{18}$ Cl $_2$ Beil. S.N. 10 CH $_3$.CH $_2$.CH $_3$.CH $_4$.CH $_4$.CH $_4$.CH $_5$.CH $_$

No data on C have apparently been reported.

[For prepn. of \bar{C} from nonene-1 (1:8385) by actn. of HOCl (together with 1-chlorononanol-2) see (1).]

3:9632 (1) Kiss (to Shell Development Co.), U.S. 1,767,291, June 24, 1930; Cent. 1930, II 1475.

 $\bar{\bf C}$ has not as yet been reported, although both the optical isomerides are known. The dextrorotatory form of $\bar{\bf C}$, from levorotatory nonanol-3 with HCl at 100° (1), or from levorotatory 3-iodononane with LiCl in MeOH (2), has b.p. 98° at 33 mm. (2), 87-89° at 24 mm. (1), $D_4^{17}=0.8588$ (1). The levorotatory form of $\bar{\bf C}$, from dextrorotatory nonanol-3, with HCl at 100° (1), has b.p. 101° at 40 mm., $D_4^{17}=0.8540$ (1).

3:9638 (1) Pickard, Kenyon, J. Chem. Soc. 99, 71 (1911). (2) Levene, Rothen, Kuna, J. Biol. Chem. 120, 786 (1937).

B.P. 85-87° at 14 mm. (1)
$$D_4^{15} = 0.8639$$
 (1) $n_D^{15} = 1.4314$ (1)

[For prepn. of C from 5-bromononane by conversion to RMgBr and subsequent treatment with Cl.CN (68% yield) see (1).]

3:9640 (1) Grignard, Ono, Bull. soc. chim. (4) 39, 1592 (1926).

B.P. 72.7-74.0° at 15 mm. (1)
$$D_4^{25} = 0.8680 \text{ (1)} \quad n_D^{25} = 1.4330 \text{ (2)} \\ n_D^{20} = 1.4351 \text{ (2)} \\ 1.4347 \text{ (1)}$$

[For prepn. of C from 3-methyloctanol-3 (n-amyl-ethyl-methyl-carbinol) (1) with HCl gas (72% yield) see (1).]

3:9642 (1) Whitmore, Williams, J. Am. Chem. Soc. 55, 408-409 (1933). (2) Smart, Quayle, J. Am. Chem. Soc. 67, 21 (1945).

B.P. 70.8-71.4° at 14.5 mm. (1)
$$D_4^{25} = 0.8690$$
 (1) $n_D^{25} = 1.4338$ (2) $D_4^{20} = 0.8723$ (1) $n_D^{20} = 1.4360$ (2)

[For prepn. of \tilde{C} from 4-methyloctanol-4 (n-butyl-methyl-n-propyl-carbinol) [Beil. I₁-(211)] (1) with dry HCl at -10° see (1).]

3:9644 (1) Whitmore, Woodburn, J. Am. Chem. Soc. 55, 363-364 (1933). (2) Smart, Quayle, J. Am. Chem. Soc. 67, 21 (1945).

B.P. 46.0° at 3 mm. (1)
$$D_4^{25} = 0.8822$$
 (1) $D_4^{20} = 0.8856$ (1) $n_D^{20} = 1.4400$ (1)

[For prepn. of \tilde{C} from 3-ethylheptanol-3 (n-butyl-diethyl-carbinol) [Beil. I₁-(211), I₂-(457)] (1) with dry HCl gas at -10° see (1).]

3:9646 (1) Whitmore, Woodburn, J. Am. Chem. Soc. 55, 363-364 (1933).

B.P. 67-68° at 12 mm. (1)
$$D_4^{20} = 0.8821$$
 (1) $n_D^{20} = 1.4438$ (2) 0.884 (2) 0.884 (2) 0.884 (2) 0.884 (2) 0.884 (1) 0.884 (2) 0.884 (2) 0.884 (1)

[For prepn. of \tilde{C} from 4-ethylheptanol-4 (ethyl-di-n-propyl-carbinol) [Beil. I-424, I₁-(212), I₂-(457)] by saturation with HCl gas see (1); for formn. of \tilde{C} from 3-n-propylhexene-2 (2) with conc. HCl see (2).]

[For data on density and parachor of C at 0°, 15°, 25°, and 65° see (3).]

[Č with AlCl₃ + C₆H₆ gives 67% yield 4-ethyl-4-phenylheptane, b.p. 127-128° at 15 mm., $D_4^{20} = 0.8698$, $n_D^{15} = 1.49211$ (1).]

3:9648 (1) Halse, J. prakt. Chem. (2) 89, 456-457 (1914). (2) Nasarov, Ber. 70, 624 (1937). (3) Quayle, Owen, Beavers, J. Am. Chem. Soc. 61, 3107-3111 (1939).

1328

B.P. 54° at 8 mm. (1)
$$D_{4}^{23} = 0.8809$$
 (1) $D_{2}^{20} = 0.885$ (1) $n_{\rm D}^{20} = 1.4391$ (1)

[For prepn. of Č from 2,3-dimethylheptanol-3 (n-butyl-isopropyl-methyl-carbinol) (1) with dry HCl at 0° (86% yield) see (1).]

3:9650 (1) Whitmore, Evers, J. Am. Chem. Soc. 55, 813 (1933).

B.P. 63-64° at 15 mm. (1)
$$D_4^{18.5} = 0.8692$$
 (1) $n_D^{15} = 1.43457$ (1)

[For prepn. of \bar{C} from 2,5-dimethylheptanol-5 (ethyl-isoamyl-methyl-carbinol) [Beil. I-425, I_1 -(212)] by saturation with dry HCl gas (75% yield (1)) see (1).]

[Č with AlCl₃ + C₆H₆ yields (1) 5-phenyl-2,5-dimethylheptane, b.p. 122-123° at 14 mm., $D_4^{16} = 0.8788$, $n_D^{13} = 1.49894$ (1).]

3:9652 (1) Halse, J. prakt. Chem. (2) 89, 455 (1914).

3:9654 d,l-3-CHLORO-2,2,3-TRIMETHYLHEXANE C₂H₁₀Cl Beil. S.N. 10

(ter-Butyl-methyl-n-propyl-carbinyl Cl CH₃

chloride) CH₃.CH₂.CH₂ CH₃

CH₃ CH₃

B.P. 64.2-65.5° at 12.5-13 mm. (1)
$$D_4^{20} = 0.8973$$
 (1) $n_D^{20} = 1.4468$ (1)

[For prepn. of \bar{C} from 2,2,3-trimethylhexanol-3 (ter-butyl-methyl-n-propyl-carbinol) [Beil. I₂-(458)] (1) by saturation with dry HCl at 0° see (1).]

3:9654 (1) Petrov, Karasev, Cheltzova, Bull. soc. chim. (5) 3, 172-173 (1936).

3:9656 3-CHLORO-2,2-DIMETHYL-3-ETHYLPENTANE C₂H₁₂Cl Beil. S.N. 10 (ter-Butyl-diethyl-carbinyl chloride) Cl CH₃

CH₃.CH₂—C—C—CH₃

B.P. 53-54° at 6 mm. (1)

[For prepn. of \bar{C} from 2,2-dimethyl-3-ethylpentanol-3 (ter-butyl-diethyl-carbinol) (1) with dry HCl gas at 0° see (1).]

C on distn. at 150 mm. loses HCl (1) yielding a nonene, b.p. 80.6-81° at 150 mm. (1).

3:9656 (1) Bartlett, Knox, J. Am. Chem. Soc. 61, 3119 (1939).

Beil. S.N. 640

3:9658 PHENYLPROPIOLYL CHLORIDE

B.P. 130-133° at 25-30 mm. (1) 115-116° at 17 mm. (2) 119° at 12 mm. (3)

[For prepn. of \bar{C} from phenylpropiolic acid (1:0745) with PCl₅ (1) (2) cf. (3), or refluxed with 7 pts. SOCl₂ (90-95% yield (4)) (3), or from sodium propiolate (available from pharmaceutical industry (5)) with SOCl₂ (5) but not PCl₃ (2), see indic. refs. Note that phenylpropiolic acid (1:0745) dislvd. in 2 pts. POCl₃ at 100° and htd. 3 min. beyond first sepn. of cryst. (6), or the acid refluxed with Ac₂O (7), gives good yield 1-phenylnaphthalene-2,3-dicarboxylic anhydride [Beil. XVII-541, XVII₁-(275)], ndls. from $C_6H_6 + \lg r$., m.p. 255°.]

[For reactn. of \bar{C} with AlCl₃ + anisole (1:7445) yielding (1) (3) p-methoxyphenyl phenylethynyl ketone [Beil. VIII-199], m.p. 100° (1) (3) (dibromide, m.p. $138-140^{\circ}$ (3)), see indic. refs.; for reactn. of \bar{C} with AlCl₃ + methyl p-tolyl ether (1:7495) giving (60% yield (5)) 2-hydroxy-5-methyl- β -chlorochalcone, deep yel. ndls. from pet. eth., m.p. 95.5° (which in alc. on dropwise treatment with dil. aq. NaOH ring-closes by loss of HCl to give quant. (5) 6-methylflavone [Beil. XVIII-(206)], m.p. 122° (5)), see (5); for reactn. of \bar{C} with AlCl₃ + resorcinol (1:1530) in nitrobenzene to give 7-hydroxyflavone [Beil. XVIII-58], m.p. 241°, see (8).]

[For reactn. of C with diethyl sodio-malonate (4), ethyl sodio-acetoacetate (4), sodio-acetylacetone (4), with Na phenylacetylene or phenyl-ethynyl MgBr (9) see indic. refs.]

 \tilde{C} on hydrolysis (presumably) yields phenylpropiolic acid (1:0745), m.p. 136°. For the amide, anilide, p-toluidide, and other derivs. corresp. to \tilde{C} see the acid (1:0745).

3:9658 (1) Stockhausen, Gattermann, Ber. 25, 3537-3538 (1892). (2) Rupe, Ann. 369, 329 (1909). (3) Watson, J. Chem. Soc. 85, 1324-1325 (1904). (4) Ruhemann, Merriman, J. Chem. Soc. 87, 1389-1395 (1905). (5) Simonis, Lear, Ber. 59, 2908-2913 (1926). (6) Michael, Ber. 39, 1911-1912 (1906). (7) Michael, Bucher, Am. Chem. J. 20, 91-92 (1898). (8) Seka, Prosche, Monatsh. 69, 289 (1936). (9) Hess, Weltzien, Ber. 54, 2515-2516 (1921).

3:9660 o-METHYLPHENACYL CHLORIDE (Chloromethyl o-tolyl ketone;

(Chloromethyl o-tolyl ketone; ω -chloro-o-methylacetophenone)

C₉H₉OCl CH₃ CO.CH₂Cl

B.P. 129-130° at 11 mm. (1)

Clear pale yel. liq. (1). — Strong lachrymator!

[For prepn. from benzyl MgCl + chloroacetic acid anhydride (3:0730) (42% yield (1)) see (1): from o-toluyl chloride (3:8740) + diazomethane see (2).]

C on oxidn, with NaOCl gives (56% yield (1)) o-toluic ac. (1:0690), m.p. 104° (1).

© Chloromethyl o-tolyl ketone semicarbazone: m.p. 103-105° (1).

3:9660 (1) Austin, Johnson, J. Am. Chem. Soc. 54, 656 (1932). (2) Mercer, Robertson, Cahn, J. Chem. Soc. 1935, 1000.

--- p-CHLOROPHENYL ETHYL C₉H₉OCl Beil. VII - 301
KETONE Cl ——CO.CH₂CH₃ VII₁—

B.P. 152° at 30 mm.

M.P. 35-36°

See 3:0340. Division A: Solids.

3:9664 a-CHLOROETHYL PHENYL KETONE H C9H9OCl Beil. S.N. 640 (a-Chloropropiophenone) CH3-C-CO-

B.P. 131-133° at 26 mm. (1)

[For prepn. (66.4% yield (1)) from α -chloropropionyl chloride (3:5320) + C₆H₆ + AlCl₃ see (1).]

3:9664 (1) Baker, Barkenbus, J. Am. Chem. Soc. 58, 263 (1936).

3:9680 AZELAYL (DI)CHLORIDE $C_9H_{14}O_2Cl_2$ Beil. II - 709 II_1-C_1 II_2-C_1 II_2-C_1

B.P. 180-183° at 35 mm. (1) 166° at 18 mm. (2) 165° at 13 mm. (1) 140° at 0.4 mm. (3)

[For prepn. of \tilde{C} from azelaic acid (1:0695) with PCl₅ (1) or with SOCl₂ (2) (3) see indic. refs.]

[Č with 1 mole MeOH should yield 8-carbomethoxyoctanoyl chloride-1, b.p. 150-155° at 15 mm. (7), usually prepd. from methyl hydrogen azelate, b.p. 190-195° at 15 mm., m.p. 21-24° (7), with SOCl₂ (7).]

Č on htg. with disodium azelate yields (1) azelaic anhydride, m.p. 54-56° (1) (this prod. is probably the linear polymeric α-anhydride (see 1:0695)).

[\bar{C} with $C_6H_6 + AlCl_3$ yields (1) 1,9-diphenylnonanedione-1,9, m.p. 44° (1); \bar{C} with toluene + AlCl₃ yields (4) 1,9-di-p-tolylnonanedione-1,9, m.p. 78-79° (4).]

C with phenol yields (5) (6) diphenyl azelate, m.p. 59-60° (6), 49-50° (5).

[C with MeZnI yields (2) undecanedione-2,10, m.p. 64° (2).]

Č on hydrolysis yields azelaic acid (1:0695), m.p. 106° (for the diamide, dianilide, di-p-toluidide, and other derivs. corresp. to Č see 1:0695).

3:9680 (1) Etaix, Ann. chim. (7) 9, 397-401 (1896). (2) Blaise, Koehler, Bull. soc. chim. (4) 5, 692 (1909). (3) Rusicka, Boekenoogen, Helv. Chim. Acta 14, 1332 (1931). (4) Borsche, Ber. 52, 2081-2082 (1919). (5) Bouchonnet, Compt. rend. 140, 1599 (1905). (6) Marangoni, Atti ist. Veneto sci. Pt. 2, Sci. math. nat. 97, 209-218 (1937-38); Cent. 1939, I 96; C.A. 34, 6934-6935 (1940). (7) Morgan, Walton, J. Chem. Soc. 1936, 903.

This compound is apparently unreported although the corresp. 2,3,6-trimethylbenzyl bromide, b.p. 146° at 23 mm., 130–132° at 14 mm., has been obtd. (41% yield (1)) from prehnitene (1,2,3,4-tetramethylbenzene) (1:7548) by bromination.

Certain derivatives of Č are, however, recorded here because of the desirability of comparison with the corresp. derivs. of 2,4,5-trimethylbenzyl chloride (3:9702) and of 2,4,6-trimethylbenzyl chloride (3:0372).

- 2,3,6-Trimethylbenzyl alcohol: m.p. 83.5-85° (1).
- 2,3,6-Trimethylbenzyl acetate: oil, b.p. 152° at 23 mm. (1).

3:9701 (1) Smith, Agre, J. Am. Chem. Soc. 60, 652-653 (1938).

3:9702 2,4,5-TRIMETHYLBENZYL CHLORIDE C₁₀H₁₃Cl Beil. V — V₁— V₂ - (329)
CH₂CH₂Cl

3:9702-3:9712

B.P. 130° at 15 mm. (1) 111-116° at 6 mm. (2) 110° at 5 mm. (2) 98-108° at 1 mm. (3)

[See also the isomeric 2,4,6-trimethylbenzyl chloride (3:0372).]

[For prepn. of \bar{C} from 1,2,4-trimethylbenzene (pseudocumene) (1:7470) by chloromethylation with formalin (1:0145) + conc. HCl + HCl gas (yields: 70% (2), 40-43% (3)), or with paraformaldehyde + HCl + ZnCl₂ (4), or with chloromethyl methyl ether (3:7085) in AcOH without cat. (yields: 60% (1), 50-60% (5)) (note that some bis (chloromethylated) product is also formed) see indic. refs.; for prepn. of \bar{C} from 2,4,5-trimethylbenzyl alc. (see below) with conc. HCl under reflux 5 hrs. see (2).]

[Č on catalytic hydrogenation presumably yields 1,2,4-trimethylbenzene (pseudocumene) (1:7470) although this particular reaction is not actually reported cf. (1)]

[C on hydrolysis presumably yields 2,4,5-trimethylbenzyl alcohol, cryst. from alc., m.p. 83.0-83.5° (2); note, however that this reaction is not actually reported, the alc. having been obtd. by hydrolysis of its acetate, oil, b.p. 141-150° at 9 mm. (2).]

Č in alc. with aq. NaCN refluxed 5 hrs. gives (85% yield (2)) 2,4,5-trimethylbenzyl cyanide, m.p. 9-10°, b.p. 133-147° at 4 mm. (2); note that this nitrile upon hydrolysis with 50% H₂SO₄ at 100° for 2½ hrs. gives 2,4,5-trimethylphenylacetic acid, crude m.p. 116-118° (2), pure m.p. 128-129° (2) (corresp. dinitro deriv., m.p. 203-203.5° (2)).

[For condensation of C with ethyl sodio-acetoacetate see (3).]

3:9762 (1) Vavon, Bolle, Calin, Bull soc. chim. (5) 6, 1025-1033 (1939). (2) Smith, MacMullen, J. Am. Chem. Soc. 58, 633-635 (1936). (3) John, Gunther, Ber. 74, 887-888 (1941). (4) Bert, Comp. rend. 186, 373-374 (1928). (5) Vavon, Bolle, Comp. rend. 204, 1826-1828 (1937).

B.P. 82° at 17 mm. (1)
$$D_4^{20} = 0.8968$$
 (1) $n_D^{20} = 1.4543$ (1)

[For prepn. of \bar{C} from 3-methylnonyn-4-ol-3 (1) by saturation with HCl gas (72% yield) see (1).]

[\tilde{C} with MeMgBr gives 73% yield 3,3-dimethylnonyne-4, b.p. 82° at 40 mm., $D_4^{20} = 0.7658$, $n_D^{20} = 1.4313$ (1).]

3:9710 (1) Campbell, Eby, J. Am. Chem. Soc. 62, 1799-1800 (1940).

3:9712 5-CHLORODECENE-5 Cl C₁₀H₁₉Cl Beil. S.N. 11
CH₃.CH₂.CH₂.CH₂.CH₂.CH₂.CH₂.CH₂.CH₃.

B.P. 99-100° at 28 mm. (1)
$$D_4^{25} = 0.8753$$
 (1) $n_D^{25} = 1.4448$ (1)

Two geom. stereoisomers of \tilde{C} are possible, but only this one has as yet been recognized. [For prepn. of \tilde{C} from decyne-5 (di-n-butylacetylene) [Beil. I₂-(239)] with AcCl + SnCl₄

(4-chloro-3-n-butylocten-3-one-2, b.p. 140-146° at 28 mm., $D_4^{25} = 0.9459$, $n_D^{25} = 1.4612$, is also formed (1)) see (1).]

3:9712 (1) Kroeger, Sowa, Nieuwland, J. Org. Chem. 1, 163-169 (1936).

B.P. 83-84° at 12 mm. (1)

[For prepn. of C from 2,6-dimethylocten-6-ol-5 [Beil. I-452, I₁-(232)] with 6 N HCl see (1).]

3:9714 (1) Abelmann, Ber. 43, 1583 (1910).

B.P. 70-72° at 10 mm. (1)

For prepn. of \bar{C} from 3,4-diethylhexene-3 (1) with $Cl_2 + NaHCO_3$ at 0° (60% yield accompanied by 40% yield of 3,4-dichloro-3,4-diethylhexane (3:9724)) see (1).]

Beil. S.N. 10

C on treatment with O₃ yields (1) acetaldehyde (1:0100) q.v.

3:9716 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4222; C.A. 33, 4190 (1939).

B.P. 147-148° at 11 mm. (1)
$$D_4^{22} = 0.9941$$
 (1)

[For prepn. of C from decanediol-1,10 (decamethylene glycol) (1:5961) by htg. 1 day with excess SOCl₂ see (1).]

C with NaI in acetone refluxed 4 hrs., acetone evaporated, residual material htd. for 3 hrs. at 140-150° with thiourea in isoamyl alc., yields (1) decamethylene ω, ω' -bis-(isothiourea hydrochloride), m.p. 186° (1).

3:9720 (1) Kawai, Hosono, Shikinami, Yonechi, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 16, Nos. 306-309, 9-16 (1931); Cent. 1931, II 1694; C.A. 25, 5665 (1931).

3:9724 3,4-DICHLORO-3,4-DIETHYLHEXANE
$$C_{10}H_{20}Cl_2$$
 Beil S.N. 10 Cl Cl $CH_2.CH_2$ $CH_3.CH_3$ C_2H_5 C_2H_5

B.P. 101-103 at 10 mm. (1)

 $D_4^{10} = 1.022 (1) \quad n_5^{15} = 1.47485 (1)$

[For prepn. of Č from 3,4-diethylhexene-3 (1) with Cl₂ + NaHCO₃ at 0° (yield 40% accompanied by 60% 4-chloro-3,4-diethylhexene-2 (3:9716)) see (1).]

3:9724 (1) Tishchenko, J. Gen. Chem. (U.S.S.R.) 8, 1232-1246 (1938); Cent. 1939, II 4222; C.A. 33, 4190 (1939).

B.P. 43-45° at 1 mm. (1)
$$D_4^{25} = 0.8663$$
 (1) $n_D^{25} = 1.4369$ (2) $n_D^{20} = 1.4389$ (2) 1.4375 (1)

[For prepn. of \tilde{C} from 4-methylnonanol-4 (n-amyl-methyl-n-propyl-carbinol) (1) with HCl gas (85% yield (1)) see (1).]

3:9730 (1) Whitmore, Williams, J. Am. Chem. Soc. 55, 408-409 (1933). (2) Smart, Quayle, J. Am. Chem. Soc. 67, 21 (1945).

B.P. 75-77° at 10 mm. (3)
$$D_4^{25} = 0.8676$$
 (1) $D_4^{20} = 0.8707$ (1) $D_D^{20} = 1.4382$ (1)

[For prepn. of \tilde{C} from 5-methylnonanol-5 (di-n-butyl-methyl-carbinol [Beil. I₁-(213), I₂-(460)] (1) by saturation with dry HCl gas at -10° see (1).]

Č on refluxing with 2½ pts. aq. for 9 hrs. gives 14% of its halogen as halide ion (1) (the resultant olefin was not isolated).

[For behavior of \ddot{C} with naphthalene + AlCl₃ in CS₂ see (3).]

3:9732 (1) Whitmore, Woodburn, J. Am. Chem. Soc. **55**, 363-364 (1933). (2) Woodburn, Whitmore, J. Am. Chem. Soc. **56**, 1394-1395 (1934). (3) Petrov, Kurbskii, J. Gen. Chem. (U.S.S.R.) **14**, 492-494 (1944); C.A. **39**, 4600 (1945).

3:9734
$$d$$
, l -3-CHLORO-3-ETHYLOCTANE $C_{10}H_{21}Cl$ Beil S.N. 10 (n -Amyl-diethyl-carbinyl chloride) Cl CH_3 . CH_2 . CH_2 . CH_3 . CH_2 . CH_3 . CH_4 . CH_5

B.P. 42-43° at 0.5 mm. (1)
$$D_4^{25} = 0.8792$$
 (1) $n_D^{20} = 1.4423$ (1)

[For prepn. of C from 3-ethyloctanol-3 (n-amyl-diethyl-carbinol) [Beil. I-426] (1) with HCl gas (72% yield (1)) see (1).]

3:9734 (1) Whitmore, Williams, J. Am. Chem. Soc. 55, 408-409 (1933).

[For prepn. of \tilde{C} from 4-ethyloctanol-4 (n-butyl-ethyl-n-propyl-carbinol) [Beil. I₂-(460)] (1) by saturation with dry HCl gas at -10° see (1).]

3:9736 (1) Whitmore, Woodburn, J. Am. Chem. Soc. 55, 363-364 (1933).

B.P. 53-55° at 3 mm. (1)
$$D_4^{20} = 0.8818$$
 (1) $n_D^{20} = 1.4420$ (1)

[For prepn. of \bar{C} from 2,3-dimethyloctanol-3 (1) with dry HCl gas at 0° (77% yield) see (1).]

3:9738 (1) Whitmore, Evers, J. Am. Chem. Soc. 55, 813-814 (1933).

B.P. 88-89° at 12 mm. (1) 85-86° at 10 mm. (2)

[For prepn. of \bar{C} from 2,6-dimethyloctanol-8 [Beil. I-426, I_{1} -(214), I_{2} -(461)] (1) with dry HCl (1) or with PCl₅ (2) see indic. refs.]

[For conversion of \bar{C} to corresp. RMgCl and reactn. of latter with chloromethyl methyl ether (3:7085) to give (70% yield (1)) 1-methoxy-4,8-dimethylnonane, b.p. 94-94.5° at 14.5 mm., $n_D^{20} = 1.4240$ see (1).]

3:9749 (1) Smith, Ungnade, Austin, Prichard, Opie, J. Org. Chem. 4, 338-340 (1939). (2) Ishizaka, Ber. 47, 2454 (1914).

B.P. 80° at 12 mm. (1)
$$D_4^{20} = 0.8779$$
 (1) $n_D^{16} = 1.44209$ (1)

. [For prepn. of Č from 4-n-propylheptanol-4 [Beil. I-426, I₁-(214), I₂-(461)] by saturation with dry HCl see (1).]

[For data on density and parachor of C at 0°, 15°, 25°, 50°, and 75° see (2).]

[For reactn. of \bar{C} with AlCl₃ + C₆H₆ yielding 4-phenyl-4-n-propylheptane, b.p. 140-141° at 15 mm., $D_4^{20} = 0.8694$, $n_D^{15} = 1.4924$, see (1).]

3:9742 (1) Halse, J. prakt. Chem. (2) 89, 459 (1914). (2) Quayle, Owen, Beavers, J. Am. Chem. Soc. 61, 3107-3111 (1939).

B.P. 82-83° at 25 mm. (1)

$$D_4^{20} = 0.8657$$
 (1) $n_D^{15} = 1.43336$ (1)

[For prepn. of \bar{C} from 2,4,6-trimethylheptanol-4 (di-isobutyl-methyl-carbinol) [Beil. I-427, I₁-(215)] (1) by saturation with dry HCl gas see (1).]

[For reactn. of \tilde{C} with AlCl₃ + C_6H_6 to give 4-phenyl-2,4,6-trimethylheptane, b.p. 143-144° at 18 mm., $D_4^{20}=0.8753, n_D^{15}=1.49497$ see (1).]

3:9744 (1) Halse, J. prakt. Chem. (2) 89, 458-459 (1914).

3:9750 2,4,6-TRIMETHYLBENZOYL CHLORIDE
$$C_{10}H_{11}OCl$$
 Beil. S.N. 943 (Mesito'yl chloride; CH_3 CH_3

B.P.
$$143-146^{\circ}$$
 at 60 mm. (1) $D_4^{25}=1.0967$ (3) $n_D^{25}=1.5263$ (3) $118-119^{\circ}$ at 19 mm. (2) $115.5-116.5^{\circ}$ at 18 mm. (3) $85.0-85.5^{\circ}$ at 4 mm. (4) $85.5-86.5^{\circ}$ at 2-3 mm. (5)

[For prepn. of \bar{C} from 2,4,6-trimethylbenzoic acid (mesitoic acid) [Beil. IX-553, IX₁-(214)] (1) with SOCl₂ (90-97% yield (1)) (2) (3) (5) (6) see indic. refs.]

[\tilde{C} with MeOH yields (3) (4) methyl-2,4,6-trimethylbenzoate (mesitoate) [Beil. IX-553], b.p. 242°, 102-103° at 5.5 mm. (3), 101-102° at 3 mm., $n_D^- = 1.4970$ (4).]

[C with 2,4,6-trimethylphenyl MgBr yields (5) (6) 2,4,6,2',4',6'-hexamethylbenzophenone (dimesityl ketone), m.p. 138-139° (5), 136-137° (6); C with 2,4,6-trimethylphenacyl MgBr gives (7) 2,4,6,2',4',6'-hexamethyldibenzoylmethane (dimesitoylmethane), m.p. 96-97° (7).]

C on hydrolysis yields (4) 2,4,6-trimethylbenzoic acid, m.p. 152° (amide, m.p. 189° (9), 188–188.5° (4), 187–188° (8)).

3:9750 (1) Barnes, Org. Syntheses 21, 77-79 (1941). (2) Murray, Cleveland, Saunders, J. Am. Chem. Soc. 63, 3121 (1941). (3) Kadesch, Weller, J. Am. Chem. Soc. 63, 1311 (1941). (4) Norris, Young, J. Am. Chem. Soc. 57, 1424 (1935). (5) Nauta, Wuis, Rec. trav. chim. 56, 537-538 (1937). (6) Kohler, Baltaly, J. Am. Chem. Soc. 54, 4023 (1932). (7) Fuson, Fugate, Fisher, J. Am. Chem. Soc. 61, 2363 (1939). (8) Wheeler, Am. Chem. J. 23, 468 (1900). (9) Hantssch, Lucas, Ber. 28, 748 (1895).

3:9760 2-CHLORO-4-ter-BUTYLPHENOL

C₁₀H₁₈OCl

Beil. S.N. 530-a

B.P. 113-115° at 8 mm. (1)

85-86° at 3-4 mm. (2)

84.5-85° at 3-4 mm. (3)

[For prepn. of \bar{C} from *p-ter*-butylphenol (1:1510) by chlorination with *N*-chloroacetamide (cf. (4) (5)) see (1); for other methods see (2) (3).] [For study of mercuration of \bar{C} see (6).]

4-ter-Butyl-2-chlorophenyl p-nitrobenzyl ether: colorless pl. from EtOH, m.p. 90° (1).

3:9760 (1) Jones, J. Chem. Soc. 1942, 678. (2) Mills (to Dow Chem. Co.), U.S. 2,176,010, Oct. 10, 1939; C. A. 34, 858 (1940). (3) Mills (to Dow Chem. Co.), U.S. 2,221,807, Nov. 19, 1940; C.A. 35, 1936 (1941). (4) Orton, King, J. Chem. Soc. 99, 1185-1192 (1911). (5) Orton, Bradfield, J. Chem. Soc. 1927, 993. (6) Moness, Christiansen (to E.R. Squibb), U.S. 2,137,236, Nov. 22, 1938; Cent. 1939, I 5007; C.A. 33, 1885-1886 (1939).

4-CHLORO-5-ISOPROPYL-2- Cl C₁₀H₁₃OCl Beil. S.N. 531
METHYLPHENOL (CH₃)₂CH CH₃ ?

B.P. 158° at 52 mm.

M.P. 42-43°

See 3:0480. Division A: Solids,

113-120° at 1 mm. (3)

3:9770 β -CHLOROETHYL- β '-PHENOXYETHYL $C_{10}H_{13}O_2C!$ Beil. VI — VI₁— $C_{10}H_{13}O_2C!$ Beil. VI — VI₁— VI₂— (150) chloride]

B.P. 149° at 10 mm. (1) $D_{15}^{15} = 1.149$ (1) 138–143° at 8 mm. (2)

[For prepn. (60% yield (1)) from β,β' -dichlorodiethyl ether (3:6025) with alc. NaOC₆H₅ (1 mole) see (1).]

[For reaction of C in CS₂ or C₆H₆ with AlCl₃ + phthalic anhydride, succinic anhydride, maleic anhydride, acetic anhydride see (4).]

[For condensation with amines and phenols see (5); for use as plasticizer see (6).]

S:9770 (1) Cretcher, Koch, Pittenger, J. Am. Chem. Soc. 47, 1174 (1925). (2) Eastman Organic Chemicals, List No. 33 (1942). (3) Bruson (to Röhm and Haas Co.), U.S. 2,249,111, July 15, 1941; C.A. 35, 6698 (1941). (4) Bruson, Eastes, J. Am. Chem. Soc. 60, 2502-2505 (1938). (5) Röhm and Haas Co., French 824,887, Feb. 17, 1938; Cent. 1938, II 1861; C.A. 32, 6258 (1938). (6) Murray, Kenyon (to Eastman Kodak Co.), U.S. 1,946,635, Feb. 13, 1934; Cent. 1934, II 2153; C.A. 28, 2532 (1934).

3:9780 SEBACYL (DI)CHLORIDE
$$C_{10}H_{16}O_{2}Cl_{2}$$
 Beil. II - 719 $C_{10}CC_{10}$ $C_{10}CCC_{10}$ $C_{10}CCC_{10}$ $C_{10}CCC_{10}$ $C_{10}CCC_{10}$ $C_{$

168-170° at 16 mm. (4) 152° at 15 mm. (5) 162-167° at 11 mm. (6) 155-156° at 8 mm. (7) 109-110° at 1-2 mm. (11)

[For prepn. of \bar{C} from sebacic acid (1:0730) with PCl₅ (90-95% yield (5) (2)) (4), with PCl₃ (3), with SOCl₂ (yield: 100% (1), 86% (6), 84% (7)) (8), 83% (11), or with SiCl₄ in C_6H_6 + ether (37% yield (9)) see indic. refs.]

Č with MeOH (1 mole) followed by Na₂CO₃ yields (1) methyl hydrogen sebacate, m.p. 36° (1); Č with abs. EtOH (1 mole) yields (7) 9-carbethoxynonanoyl chloride (C₂H₅OOC.(CH₂)₈.CO.Cl), b.p. 158−160° at 7 mm. (7) (corresp. 9-carbethoxynonanoic anilide, m.p. 60−61° (7)); Č with excess phenol yields (8) diphenyl sebacate, m.p. 65−66° (8).

[\bar{C} with AlCl₃ + C_6H_6 (1:7400) gives (50% yield (2)) (4) 1,8-dibenzoyloctane, m.p. 91-92° (4), 88-89° (2); \bar{C} with AlCl₃ + m-xylene (1:7420) gives (10) 1,8-bis-(2,4-dimethylbenzoyl)octane.]

[\bar{C} with n- $C_6H_{13}MgBr$ gives (28% yield (7)) 10-ketopalmitic acid, m.p. 75-75.8° (7); \bar{C} with n- $C_8H_{17}MgBr$ gives (12% yield (7)) 10-ketostearic acid, mp.. 82-82.8° (7); \bar{C} with AgNCO yields (11) sebacyl di-isocyanate.

[C in xylene on cat. hydrogenation over Pd/CaCO₃ (6) or Pd/diatomaceous earth (5) gives (30-40% yield (5)) corresp. dialdehyde, decandial-1,10 [Beil. I₂-(849)].]

 $\tilde{\mathbf{C}}$ on hydrolysis yields sebacic acid (1:0730); for the diamide, dianilide, di-p-toluidide, and other derivs. corresp. to $\tilde{\mathbf{C}}$ see 1:0730.

3:9780 (1) Meyer, Monatsh. 22, 421 (1901). (2) Auger, Ann. chim. (6) 22, 361-364 (1891). (3) Borsche, Wollemann, Ber. 44, 3185-3186 (1911). (4) von Auwers, Schmidt, Ber. 46, 480 (1913). (5) Rosenmund, Zetsche, Ber. 55, 609-612 (1922). (6) Waser, Helv. Chim. Acta 8, 124-125 (1925). (7) Fordyce, Johnson, J. Am. Chem. Soc. 55, 3369-3370 (1933). (8) Marangoni, Atti ist. Veneto sci. Pt. 2. Sci. mat. nat. 97, 209-218 (1937-1938); Cent. 1939, I 96; C.A. 34, 6934-6935 (1940). (9) Montonna, J. Am. Chem. Soc. 49, 2115 (1927). (10) Borsche, Ber. 52, 2078, 2082 (1919).

(11) Lieser, Macura, Ann. 548, 226-254 (1941); Cent. 1942, II 146-148; C.A. 37, 4699 (1942).

3:9792 METHYL ω -(CHLOROFORMYL)PELARGONATE Beil. S.N. 178 (ω -(Carbomethoxy)pelargonyl chloride) O $C_{11}H_{19}O_3Cl$

CH₃OOC—(CH₂)₈—C—Cl

B.P. 177° at 23 mm. (1) 158-160° at 10 mm. (2)

Note that C is both an acid chloride and an ester.

[For prepn. of \tilde{C} from methyl hydrogen sebacate (itself obtd. (52-61% (2)) from sebacic acid (1:0730) + MeOH (1:6120)) by action of SOCl₂ (yields: 83-86% (2), 60-70% (1)) set indic. refs.]

- ω-(Carbomethoxy)pelargonamide (methyl sebacamate): cryst. from aq., m.p. 77.4° (3), 72–74° (2). [From Č with conc. aq. NH₄OH at 8° (yields: 93–95% (2), 90% (3)); for dehydration of this prod. (64–71% yield) (3) with P₂O₅ in acetylene tetrachloride to methyl ω-cyanopelargonate, b.p. 170° at 14 mm., $n_D^{25} = 1.4398$ (3), and use of latter in prepn. of high-mol.-wt. linear polymers (4), see indic. refs.]
- **3:9792** (1) Morgan, Walton, J. Chem. Soc. 1936, 904. (2) Bishop, Org. Syntheses 25, 71-72 (1945). (3) Biggs, Bishop, J. Am. Chem. Soc. 63, 944 (1944). (4) Bishop (to Bell Telephone Laboratories, Inc.), U.S. 2,277,033, March 24, 1942; C.A. 36, 4636 (1942).

3:9800 *n*-UNDECANOYL CHLORIDE
$$C_{10}H_{21}OCl$$
 Beil. S.N. 162 (*n*-Hendecanoyl chloride) $CH_{3}.(CH_{2})_{9}.C=O$ Cl B.P. 119–120° at 40 mm. (1) $n_{D}^{5}=1.4465$ (3)

123° at 11 mm. (2) 90° at 1 mm. (3)

Care must be taken to avoid confusion of \tilde{C} with *n*-undecyl chloride (1-chloroundecane) (3:8803).

[For prepn. of \tilde{C} from *n*-undecylic acid (1:0573) with SOCl₂ (yield: 95.5% (1)) (3) (4) see indic. refs.]

[\bar{C} with $C_6H_6+AlCl_3$ should give *n*-undecyl phenyl ketone, but this compd. is unreported in the literature. — \bar{C} with toluene (1:7405) + AlCl₃ gives (80% yield (5)) *n*-undecyl *p*-tolyl ketone, m.p. 32°, b.p. 196–197° at 12 mm.(?)]

[\bar{C} with MeOH presumably gives methyl *n*-undecylate [Beil. II₁-(154), II₂-(314)], b.p. 123° at 9-10 mm. (6); similarly, \bar{C} with EtOH presumably gives ethyl *n*-undecylate [Beil. II-358, II₁-(154)] (known in polymorphic forms for which see (7) (8) (9)); note, however, that prepn. of these esters by this means is not actually reported in the literature).]

 $[\bar{C}]$ with phenol presumably gives phenyl *n*-undecylate, but neither this cpd. nor either of the *n*-undecyl hydroxyphenyl ketones to be expected from its rearr. with AlCl₃ is reported in the literature. — However, for reaction of \bar{C} with hydroquinone (1:1590) see (10).]

[Č with sodium undecylate on htg. presumably gives undecylic anhydride, m.p. 36.7° (11), 35° (12), but this cpd. is actually reported only by other methods (11) (12).]

[For reaction of \hat{C} with diethyl sodioacetosuccinate [Beil. III-801, III₁-(280), III₂-(486)] and subsequent hydrolysis of prod. to γ -ketomyristic acid see (4).]

[\bar{C} with vanilly lamine (4-hydroxy-3-methoxybenzy lamine) gives (2) cf. (13) N-(vanilly l)-myristamide, α -form, m.p. 69.5° (2); β -form, m.p. 62.0-62.5° (2); the m.p. of 54-56° reported earlier (13) may have been a mixture, but that of 73-74° by other workers (14) is unexplained.]

 \bar{C} on hydrolysis yields undecylic acid (1:0573), m.p. 29.3°; for the amide, anilide, p-toluidide, and other derivatives corresp. to \bar{C} see undecylic acid (1:0573).

S:9900 (1) Fierz-David, Kuster, Helv. Chim. Acta 22, 86-89 (1939). (2) Ford-Moore, Phillips, Rec. trav. chim. 53, 856 (1934). (3) Haskelberg, Bergmann, J. Soc. Chem. Ind. 60, 166-168 (1941). (4) Robinson, J. Chem. Soc. 1930, 747-748. (5) Hasan, Stedman, J. Chem. Soc. 1931, 2120. (6) Lesser, Weiss, Ber. 47, 2519 (1914). (7) van Bellinghen, Bull. soc. chim. Belg. 47, 647, 659, 673, 674, 676, 677, (1938). (8) Mumford, Phillips, Rec trav. chim. 52, 181-194 (1933). (9) Meyer, Reed, J. Am. Chem. Soc. 55, 1582 (1933). (10) Asano, Hase, J. Pharm. Soc. Japan 60, 650-659 (1940); 61, 1-6 (1941); C.A. 36, 82 (1942).

(11) Wallace, Copenhaver, J. Am. Chem. Soc. 63, 699 (1941). (12) Backer, van der Baan, Rec. trav. chim. 56, 1166 (1937). (13) Nelson, J. Am. Chem. Soc. 41, 2125-2126 (1919). (14) Kobayashi, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 6, 166-184 (1927); Cent. 1928, I 1029.

3:9850 2,3-DICHLOROBIPHENYL

Cl Cl Beil. S.N. 479

B.P. 172° at 30 mm. (1) 170-176° at 19 mm. (2)

[For prepn. from 2-amino-3-chlorobiphenyl via diazo reactn. see (1); for other methods see (2).]

 \bar{C} on oxidn. with $CrO_3 + AcOH$ yields (1) 2,3-dichlorobenzoic acid (3:4650), m.p. 160° (1).

3:9850 (1) de Crauw, Rec. trav. chim. 50, 776-777 (1931). (2) Zerweek, Schütz (to General Aniline and Film Corp.), U.S. 2,280,504, April 21, 1942; C.A. 36, 5658 (1942).

- 2,4'-DICHLOROBIPHENYL C₁₂H₈Cl₂ Beil. S.N. 479

B.P. 191° at 30 mm.

M.P. 46°

See 3:0670. Division A: Solids.

3:9854 2,5-DICHLOROBIPHENYL Cl C₁₂H₈Cl₂ Beil. V — V₁— V₂-(483)

B.P. 182° at 30 mm. (1)

171° at 15 mm. (2)

147-148° at 8 mm. (3)

[For prepn. of C from 2-amino-5-chlorobiphenyl (1) (2), 4,4'-diamino-2,5-dichlorobiphenyl (20% yield (1)), or 2,5-dichloroaniline (3) via appropriate diazo reactions see (1) (2) (3).] C on oxidn. with CrO₃ + AcOH yields (1) (2) 2,5-dichlorobenzoic acid (3:4340), m.p. 152° (1), 154° (2).

[For study of reaction of C with NaOMe see (4).]

3:9854 (1) de Crauw, Rec. trav. chim. 50, 776-777 (1931). (2) Scarborough, Waters, J. Chem. Soc. 1927, 94. (3) I.G., French 851,131, Jan. 3, 1940; C.A. 36, 1950 (1942). (4) Ref. 1, pp. 784-785, 789.

— 3,4-DICHLOROBIPHENYL Cl Cl Cl₁₂H₈Cl₂ Beil. V — V₁— V₂—(483)

B.P. 195-200° at 15 mm.

M.P. 46°

See 3:0685. Division A: Solids.

-- 3,5-DICHLOROBIPHENYL Cl C₁₂H₈Cl₂ Beil. V -- V₁-- V₂-(484)

B.P. 180° at 15 mm.

M.P. 36°

See 3:0360. Division A: Solids.

Beil. S.N. 539

B.P. 176.6° at 5 mm.

M.P. 77°

See 3:1900. Division A: Solids.

3:9856
$$\alpha$$
-NAPHTHYLACETYL CHLORIDE $C_{12}H_{9}OCl$ Beil. IX — IX₁-(278)

[For prepn. of \tilde{C} from α -naphthylacetic acid (1:0728) with PCl₅ (4) (1), or with SOCl₂ alone (2) (5) or in C₆H₅ (6), see indic. refs.]

Č with AlCl₃ in nitrobenzene (1) (but *not* by SnCl₄ in CS₂ at room temp. (2)) losses HCl and ring-closes yielding acenaphthenone (1:5200), m.p. 121° cor.

[\bar{C} with aminoacetic acid (glycine) yields (5) N-(α -naphthylacetyl) glycine, m.p. 153-154° (5). (For reactn. of \bar{C} with other amino acids and use as plant hormone see (5)).]

 \bar{C} on hydrolysis yields α -naphthylacetic acid (1:0728) q.v. for the corresp. amide and anilide.

3:9856 (1) Badische Anilin- und Soda-Fabrik, Ger. 230,237, Jan. 20, 1910; Cent. 1911, I 358. (2) Cook, Hewett, J. Chem. Soc. 1933, 1108. (3) Wolfram, Schörnig, Hausdörfer (to I.G.), Ger. 562,391, Nov. 1, 1932; Cent. 1933, I 849. (4) Boessneck, Ber. 16, 641 (1883). (5) Isler (to Hoffmann-LaRoche Inc.), U.S. 2,179,979, Nov. 14, 1939; C.A. 34, 1808 (1940); Brit. 510,138, July 27, 1939; Cent. 1939, II 3872; C.A. 34, 4080 (1940); Swiss 203,078, May 16, 1939; Cent. 1939, II 3872. (6) Gilman, Kirby, J. Am. Chem. Soc. 51, 3477, Note 18 (1929). (7) King, Henshall, J. Chem. Soc. 1945, 418.

Note that care must be taken to avoid confusion of \tilde{C} with *n*-lauryl chloride (1-chlorododecane) (3:8810).

PREPARATION OF C

[For prepn. of \tilde{C} from *n*-lauric acid (1:0605) with PCl₅ (yields: 91.5% (10), 66% (13)) (6) (15) (32), with PCl₅ + ZnCl₂ (45% yield (13)), with PCl₃ (yields: 80% (8), 72% (13)) (4) (16), with PCl₃ + ZnCl₂ (79% yield (13)), with SOCl₂ (yields: 92% (9), 80-84% (11), 83% (13), 80% (20)) (1) (5) (17) (32) (33), with oxalyl (di)chloride (3:5060) (99% yield (3)) (2), or with carbonyl chloride (phosgene) (3:5000) at 140-150° (85-90% yield (18)) see indic. refs.]

[For prepn. of \bar{C} from α, β -dichloroethyl laurate (19) on distn. with 0.1% ZnCl₂ (chloroacetaldehyde (3:7212) is also formed) see (19).]

CHEMICAL BEHAVIOR OF C

BEHAVIOR WITH INORGANIC REACTANTS

Hydrogenation of \tilde{C} . [\tilde{C} with $H_2 + Pt$ cat. at 200-320° and 50-180 mm. or with $H_2 + Raney$ Ni at 160° and 50 mm. fails (8] to give the expected lauraldehyde (1:0017); this result is apparently due to side reactions of the latter since undecane (1:8820) and tricosane, $C_{23}H_{48}$, were isolated (8).]

Behavior with sodium. [Č (1 mole) with metallic sodium (1.2 moles) in dry ether refluxed (with stirring) for 4 hrs. gives (60% yield (20)) tetracosen-12-diol-12,13 dilaurate, i.e., the dilaurate ester of CH₃.(CH₂)₁₀.C(OH)=C(OH).(CH₂)₁₀.CH₃, cryst. from acetone/C₆H₆ (3:1), m.p. 42-43° (20).]

Behavior with Na_2O_2 . [\bar{C} with aq. Na_2O_2 below 50° gives (21) dilauroyl peroxide, but no constants for either this prod. or for lauroyl hydrogen peroxide can be found in the literature; for use of dilauroyl peroxide as cat. for drying oils see (22).]

Behavior with NaN₃. [\tilde{C} with NaN₃ in C₆H₆ reacts to give lauroyl azide (not isolated (23)), which loses N₂ and rearr. giving (81–86% yield (23)) undecyl isocyanate, b.p. 103° at 3 mm. (23).]

BEHAVIOR WITH ORGANIC REACTANTS

With hydrocarbons. [\bar{C} with $C_6H_6+AlCl_3$ gives (yields: 100% (14), 71% (11)) (24) (25) (26) (27) phenyl undecyl ketone (laurophenone) [Beil. VII-345, VII₁-(186)], m.p. 47° (24) (28), 46° (14) (25), 45° (26), 44-45° (11); b.p. 222-223° at 21 mm. (25), 201-202° at 9 mm. (26), 193-194° at 9 mm. (11), 174° at 3 mm. (29) (corresp. oxime, m.p. 64.5° (11); semicarbazone, m.p. 98° (11); 2,4-dinitrophenylhydrazone, m.p. $101-102^\circ$ (11)). — For analogous reactions of \bar{C} in pres. of AlCl₃ with biphenyl (1:7175), diphenyl ether (1:7125), diphenylene oxide (1:7205), carbazole, thiophene, and furan see (30); for use of these products as waxes, addition agents for lubricants, etc., see (30) (31).]

With alcohols. \bar{C} with alcohols gives in general the corresp. alkyl laurates [e.g., \bar{C} with MeOH gives methyl laurate, m.p. +5°, b.p. 148° at 18 mm. (10); \bar{C} with EtOH gives ethyl laurate (1:4196), m.p. -1.7 b.p. 269°; etc. $-\bar{C}$ with benzyl alc. (1:6480) gives (32) benzyl laurate; \bar{C} with menthol (1:5940) gives (33) menthyl laurate; etc.].

C (2 moles) with dihydric alcs. on htg. gives the corresp. neutral esters [e.g., C with ethylene glycol (1:6465) gives (34) ethylene glycol dilaurate (1:2157), m.p. 52°; C with propanediol-1,2 (1:6455) gives (34) propylene glycol dilaurate, m.p. 35°; C with butanediol-1,3 (1:6482) gives (34) 1,3-butylene glycol dilaurate, m.p. about 16.5°; C with butanediol-1,4 (1:6516) gives (34) tetramethylene glycol dilaurate, m.p. 45.5°].

Č has also been much employed in the prepn. of mixed glycerides, but this topic cannot be expanded in detail in this text.

With phenols. $\bar{\mathbb{C}}$ on htg. with phenols splits out HCl yielding the corresp. esters. [E.g., $\bar{\mathbb{C}}$ with phenol (1:1420) gives (6) phenyl laurate, m.p. 24.5° (6), b.p. 210° at 15 mm. (6), 159–161° at 1 mm. (35); $\bar{\mathbb{C}}$ with p-cresol (1:1410) gives (6) p-tolyl laurate, m.p. 28° (6), b.p. 219.5° at 15 mm. (6). $-\bar{\mathbb{C}}$ (2 moles) with pyrocatechol (1:1520) at 110° for 2 hrs. gives (36) pyrocatechol dilaurate, m.p. 35.5°; $\bar{\mathbb{C}}$ (2 moles) with resorcinol (1:1530) at 110° for 2 hrs. gives (36) resorcinol dilaurate, m.p. 43–44.5°; $\bar{\mathbb{C}}$ (2 moles) with hydroquinone (1:1590) at 110° for 2 hrs. gives (36) hydroquinone dilaurate, m.p. 85–86°.]

[\tilde{C} with phenol (1:1420) + AlCl₃ in sym.-tetrachloroethane (3:5750) as solvent, however, gives (37) (35) (38) a mixt. of the corresp. hydroxylaurophenones; viz., 32.6% yield (37) o-hydroxyphenyl undecyl ketone, m.p. 44-45.5° (corresp. 2,4-dinitrophenylhydrazone, m.p. 92-93°) and 24.6% yield (37) p-hydroxyphenyl undecyl ketone, m.p. 71-72° (corresp. 2,4-dinitrophenylhydrazone, m.p. 150-151°); for study of influence upon o/p ratio of use of nitrobenzene and CS₂ as solvents see (38); for prepn. of these hydroxylaurophenones from phenyl laurate by BF₃ rearr. see (39); for their methyl ethers see (44).]

With salts of organic acids. [Č with Na laurate at 100° with protection from moist air gives (40) lauric anhydride (1:0601), m.p. 44° (41), 42.1° (42), 41.8° (43), 41° (40), but the latter is usually prepd. from lauric acid (1:0605) by htg. with Ac₂O (41) (42) (43).]

With Grignard reagents. \bar{C} with RMgX reagents derived from tertiary halides not only undergoes the normal reaction to give the corresp. secondary alcohol but also suffers reduction [e.g., \bar{C} with ter-BuMgCl gives (7) the expected 2,2-dimethyltetradecanol-3 (67% yield) together with lauryl alc. (1:5900) (13.7%) and ter-butyl-undecyl-carbinyl laurate (10.4%); similarly, \bar{C} with ter-AmMgCl gives (7) lauryl alc. (1:5900) (54.8%) and 3,3-dimethylpentadecanol-4 (17.7%)].

With organic amines. \bar{C} with organic primary amines yields the corresp. amides [e.g., \bar{C} with p-cymidine (2-methyl-5-isopropylaniline) gives (1) lauro-(2-methyl-5-isopropyl)-anilide, m.p. 82-83°; \bar{C} with vanillylamine (4-hydroxy-3-methoxybenzylamine) gives (12) N-(vanillyl)lauramide, α -form, m.p. 72.5-73°, β -form, m.p. 67-67.5°].

 $\bar{\mathbf{C}}$ on hydrolysis yields lauric acid (1:0605), m.p. 43-44°; for the amide, anilide, p-toluidide, and other derivatives corresp. to $\bar{\mathbf{C}}$ see lauric acid (1:0605).

3:9858 (1) Hann, Jamieson, J. Am. Chem. Soc. 50, 1443 (1928). (2) Averill, Roche, King, J. Am. Chem. Soc. 51, 868 (1929). (3) Adams, Ulich, J. Am. Chem. Soc. 42, 604 (1920). (4) Caspari, Am. Chem. J. 27, 305 (1902). (5) Gault, Ehrmann, Bull. soc. chm. (4) 39, 875-876 (1926). (6) Krafft, Burger, Ber. 17, 1378 (1884). (7) Whitmore, Wintaker, J. Am. Chem. Soc. 63, 649-650 (1941). (8) Escourrou, Bull soc. chim. (5) 6, 1177-1180 (1939). (9) Fierz-David, Kuster, Helv. Chim. Acta 22, 89 (1939). (10) Guerin, Bull soc. chim. (3) 29, 1121 1123 (1903).

(11) Ju, Shen, Wood, J. Inst. Petroleum Tech. 26, 514-520 (1940). (12) Ford-Moore, Phillips, Rec. trav. chim. 53, 856 (1934). (13) Clark, Bull, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (14) Darzens, Mentzer, Compt. rend. 213, 268-271 (1941). (15) Ralston, McCorkle, Vander Wal (to Armour and Co.), U.S. 2,262,431, Nov. 11, 1941; C.A. 36, 1513 (1942). (16) Tilak, Venkataraman, J. Sci. Ind. Research (India) 3, 193-197 (1944); C.A. 39, 4242 (1945). (17) Izard, Biochem. Z. 40, 401 (1912). (18) Prat, Étienne, Bull. soc. chim. (5) 11, 30-34 (1944); C.A. 38, 6274 (1944). (19) Soc. des Usines Chim. Rhone-Poulenc, Ger. 527,874, June 22, 1931; Cent. 1931, II 1350; C.A. 25, 1575 (1931): Brit. 329,721, June 19, 1930; Cent. 1930, II 1611; C.A. 24, 5767 (1930): Brit. 330,511, July 10, 1930; Cent. 1930, II 2184; C.A. 24, 5767 (1930). (20) Ralston, Selby, J. Am. Chem. Soc. 61, 1019-1020 (1939).

(21) Stoddard, Kokatnur (to Pilot Lab., Inc.), U.S. 1,718,609, June 25, 1929; Cent. 1929, II 2261; [C.A. 23, 4093 (1929)]. (22) Hooft (to Lucidol Corp.), U.S. 2,032,554, March 3, 1936; Cent. 1936, I 4813; [C.A. 30, 2781 (1936)]. (23) Allen, Bell, Org. Syntheses 24, 94-95 (1944). (24) Kipping, Russell, J. Chem. Soc. 67, 508 (1895). (25) von Auwers. Ber 45, 2772 (1912). (26) Haller, Bauer, Compt. rend. 149, 7 (1909). (27) I.G., Brit. 453,778, Oct. 15, 1936; Cent 1937, I 727; C.A. 31, 1122 (1937). (28) Sabatier, Mailhe, Compt. rend. 158, 834 (1914). (29) I.G., French 801,499, Aug. 5, 1936; Cent. 1937, I 1016; C.A. 31, 483 (1937). (30) Ralston, Christensen, Ind. Eng. Chem. 29, 194-196 (1937).

(31) Ralston, Christensen (to Armour and Co.), U.S. 2,033,544, March 10, 1936; Cent 1936, II 897; [C.A. 30, 3134 (1936)]. (32) Shonle, Row, J. Am. Chem. Soc. 43, 363 (1921). (33) Brauns, J. Am. Chem. Soc. 42, 1479 (1920). (34) Staudinger, Schwalenstöcker, Ber. 68, 728-742 (1935). (35) Ralston, McCorkle, Bauer, J. Org. Chem. 5, 658 (1940). (36) Marangoni, Atti ist. Veneto sci., Pt. 2. Sci. mat. nat. 97, 209-218 (1937/8); Cent. 1939, I 95-96; C.A. 34, 6934 Verieto Sci., Fi. 2. Sci. mat. at. 25, 250-216 (1937/8); Cent. 1838, 193-96; C.A. 25, 0934 (1940).
 (37) Raiston, Bauer, J. Org. Chem. 5, 165-170 (1940).
 (38) Raiston, Ingle, McCorkle, J. Org. Chem. 7, 457-461 (1942).
 (39) Balle, Heimke (to I.G.), Ger. 637,808, Nov. 4, 1936; Cent. 1937, I 4581; C.A. 31, 5379 (1937).
 (40) Kraft, Rosiny, Ber. 33, 3577-3578 (1900).
 (41) Mannich, Nadelmann, Ber. 63, 797 (1930).
 (42) Wallace, Copenhaver, J. Am. Chem. Soc.
 63, 699 (1941).
 (43) Holde, Gentner, Ber. 58, 1423 (1925).
 (44) Paranipe, Phalnikar, Nargund,

J. Univ. Bombay 11, Pt. 3, 120-123 (1942); C.A. 37, 1999 (1943).

BENZOHYDRYL CHLORIDE C₁₃H₁₁Cl Beil. V - 590 V1-(278) V₂-(500)

B.P. 190-191° at 247 mm. M.P. 18°

1343

 $D_4^{19.5} = 1.1398$ $n_{\rm D}^{19.5} = 1.5959$ See 3:0060. Division A: Solids.

3:9859 1-CHLOROTRIDECANE CH₃. (CH₂)₁₁.CH₂Cl $C_{13}H_{27}Cl$ Beil. S.N. 10 (n-Tridecyl chloride)

 $D_4^{20} = 0.8668 (1) \quad n_5^{20} = 1.4460 (1)$ B.P. 135.7-136.0° at 9 mm. (1)

[For prepn. of C from N-benzoyl-n-tridecylamine (N-(n-tridecyl)benzamide) with PCls at 160-210° (67% yield) see (1).]

Č with Mg in dry ether gives n-C₁₃H₂₇MgCl (1) [this prod. with allyl bromide as directed gives (48% yield (1)) hexadecene-1 (cetene) (1:7000)].

- ----n-Tridecyl p-nitrobenzoate: m.p. 37.4° cor. (2). [Prepd. indirectly (2).]
- ----n-Tridecvl 3.5-dinitrobenzoate: unreported.
- ----N-(n-Tridecvl)phthalimide: unreported.

3:9859 (1) Suida, Drahowzal, Ber. 75, 996 (1942). (2) Armstrong, Copenhaver, J. Am. Chem. Soc. 65, 2252-2253 (1943).

2.4'-DICHLOROBENZOPHENONE $C_{13}H_8OCl_2$ Beil. VII - 420 VII₁---

B.P. 214-215° at 22 mm.

M.P. 66-67°

See 3:1565. Division A: Solids.

3:9859-A 2,3'-DICHLOROBENZOPHENONE C12HaOCl2 Beil. S.N. 652 (o-Chlorophenyl m-chlorophenyl ketone)

B.P. 140-142° at 1 mm. (1)

[For prepn. of \bar{C} from *m*-chlorobromobenzene [Beil. V-209, V₁-(115), V₂-(161)] (2) by conversion to *m*-chlorophenyl MgBr (cf. (3)) and reaction with *o*-chlorobenzonitrile [Beil. IX-336] (4) (5) followed by hydrolysis (73% yield) see (1).]

1) 2,3'-Dichlorobenzophenone 2,4-dinitrophenylhydrazone: m.p. 255-257° (1).

3:2859-A (1) Haller, Bartlett, Drake, Newman, Cristol, et al., J. Am. Chem. Soc. 67, 1601-1602 (1945). (2) Hartwell, Org. Syntheses 24, 22-24, Note 5 (1944). (3) Hein, Retter, Ber. 71, 1968 (1938). (4) Norris, Klemka, J. Am. Chem. Soc. 62, 1433 (1940). (5) Baudet, Rec. trav. chem. 43, 707-708 (1924).

3:9860 TRIDECANOYL CHLORIDE

$$C_{13}H_{25}OCl$$

Beil. S.N. 162

1

B.P. 145-146° at 11 mm. (1)

145-147° at 10 mm. (2)

144-145° at 10 mm. (3)

[For prepn. of \bar{C} from tridecanoic acid (1:0600) with SOCl₂ (3) (96.5% yield (2)) see indic. refs.]

[For reactn. of \bar{C} with $C_6H_6+AlCl_3$ yielding phenyl *n*-dodecyl ketone, m.p. 41-42°, b.p. 170° at 0.1 mm. (semicarbazone, m.p. 101°), see (3); for reactn. of \bar{C} with vanillylamine see (1); for reactn. of \bar{C} with 1,7-aminonaphthol see (4).]

 $\bar{\mathbf{C}}$ on hydrolysis yields tridecanoic acid (1:0600) (for the amide, anilide, p-toluidide, and other derivatives corresp. to $\bar{\mathbf{C}}$ see 1:0600).

3:9869 (1) Ford-Moore, Phillips, Rec. trav. chim. 53, 856-857 (1934). (2) Fierz-David, Kuster, Helv. Chim. Acta 22, 86-89, 101 (1939). (3) Ziegler, Dersch, Wollthan, Ann. 511, 38-39 (1934).

3:9863 1,1-DICHLORO-2-(m-CHLOROPHENYL)-2- C₁₄H₈Cl₄ Beil. S.N. 480 (p-CHLOROPHENYL)ETHYLENE

CI CI CI

B.P. 158-162° at 1 mm. (1)

[For prepn. of \bar{C} from "m,p-DDT" (3:9867) by elimination of 1 HCl with alc. KOH (80% yield) see (1).]

C on oxidn. with CrO₃ gives (41% yield, (1)) 3,4'-dichlorobenzophenone (3:3415), m.p. 113°.

3:9863 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., J. Am. Chem. Soc. 67, 1600 (1945).

3:9865 1,1,1-TRICHLORO-2,2-bis-(o-CHLOROPHENYL)ETHANE ("o.o'-DDT")

This compound is the so-called o,o'-isomer of "DDT" (3:3298). Although it is known to be a contaminant of "DDT" (e.g., 6% (1)) no accurate information regarding it is at present available.

3:9865 (1) Gunther, J. Chem. Education 22, 239 (1945).

3:9867 1,1,1-TRICHLORO-2-(m-CHLOROPHENYL)-2- C₁₄H₉Cl₅ Beil. S.N. 479 (b-CHLOROPHENYL)ETHANE Cl

(" m,p'-DDT ")

B.P. 181-185° at 1 mm. (1)

[For prepn. of \bar{C} from 2,2,2-trichloro-1-(m-chlorophenyl)ethanol (1) by condensation with chlorobenzene (3:7903) in presence of fumg. H₂SO₄ (48% yield) see (1).]

[C with alc. KOH loses HCl giving (80% yield (1)) 1,1-dichloro-2-(m-chlorophenyl)-2-(p-chlorophenyl)ethylene (3:9863).]

 \bar{C} on dinitration with equal wt. fumg. HNO₃ gives (90% yield (1)) a dinitro cpd., m.p. 118.8-120.1° (1)..

3:9867 (1) Haller, Bartlett, Drake, Newman, Cristol, J. Am. Chem. Soc. 67, 1600 (1945).

3:9870 1,1-DIPHENYLETHYL CHLORIDE

C₁₄H₁₃Cl Beil. S.N. 479

(Chloro-diphenyl-methyl-methane)

C—CH₃

[See also 2,2-diphenylethyl chloride (3:9871).]

 \bar{C} cannot be obtd. in cryst. form; at room temp. \bar{C} slowly dec. (1) to give HCl and 1,1-diphenylethylene [Beil. V-639, V₁-(308), V₂-(543)], b.p. 277°, accompanied (1) (3) by a small amt. of 1,1,3,3-tetraphenylbutene-1, m.p. 113-114° (the unsatd. dimer of 1,1-diphenylethylene).

[For prepn. of \bar{C} from diphenyl-methyl-carbinol [Beil. VI-685, VI₁-(330)] in C_6H_6 (1) or pet. ether (2) in pres. of $CaCl_2$ by saturation at 0-10° with dry HCl gas and stdg. overnight see indic. refs.]

 \bar{C} in C_6H_6 stood at room temp. gives (95-97% yield in 1 week, 80% in 1 day (1)) 1,1,3-triphenyl-3-methylhydrindene (the saturated dimer of 1,1-diphenylethylene), colorless cryst. from alc., m.p. 143° (1); note that attempts to accelerate this reaction by warming give decreased yield together with formation of 1,1-diphenylethylene and its unsaturated dimer (mentioned above).

3:9870 (1) Schoepfle, Ryan, J. Am. Chem. Soc. 52, 4025-4027 (1930). (2) Schoepfle, Ryan, J. Am. Chem. Soc. 54, 3692 (1932). (3) Blicke, Powers. J. Am. Chem. Soc. 52, 3383 (1929).

3:9871 2,2-DIPHENYLETHYL CHLORIDE

C₁₄H₁₃Cl

Beil. V - 606 V₁-(285)

CH—CH

[See also 1.1-diphenylethyl chloride (3:9870).]

Oil, which on attempted distillation dec. (1) (2) into HCl + 1,2-diphenylethylene (stilbene) (1:7250). — \bar{C} can, however, be distilled with steam (1).

[For prepn. of \bar{C} from C_6H_6 with chloroacetaldehyde (3:7212) (generated in mixt. by use of α,β -dichloroethyl ethyl ether (3:5640)) + conc. H_2SO_4 see (2); for formn. in very small amt. from 1,1,1-trichloro-2,2-diphenylethane [Beil. VI-606, VI₁-(285)] during electrolytic reduction in alc./HCl see (3).]

 \bar{C} with alc. KOH loses HCl yielding (1) 1,1-diphenylethylene [Beil. V-639, V₁-(308), V₂-(543)], b.p. 277°, accompanied by its polymers.

3:9871 (1) Hepp, Ber. 7, 1409-1413 (1874). (2) Hepp, Ber. 6, 1439 (1873). (3) Brand, Z. Elektrochem. 16, 670 (1910).

B.P.
$$154-155^{\circ}$$
 at 15 mm. (1) $D_4^{20} = 0.8589$ (2) $n_D^{20} = 1.4450$ (2) $139-142^{\circ}$ at 4 mm. (2) $44-53^{\circ}$ at 2×10^{-4} mm. (2)

Care must be taken to avoid confusion of \bar{C} with the acid chloride of *n*-tetradecanoic acid (myristic acid), commonly designated as *n*-myristoyl chloride (3:9885).

[For prepn. of \bar{C} from tetradecanol-1 (1:5935) with conc. HCl + ZnCl₂ or by htg. in s.t. with fumg. HCl see (1); for formn. of \bar{C} (31% yield) from tetradecanol-1 (1:5935) with PCl₃ in pres. of mesityl oxide and Ac₂O see (2).]

[\bar{C} (1 mole) with pyridine (1 mole) in s.t. at 110° for 15 hrs. gives (3) the corresp. quaternary salt, viz., N-(n-tetradecyl)pyridinium chloride, cryst. from alc./ether or from C_6H_6 as monohydrate, m.p. 85.5° (3), 75.5° (5) (this prod. on cat. hydrogenation gives (3) N-(n-tetradecyl)piperidinium hydrochloride, m.p. 186–187° (3). — For analogous reactn. of \bar{C} with isoquinoline see (3).]

[For study of rate of reactn. of \bar{C} with KI in acetone at 50° and 60° see (1).]

- --- n-Tetradecyl p-nitrobenzoate: m.p. 51.2° cor. (4). [Prepd. indirectly.]
- ---- n-Tetradecyl 3,5-dinitrobenzoate: unreported.
- --- N-(n-Tetradecyl)phthalimide: unreported.
- ---- S-(n-Tetradecyl)isothiourea picrate: unreported.
- ---- n-Tetradecyl mercuric chloride: unreported (but see (6)).

3:9874 (1) Conant, Hussey, J. Am. Chem. Soc. 47, 483, 485 (1925). (2) Drake, Marvel, J. Org. Chem. 2, 394 (1937). (3) Karrer, Kahnt, Epstein, Jaffé, Ishii, Helv. Chim. Acta 21, 233-234 (1938). (4) Armstrong, Copenhaver, J. Am. Chem. Soc. 65, 2252-2253 (1943). (5) Lottermoser, Froscher, Kolloid-Beihefte 45, 305-306, 315, 319, 323, 339 (1937). (6) Meals, J. Org. Chem. 9, 215 (1944).

o-BENZOYLBENZOYL CHLORIDE --- A 3:9880 3-CHLORO-3-PHENYLPHTHALIDE—B

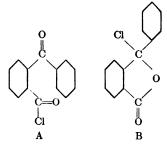
(o-Benzovlbenzovl pseudo-chloride)

C₁₄H₉O₂Cl

A. Beil. X-749 X1----

> B. Beil. XVII - 361 XVII₁---

3:9880



C appears to react in two tautomeric forms corresp. to structures A and B, the independent existence of which, however, has not (as yet) been definitely established. same method of prepn. has in various laboratories given results sometimes suggesting a preponderance of A, sometimes of the tautomer B. The constants reported for C show a correspondingly wide variation, e.g., m.p. 82-83° (1), abt. 70° (2), 59-60° (3); b.p. 170-171° at 1 mm. (1); other workers, e.g. (5) (6), have sometimes obtd. C in crystn form and sometimes not and have failed to report constants.

[For prepn. of C from o-benzoylbenzoic acid (1:0720) with PCl₅ in CS₂ (2) (3) (4) (5), or PCl₅ (7), PCl₃ (7) (4), or SOCl₂ (7) (4) (5) (6) (1) (8) (11), see indic. refs.; for prepn. of C from 3-phenylphthalide with Cl₂ at 115-120° see (5)

Č-A on htg. above 130° loses HCl and ring-closes yielding (9) (10) anthraquinone (1:9095). C-A with conc. aq. NH4OH at 0° yields (9) o-benzoylbenzamide, m.p. 165° cor. (9); with aniline yields (11) o-benzoylbenzanilide, m p. 195° (11).

C-A with MeOH yields (2) (7) (4) methyl o-benzoylbenzoate, m p. 51.5° (4), 51.7° (4). 51-52° (2), 52° (12); C-B with MeOH yields (7) methyl pseudo-o-benzoylbenzoate (3methoxy-3-phenylphthalide), m.p. 80-81° (7).

Č-A with EtOH should yield ethyl o-benzoylbenzoate, m.p. 58° (13) (12); Č-B with EtOH yields (14) ethyl pseudo-o-benzoylbenzoate (3-ethoxy-3-phenylphthalide), m.p. 51-53° (14), 56° (13).

C-A with K phenolate or with phenol in pyridine yields (5) phenyl o-benzoylbenzoate, m.p. 162-163° (5); C-B under same circumstances yields phenyl pseudo-o-benzoylbenzoate (3-phenoxy-3-phenylphthalide), m.p. 80-82° (5). [For analogous behavior of other phenols see (5).]

Č-B with phenol yields (6) 3-(p-hydroxyphenyl)-3-phenylphthalide, m.p. 168-170° (6). [For analogous reactn. with other phenols and phenol ethers see (6).]

[For reactn. of \bar{C} with α -methylnaphthalene see (15).]

3:9880 (1) Norris, Ware, J. Am. Chem. Soc. 61, 1418-1420 (1938). (2) Haller, Guyot, Bull. soc. chsm. (3) 25, 49-56 (1901). (3) Martin, J. Am. Chem. Soc. 38, 1142-1144 (1916). (4) McMullen, J. Am. Chem. Soc. 38, 1228-1230 (1916). (5) Blicke, Swisher, J. Am. Chem. Soc. 56, 902-904 (1934). (6) Blicke, Swisher, J. Am. Chem. Soc. 56, 923-925 (1934). (7) Meyer, Monatsh. 25, 475-486 (1904). (8) Samdahl, Christiansen, Bull. soc. chim. (5) 5, 1577 (1938). (9) Graebe, Ullmann, Ann. 291, 10-12 (1896). (10) Meyer, Monatsh. 25, 1181-1184 (1904).

(11) Meyer, Monatsh. 28, 1226-1227 (1907). (12) Plascuda, Ber. 7, 987 (1874). (13) von Auwers, Heinze, Ber. 52, 599 (1919). (14) Egerer, Meyer, Monatsh. 34, 77-79 (1913). (15) Clar, Ber. 63, 116 (1930).

---- α-CHLORO-DIPHENYLACETYL CHLORIDE C₁₄H₁₀OCl₂ Beil. IX - 675 IX₁-(283)

B.P. 180° at 14 mm. M.P. 50°

See 3:0885. Division A: Solids.

3:9885 n-TETRADECANOYL CHLORIDE C₁₄H₂₇OCl Beil. II - 368 (n-Myristoyl chloride) CH₃.(CH₂)₁₂.C=O II₁-(162) II₂-(329)

Care must be taken to avoid confusion of $\bar{\mathbf{C}}$ with *n*-myristyl chloride (1-chlorotetradecane) (3:9874).

PREPARATION OF C

[For prepn. of \bar{C} from myristic acid (1:0630) with SOCl₂ (yields: 91% (8), 80% (3), 80-84% (9), 79% (6)) (12) (2) (13) (14) (15); with PCl₅ (89% yield (6)) (7) (14); with PCl₃ (11) (1) (17); with PCl₃ + ZnCl₂ (79% yield (6)); or with oxalyl (di)chloride (3:5060) (10) see indic. refs.]

CHEMICAL BEHAVIOR OF C

BEHAVIOR WITH INORGANIC REACTANTS

Hydrogenation of \bar{C} . [\bar{C} with $H_2 + Pt$ cat. at 220-230° at 60-65 mm. gives (1) not only some *n*-myristaldehyde (1:0004) and its trimer but also (by loss of CO from \bar{C}) *n*-tridecane [Beil. 1-171, I₂-(134)], b.p. 234°.]

Hydrolysis of C. C on hydrolysis with aq. presumably yields myristic acid (1:0630) + HCl although actual record of this reaction is lacking in the literature.

Behavior with sodium. [\bar{C} (1 mole) with metallic sodium (1.2 moles) in dry ether refluxed (with stirring) for 10 hrs. gives (64% yield (3)) octacosen-14-diol-14,15 dimyristate, i.e., the dimyristate ester of CH₃. (CH₂)₁₂.C(OH)=C(OH). (CH₂)₁₂.CH₃, cryst. from acetone/C₆H₆ (3:1), m.p. 54-55° (3).]

BEHAVIOR WITH ORGANIC REACTANTS

With hydrocarbons (or their equivalents). [C with C₆H₆ + AlCl₃ in CS₂ gives (69% yield (9)) phenyl n-tridecyl ketone (myristophenone) [Beil. VII₁-(186)], m.p. 52-53°

(corresp. oxime, m.p. 69.5°; corresp. 2,4-dinitrophenylhydrazone, m.p. 98.0-98.5°; corresp. semicarbazone, m.p. 101° (9)).]

[\bar{C} with thiophene + SnCl₄ gives (yield not stated (18)) 2-furyl *n*-tridecyl ketone (2-myristolythiophene), oil, b.p. 205-210° at 4 mm., $D_{25}^{25} = 0.9506$, $n_{D}^{35} = 1.4961$ (18).]

[C with carbazole + AlCl₃ gives (yield not stated (18)) 2,8-dimyristolylcarbazole, m.p. 169° (18).

With alcohols. \tilde{C} with alcohols gives in general the corresp. alkyl myristates. [E.g., \tilde{C} with MeOH gives methyl myristate (1:2013), m.p. 18.5°; \tilde{C} with EtOH gives ethyl myristate (1:4316), m.p. 11.9°, b.p. 295°; etc. — \tilde{C} with benzyl alc. (1:6480) gives (14) benzyl myristate; \tilde{C} with menthol (1:5940) gives (15) menthyl myristate; etc.]

C (2 moles) with dihydric alcs. on htg. gives the corresp. neutral esters [e.g., C with ethylene glycol (1:6465) gives (20) ethylene glycol dimyristate (1:2233), m.p. 63°; C with propanediol-1,2 (1:6455) gives (20) propylene glycol dimyristate, m.p. 41.5°; C with butanediol-1,3 (1:6482) gives (20) 1,3-butylene glycol dimyristate, m.p. 29.5-31.0°; C with butanediol-1,4 (1:6516) gives (20) tetramethyleneglycol dimyristate, m.p. 55°].

 \bar{C} has been much employed in prepn. of mixed glycerides, but this topic cannot be expanded in detail in this text [however, for examples of use of \bar{C} with the compound of glycerol + acetone (i.e., 4-hydroxymethyl-2,2-dimethyldioxolane-1,3) in prepn. of glyceryl α -monomyristate (" α -monomyristin") see (10) (5)].

With phenols. \bar{C} on htg. with phenols splits out HCl yielding the corresp. esters [e.g., \bar{C} with phenol (1:1420) on htg. gives (7) phenyl myristate, m.p. 36°, b.p. 230° cor. at 15 mm. (7); \bar{C} with p-cresol (1:1410) on htg. gives (7) p-tolyl myristate, m.p. 39°, b.p. 239.5° at 15 mm. (7); \bar{C} (2 moles) with pyrocatechol (1:1520) at 110° for 2 hrs. gives (12) pyrocatechol dimyristate, m.p. 47-48°; \bar{C} (2 moles) with resorcinol (1:1530) at 110° for 2 hrs. gives (12) resorcinol dimyristate, m.p. 53°; \bar{C} (2 moles) with hydroquinone (1:1590) at 110° for 2 hrs. gives (12) hydroquinone dimyristate, m.p. 90-90.3°].

[\overline{C} with phenol (1:1420) + AlCl₃ in sym.-tetrachloroethane (3:5750) as solvent, however, gives (11) a mixt. of the corresp. hydroxymyristophenones: viz., 31.9% yield (11) o-hydroxyphenyl n-tridecyl ketone, m.p. 52-55° (corresp. 2,4-dinitrophenylhydrazone, m.p. 92.0-92.5°) and 36.7% yield (11) p-hydroxphenyl n-tridecyl ketone, m.p. 78-80° (corresp. 2,4-dinitrophenylhydrazone, m.p. 142-143°); for prepn. of these same products by direct rearr. of phenyl myristate (above) with AlCl₃ in sym.-tetrachloroethane soln. see (19).

With salts of organic acids. [C with sodium myristate at 100° in absence of air gives (21) myristic anhydride (1:0629), m.p. 53.5° (22), 53.4° (23), 51° (21).]

With organometallic compounds. [\bar{C} with ethyl sodioacetoacetate gives (60% yield (13)) ethyl α -myristoylacetoacetate, b.p. 170–183° at 3 mm.; this prod. with NH₃ gas splits off the aceto group yielding (13) ethyl myristoylacetate, m.p. 36–37°, b.p. 187–188° at 7 mm.]

With organic amines. \tilde{C} with organic primary amines yields the corresp. amides [e.g., \tilde{C} with p-cymidine (2-methyl-5-isopropylaniline) gives (2) myristo-(2-methyl-5-isopropyl)-anilide, m.p. 88-89°; \tilde{C} with vanillylamine (4-hydroxy-3-methoxybenzylamine) gives (4) N-(vanillyl)myristamide, α -form, m.p. 82°, β -form, m.p. 76.5-77°].

C on hydrolysis yields myristic acid (1:0630), m.p. 53.86°; for the amide, anilide, p-toluidide, and other derivatives corresp. to C see myristic acid (1:0630).

3:9885 (1) Escourrou, Bull. soc. chim. (5) 6, 1177, 1180 (1939). (2) Hann, Jamieson, J. Am. Chem. Soc. 50, 1443 (1928). (3) Ralston, Selby, J. Am. Chem. Soc. 61, 1019-1020 (1939). (4) Ford-Moore, Phillips, Rec. trav. chim. 53, 857 (1934). (5) Rewadikar, Watson, J. Indian Inst. Sci. A-13, 128-140 (1930); Cent. 1930, II 3737; C.A. 25, 613 (1931). (6) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (7) Krafft, Bürger, Ber, 17, 1378-1380 (1884). (8) Fierz-David, Kuster, Helv. Chim. Acta 22, 89 (1939). (9) Ju, Shen, Wood, J. Inst. Petroleum Tech. 26, 514-520 (1940). (10) Averill, Roche, King, J. Am. Chem. Soc. 51, 868 (1929).

(11) Ralston, Bauer, J. Org. Chem. 5, 168-169 (1940). (12) Marangoni, Atti ist. Veneto eci., Pt. 2. Sci. mat. nat. 97, 209-218 (1937/8); Cent. 1939, I 95-96; C.A. 34, 6934 (1940). (13) Asano, Ohta, J. Pharm. Soc. Japan 51, 36-37, 395-401 (1931); Cent. 1931, II 1867; C.A. 25, 4267 (1931). (14) Shonle, Row, J. Am. Chem. Soc. 43, 363 (1921).
 (15) Brauns, J. Am. Chem. Soc. 42, 1479 (1920).
 (16) Izar, Biochem. Z. 40, 402 (1912).
 (17) Blau, Monatsh. 26, 95-99 (1905).
 (18) Ralston, Christensen, Ind. Eng. Chem. 29, 194-196 (1937). (19) Ralston, McCorkle, Bauer, J. Org. Chem. 5, 653, 658 (1940).
(20) Staudinger, Schwalenstöcker, Ber. 68, 732-741 (1935).
(21) Krafft, Rosiny, Ber. 33, 3577-3578 (1900).
(22) Wallace, Copenhaver, J. Am. Chem.

Soc. 63, 699 (1941). (23) Holde, Gentner, Ber. 58, 1423 (1925).

3:9890 1-CHLOROPENTADECANE $C_{15}H_{31}Cl$ Beil. I -(n-Pentadecyl chloride) CH₃.(CH₂)₁₃.CH₂Cl I₁-(68) I₂-(136)

 $D_{25}^{25} = 0.8433$ (2) $n_{\rm D}^{25} = 1.4470$ (2) B.P. 168-171° at 10 mm. (1)

[For prepn. of \bar{C} from N-benzoyl-n-pentadecylamine (N-(n-pentadecyl)benzamide) with PCl₅ on distn. (58% yield) see (1); from n-C₁₂H₂₅MgBr (1 mole) by reactn. in ether with γ-chloro-n-propyl p-toluenesulfonate (2 moles) (yield 42% on RMgBr) (note that some 1-bromo-3-chloropropane, b.p. 138-140°, is also formed) see (2).

[C with excess aniline at 100° for a long time, then treated with dil. HCl, ppts. (1) N-(npentadecyl)aniline HCl, cryst. from alc./ether, m.p. 97° (1); free base, m.p. 36° (1).]

- ---- n-Pentadecyl p-nitrobenzoate: m.p. 45.8° cor. (3). [Prepd. indirectly.]
- ---- n-Pentadecyl 3,5-dinitrobenzoate: unreported.
- ---- N-(n-Pentadecyl)phthalimide: unreported.
- --- S-(n-Pentadecyl isothiourea picrate: unreported.
- ---- n-Pentadecvl mercuric chloride: unreported.

3:9890 (1) von Braun, Solecki, Ber. 44, 1472 (1911). (2) Rossander, Marvel, J. Am. Chem. Soc. 50, 1495 (1928). (3) Armstrong, Copenhaver, J. Am. Chem. Soc. 65, 2252-2253 (1943).

3:9900 PENTADECANOYL CHLORIDE $C_{15}H_{29}OCl$ $CH_3.(CH_2)_{13}.C = O$ Beil. S.N. 162

B.P. 172-176° at 10 mm. (1) at 5 mm. (2)

[For prepn. of C from pentadecanoic acid (1:0620) with SOCl₂ (97% yield (1)) see (1). [For reactn. of C with vanillylamine see (2); with 1,7-aminonaphthol see (1).]

C on hydrolysis yields pentadecanoic acid (1:0620) q.v. (for the amide, anilide, and other derivatives corresp. to \bar{C} see 1:0620).

3:990 (1) Fierz-David, Kuster, Helv. Chim. Acta 22, 86-89, 101 (1939). (2) Ford-Moore, Phillips, Rec. trav. chim. 53, 857 (1934).

CH₃.(CH₂)₁₄.CH₂Cl C₁₆H₃₈Cl Beil. I - 172 1-CHLOROHEXADECANE (n-Hexadecyl chloride; cetyl chloride) I_{2} -(138)

B.P. 289° dec. M.P. 15°

See 3:0015. Division A: Solids.

Note that care must be taken to avoid confusion of C with palmityl chloride (1-chloro-hexadecane) (3:0015).

PREPARATION OF C

[For prepn. of \bar{C} from palmitic acid (1:0650) with PCl₅ (yields: 60% (2), 49% (12)) (5) (13) (14) (15) (16), with PCl₃ + ZnCl₂ (72% yield (12)), with SOCl₂ directly (yields: 93.5% (7), 86% (12), 80% (6)) (17) (19) (45) or in CCl₄ soln. (18), or with phospene (3:5000) at 140-155° (70-75% yield (20)) see indic. refs.)

CHEMICAL BEHAVIOR OF C

BEHAVIOR WITH INORGANIC REACTANTS

With sodium. [C (1 mole) with metallic sodium (1.2 moles) in dry ether refluxed with stirring as directed gives (70% yield (6)) dotriaconten-16-diol-16,17 dipalmitate, i.e., the dipalmitate ester of CH₃. (CH₂)₁₄. C(OH)=C(OH). (CH₂)₁₄. CH₃, cryst. from acetone/C₆H₆ (3:1), m.p. 61-62° (6).]

With sodium azide. [\bar{C} with NaN₃ in C₆H₆ gives (14) palmitoyl azide [Beil. II-375] (not isolated by (14)) which loses N₂ with rearr. to pentadecyl isocyanate [Beil. IV-202] (not isolated by (14) but from indirect prepn. reported (21) as m.p. 8-14°) [cf. corresp. behavior of lauroyl chloride (3:9858)].]

With water. \bar{C} with aq. hydrolyzes to palmitic acid (1:0650) + HCl. [For study of rate of hydrolysis with ord. H₂O and with D₂O see (22).]

BEHAVIOR WITH ORGANIC REACTANTS

With hydrocarbons. [\bar{C} with $C_6H_6+AlCl_3$ gives (60% yield (23)) (24) (25) pentadecyl phenyl ketone (penmitophenone) [Beil. VII-347, VII₁-(186)], lfts. from alc., m.p. 59° (23) (24) (26), b.p. 250.5-251.0° at 15 mm. (24) (corresp. oxime, m.p. 73-74° (26)). — \bar{C} with toluene + AlCl₃ gives (24) pentadecyl p-tolyl ketone [Beil. VII-347, VII₁-(186)], lfts. from alc., m.p. 60° (24) (26), b.p. 262° cor. at 15 mm. (24) (corresp. oxime, m.p. 60° (27), semi-carbazone, m.p. 114.5° (26), phenylhydrazone, m.p. 54-55° (26)). — For analogous behavior of \bar{C} + AlCl₃ + m-xylene (24), mesitylene (27) (2), diphenyl ether (23), and carbazole (28) see indic. refs.; for use of these products as waxes, addition agents for lubricants, etc., see (28) (29).]

With alcohols. Č with alcohols gives in general the corresp. alkyl palmitates [e.g.; Č with MeOH gives methyl palmitate (1:2055), m.p. 30°; Č with EtOH gives ethyl palmitate (1:2034), α-form, m.p. 19.4°, β-form, m.p. 24.2°, etc.; Č with bezynl alc. (1:6480) gives (30) benzyl palmitate, m.p. 36°; Č with menthol (1:5940) gives (31) menthyl palmitate, m.p. 32°].

Č (2 moles) with dihydric alcs. on htg. gives the corresp. neutral esters [e.g., C with ethylene glycol (1:6465) gives (32) ethylene glycol dipalmitate (1:2269), m.p. 70.5°; C with propanediol-1,2 (1:6455) gives (32) propylene glycol dipalmitate, m.p. 52.5-54.5°; C with butanediol-1,3 (1:6482) gives (32) 1,3-butylene glycol dipalmitate, m.p. 39-40°; C with butanediol-1,4 (1:6516) gives (32) tetramethylene glycol dipalmitate, m.p. 63°].

Č has also been much employed in the prepn. of mixed glycerides, but this topic cannot be expanded in detail in this text.

With phenols. \bar{C} on htg. with phenols splits out HCl yielding the corresp. esters. [E.g., \bar{C} with phenol (1:1420) gives (5) phenyl palmitate, m.p. 45° (5), 44.5–46.0° (33), b.p. 249.5° at 15 mm. (5); \bar{C} with p-cresol (1:1410) gives (5) p-tolyl palmitate, m.p. 47°, b.p. 258° at 15 mm. — \bar{C} (2 moles) with pyrocatechol (1:1520) at 110° for 2 hrs. gives (34) pyrocatechol dipalmitate, m.p. 58°; \bar{C} (2 moles) with resorcinol (1:1530) at 110° for 2 hrs. gives (34) resorcinol dipalmitate, m.p. 62.5–63.5°; \bar{C} (2 moles) with hydroquinone (1:1590) at 110° for 2 hrs. gives (34) hydroquinone dipalmitate, m.p. 94.5°.]

[\tilde{C} with phenol (1:1420) + AlCl₃ in sym.-tetrachloroethane (3:5750) as solvent, however, gives (35) (33) (36) a mixt. of the corresp. hydroxypalmitophenones; viz., 25.4% yield o-hydroxyphenyl pentadecyl ketone, m.p. 54-56° (corresp. 2,4-dinitrophenylhydrazone, m.p. 94-95° (35)), and 28.5% yield p-hydroxyphenyl pentadecyl ketone, m.p. 84.5-85° (35), 78° (37) (corresp. 2,4-dinitrophenylhydrazone, m.p. 141-142° (35)); for study of influence upon o/p ratio of use of nitrobenzene and of CS₂ as solvents see (36).]

With salts of organic acids. [\overline{C} with Ag palmitate at 100° for 10 min. (38) or \overline{C} with Na \overline{A} (32) (42) gives palmitic anhydride (1:0651), m.p. 64° (39), 63.9° (40), 63-64° (41), 63° (38), 62-63° (32) (43), but the latter is usually prepd. from palmitic acid (1:0650) by htg. with Ac₂O (39) (40) (41) (42) (43)]

With esters. [C with diethyl sodiomalonate would be expected to give diethyl palmitoylmalonate, but for unsuccessful attempt to realize this reaction see (44).]

[\overline{C} with ethyl sodio-acetacetate in dry ether gives (62% yield (11)) (45) ethyl α -palmitoylacetoacetate, m.p. 36-36.5° (11) (45); note that this prod. with aq. NaOH splits off the acetyl group giving (62% yield (11)) ethyl palmitoylacetate, m.p. 37-38° (11) (45).]

With amines. \bar{C} with org. prim. amines yields the corresp. amides [e.g., \bar{C} with p-cymidine (2-methyl-5-isopropylaniline) gives (1) palmito-(2-methyl-5-isopropyl)anilide, m.p. 90-91°; \bar{C} with vanillylamine (4-hydroxy-3-methoxybenzylamine) gives (8) N-(vanillyl)-palmitamide, α -form, m.p. 89-89.5°, β -form, m.p. 84-84.5°].

 \tilde{C} on hydrolysis yields palmitic acid (1:0650), m.p. 62.7°; for the amide, anilide, *p*-toluidide, and other derivs. corresp. to \tilde{C} see palmitic acid (1:0650).

3:9912 (1) Hann, Jamieson, J. Am. Chem. Soc. 50, 1443 (1928). (2) Klages, Ber. 35, 2260-2261 (1902). (3) Stephenson, Biochem. J. 7, 431 (1913). (4) Gault, Ehrmann, Bull. soc. chim. (4) 39, 876 (1926). (5) Krafft, Burger, Ber. 17, 1379-1380 (1884). (6) Ralston, Selby, J. Am. Chem. Soc. 61, 1019-1020 (1939). (7) Fierz-David, Kuster, Helv. Chim. Acta 22, 89 (1939). (8) Ford-Moore, Phillips, Rec. trav. chim. 53, 857 (1934). (9) Fischer, Bergmann, Barwind, Ber. 53, 1603 (1920). (10) Nishimura, Science Repts. Tohoku Imp. Univ. 20, 97-100 (1931); Cent. 1931, I 3671; C.A. 25, 3978 (1931).

(11) Levene, Haller, J. Biol. Chem. 63, 670-671 (1925). (12) Clark, Bell, Trans. Roy. Soc. Can. (3) 27, III 97-103 (1933). (13) von Braun, Jostes, Münch, Ann. 453, 147 (1927). (14) Naegeli, Grüntuch, Lendorff, Heis. Chim. Acta 12, 240-241 (1929). (15) Pummerer, Kranz. Ber. 62, 2624 (1929). (16) Ralston, McCorkle, Vander Wal (to Armour and Co.), U.S. 2,262,431, Nov. 11, 1941; C.A. 36, 1513 (1942). (17) Escher, Heis. Chim. Acta 12, 37-38, 45-45 (1929). (18) Bückel,

Ger. 281,364, Jan. 2, 1915; Cent. 1915, I 230; C.A. 9, 2130 (1915). (19) Izard, Brochem, Z, 40, 402 (1912). (20) Prat, Étienne, Bull. soc. chim. (5) 11, 30-34 (1944); C.A. 38, 6274 (1944).

(21) Jeffreys, Am. Chem. J. 22, 27 (1899). (22) Hughes, Rideal, J. Chem. Soc. 1934, 1107. (23) Adam, Proc. Roy. Soc. (London) A-103, 684-685 (1923). (24) Krafit, Ber 19, 2982-2983 (1886). (25) I.G., French 693,699, Nov. 24, 1930; Cent. 1931, I 1018; [C.A. 25, 1646 (1931)]. (26) Ryan, Nolan, Proc. Roy. Irish Acad. 30-B, 1-7 (1912); Cent. 1913, II 2050; C.A. 7, 1712 (1913). (27) Claus, Hafelin, J. prakt. Chem. (2) 54, 402-403 (1896). (28) Ralston, Christensen, Ind. Eng. Chem. 29, 194-196 (1937). (29) Ralston, Christensen (to Armour and Co.), U.S. 2,033,544, March 10, 1936; Cent. 1936, II 897; [C.A. 30, 3134 (1936)]. (30) Shonle, Row, J. Am. Chem. Soc. 43, 363 (1921).

(31) Brauns, J. Am. Chem. Soc. 42, 1479 (1920). (32) Staudinger, Schwalenstöcker, Ber. 68 733-742 (1935). (33) Ralston, McCorkle, Bauer, J. Org. Chem. 5, 658 (1940). (34) Marangoni, Atti ist. Veneto sci., Pt. 2. Sci. mat. nat. 97, 209-218 (1937/8); Cent. 1939, I 95-96; C.A. 34, 6934 (1940). (35) Ralston, Bauer, J. Org. Chem. 5, 165-170 (1940). (36) Ralston, Ingle, McCorkle, J. Org. Chem. 7, 457-461 (1942). (37) von Auwers, Ber. 36, 3891 (1903). (38) Whitby, J. Chem. Soc. 1926, 1462. (39) Holde, Ripper, Zadek, Ber. 57, 103 (1924). (40) Wallace, Copenhaver, J. Am. Chem. Soc. 63, 699 (1941).

(41) Holde, Gentner, Ber. 58, 1424 (1925). (42) Krafft, Rosiny, Ber. 33, 3578 (1900). (43) Autenrieth, Thomae, Ber. 57, 430 (1924). (44) von Auwers, Jacobsen, Ann. 426, 222 (1922).

(45) Helferich, Koster, Ber. 56, 2090-2091 (1923).

--- 1-CHLOROHEPTADECANE
$$CH_3(CH_2)_{15}$$
. CH_2Cl $C_{17}H_{36}Cl$ Beil. I -- $I_{1-}(69)$ I_{2-}

B.P. 192-195° at 10 mm. M.P. 24°

See 3:0100. Division A: Solids.

B.P. 176° at 4 mm. (1) 139-144° at 0.04 mm. (2)

[For prepn. of \bar{C} from margaric acid (1:0635) with SOCl₂ (84.5% yield (2)) (1) (3) see indic. refs.]

C with phenol (1:1420) on htg. gives (3) phenyl margarate, cryst. from MeOH, m.p. 37°, b.p. 240-250° dec. at 11 mm. (3).

[C with alkali margarates presumably would yield margaric anhydride, cryst. from ether or pet. ether, m.p. 67.6° cor. (4), although this reaction has not actually been reported and the margaric anhydride is readily obtd. from the acid (1:0635) with Ac₂O (4).]

[For reaction of C with vanilly lamine see (1); with 1,7-aminonaphthol see (2).]

 $\bar{\mathbf{C}}$ on hydrolysis yields margaric acid (1:0635); for the amide and other derivs, corresp. to $\bar{\mathbf{C}}$ see margaric acid (1:0635).

3:9925 (1) Ford-Moore, Phillips, Rec. trav. chim. 53, 858 (1934). (2) Fierz-David, Kuster, Helv. Chim. Acta. 22, 89, 101 (1939). (3) Skraup, Schwamberger, Ann. 462, 153 (1928). (4) Wallace, Copenhaver, J. Am. Chem. Soc. 63, 699-700 (1941).

--- 1-CHLORO-OCTADECANE CH₃.(CH₂)₁₆.CH₂Cl C₁₈H₃₇Cl Beil. S.N. 10 (n-Octadecyl chloride; stearyl chloride)

B.P. 180-190° at 12 mm. M.P. 21°

See 3:0095. Division A: Solids

[See also the trans stereoisomer, viz., elaidoyl chloride (3:9950).]

[For prepn. of \bar{C} from oleic acid (1:0565) with PCl₅ (yields: 75% (2), 48% (6), 27% (7)) (8), with PCl₃ (46% yield (6)) (9), with PCl₃ + ZnCl₂ (50% yield (7)), with SOCl₂ (yields: 82.5% (4), 80% (7), 75% (2)) (3), with oxalyl (di)chloride (3:5060) (90% yield (3)), or with COCl₂ (3:5000) (10) see indic. refs.]

Note that \tilde{C} with oleic acid (1:0565) forms a const.-boilg. mixt., b.p. about 241° at 6 mm., contg. 40% \tilde{C} (6).

The reaction of C as an acyl chloride with a wide variety of organic compounds has been reported in many patents which cannot be reviewed here.

Č has also been employed in the course of prepn. of mixed glycerides; although this topic cannot be fully reviewed in this text, see for examples (3) (11) (12).

[For behavior of C with resins derived from indene, coumarone, or dicyclopentadiene see (13).]

[Č with diazomethane gives an intermediate diazoketone which on decompn. with AcOH gives (75% yield (4)) nonadecen-10-one-2-yl-1 acetate, m p 21° (14).]

[\bar{C} with phenol (1:1420) at 160° for 4 hrs. gives (55% yield (18)) phenyl oleate, oil, b.p. 256-257° at 12 mm. (18).]

[Č with Na oleate yields (10) oleic anhydride [Beil. II-469, II₂-(441)], lfts. or scales from ether or alc., m.p. 22.2° (15), 22° (16), but the latter is usually prepared directly (15) (17) from oleic acid (1:0565).]

 $\tilde{\mathbf{C}}$ on hydrolysis yields oleic acid (1:0565); for the amide, anilide, p-toluidide, and other derivs. corresp. to $\tilde{\mathbf{C}}$ see oleic acid (1:0565).

3:9940 (1) Krafft, Tritschler, Ber. 33, 3584 (1900). (2) Sulzberger, Z. angew Chem. 27, 40 (1914).
 (3) Daubert, Frieke, Longenecker, J. Am. Chem. Soc. 65, 2143 (1943). (4) Fierz-David, Kuster, Helv. Chim. Acta 22, 89 (1939). (5) Verkade, Rec. trav. chim. 62, 393-397 (1943); Cent. 1943, II 1532; C.A. 38, 3250-3251 (1944). (6) Taufel, Kunkle, Fettchem. Umschau 42, 27-29 (1935); Cent. 1935, I 2971; C.A. 29, 3307 (1935). (7) Clark, Bell, Trans. Roy Soc. Can. (3) 27, III 97-103 (1933). (8) Shonle, Row, J. Am. Chem. Soc. 43, 363 (1921). (9) Aschan, Ber. 31, 2349 (1898). (10) Prat, Etienne, Bull. soc. chim. (5) 11, 30-34 (1944); C.A. 38, 6274 (1944).

(11) Daubert, Spiegl, Longenecker, J. Am. Chem. Soc. 65, 2144-2145 (1943). (12) Jackson, Daubert, King, Longenecker, J. Am. Chem. Soc. 66, 289-290 (1944). (13) Ralston, Vander Wal, Bower, Segebrecht, Ind. Eng. Chem. 32, 99-101 (1940). (14) Grundmann, Ann. 524, 31-39 (1936). (15) Holde, Rietz, Ber. 57, 100 (1924). (16) Levene, Rolf, J. Biol. Chem. 60, 681 (1924). (17) Holde, Smelkus, Ber. 53, 1894-1895 (1920). (18) Skraup, Beng, Ber. 60, 950 (1927).

3:9950 ELAIDYL CHLORIDE
$$C_{18}H_{33}OCl$$
 Beil II - 470 $CH_3.(CH_2)_7-C-H$ Cl $II_1-H-C-(CH_2)_7.C=O$

B.P. 216° at 13 mm. (1) sl. dec. 168-170° at 1 mm. (5) [For prepn. of C from elaidic acid (1:0610) with PCl₅ (1), with SOCl₂ (2), or with oxalyl (di)chloride (3:5060) (91% yield (5)) cf. (6) see indic. refs.]

[For reactn. of \tilde{C} with diazomethane giving (83% yield (2)) 1-diazononadecen-10-one-2, m.p. 53° (2), see (2); for reactn. of \tilde{C} with ethyl sodio-acetosuccinate see (3); for use of \tilde{C} in prepn. of synthetic glycerides see (4).]

 $\bar{\mathbf{C}}$ on hydrolysis yields elaidic acid (1:0610) (for the amide and other derivatives corresp. to $\bar{\mathbf{C}}$ see 1:0610).

3:9950 (1) Krafft, Tritschler, Ber. 33, 3582 (1900). (2) Grundmann, Ann. 524, 43 (1936). (3) Robinson, J. Chem. Soc. 1930, 750. (4) Böhmer, Kappeller, Fette u. Seifen 44, 340-343 (1937); Cent. 1938, I 573. (5) Daubert, J. Am. Chem. Soc. 66, 291 (1944). (6) Wood, Jackson, Baldwin, Longenecker, J. Am. Chem. Soc. 66, 287-289 (1944).

3:996	0 n-OCTAL (Stearoyl			L CE	ILOR	CH ₃ .(CH ₂)		: ₁₈ H ₃₅ C =O	Cl	Веіl. II - 384 II ₁ -(176) II ₂ -(360)
B.P.	215°	at	15	mm.	(1)	M.P.	24°		(2)	
	211-219°	at	15	mm.	(2)		23°		(1)	
	200-215°	at	13-15	mm.	(3)		23.2-	23.4°	(8)	
	205°	at	9	mm.	(4)					
	202-203°	at	6	mm.	(5)					
	186-190°	at	5-6	mm.	(45)					
	203°	at	5	mm.	(6)					
	185°	at	3	mm.	(7)					
	195-195.5°	at	2	mm.	(8)					
	164-166°	at (0.5-1.0	mm.	(9)					
	176-178°	at	0.5	mm.	(10)					
	165°	at	0.4	mm.	(11)					

Note that care must be taken to avoid confusion of \bar{C} with stearyl chloride (1-chloro-octadecane) (3:0095).

PREPARATION OF C

[For prepn. of \bar{C} from stearic acid (1:0660) with PCl₅ directly (1) (12) (13) (21) or in CCl₄ soln. (14), with SOCl₂ directly (yields: 97% (10), 81% (3)) (4) (7) (15) (16) (17) or in CCl₄ soln. (yield 86% (8)) (14), with PCl₃ (18), with oxalyl (di)chloride (3:5060) (11), or with phospene (3:5000) at 140-150° (70-75% yield (19)) see indic. refs.]

CHEMICAL BEHAVIOR OF C

BEHAVIOR WITH INORGANIC REAGENTS

Hydrogenation of \tilde{C} . [\tilde{C} with $H_2 + Pd/BaSO_4$ cat. in boilg. xylene gives (20) (21) stearaldehyde (1:0012).]

Behavior with bromine. [For behavior of C with Br₂ at room temp., 100°, and 135° see (22).]

Behavior with sodium. [\bar{C} (1 mole) with metallic sodium (1.2 moles) in dry ether under reflux gives (67% yield (3)) hexatriaconten-18-diol-18,19 distearate, i.e., the distearate ester of CH₃. (CH₂)₁₆.C(OH)=C(OH). (CH₂)₁₆.CH₃, m.p. 67-68°.]

With sodium azide. [\check{C} with NaN₃ in C₆H₆ gives (23) (12) stearoyl azide (not isolated) which loses N₂ with rearr. giving (43% yield (23)) heptadecyl isocyanate, b.p. 208-209°

at 17 mm. (23), 290-203° at 15 mm. (24); cf. the corresp. behavior of lauroyl chloride (3:9858).]

With water. C with aq. hydrolyzes to stearic acid (1:0660) + HCl.

BEHAVIOR WITH ORGANIC REACTANTS

With hydrocarbons (or their equivalents). [\bar{C} with $C_6H_6 + AlCl_3$ gives (yields: 65% (25), 60% (26)) (27) (18) heptadecyl phenyl ketone (stearophenone) [Beil. VII-347, VII₁-(187)], lfts. from alc., m.p. 64-65° (25), 63.5-64.5° (18), 64° (28), 59° (27) (29) (corresp. oxime, m.p. 53° (27), phenylhydrazone, m.p. 54° (28)); note that in this reaction no introduction of a second acyl radical occurs (30), and that attempts to prepare stearophenone by use (with $C_6H_6 + AlCl_3$) of the mixed anhydride from stearic acid with ketene) gave very poor yields (29). — For patents on the use of stearophenone as an electric insulator (31), on its sulfonation (32), or on its reaction with PCl₃ (33) see indic. refs.]

[\bar{C} with toluene + AlCl₃ gives (34) heptadecyl p-tolyl-ketone [Beil. VII-347, VII₁-(187)], lfts. from alc., m.p. 67° (34), 66–67° (28), b.p. 278° cor. at 15 mm. (34) (corresp. oxime, m.p. 64° (27)). — For analogous behavior of \bar{C} with naphthalene (1:7200) (18), tetralin (1:7550) (18), biphenyl (1:715) (18) (35), p-methylbiphenyl (35), p-chlorobiphenyl (3:1912) (35), diphenyl ether (1:7125) (35), p-nitrodiphenyl ether (35), furan (1:8015) (35), p-methylfuran (35), dibenzofuran (35), thiophene (35), dibenzothiophene (35), carbazole (35), etc., see indic. refs.; for use of these products as waxes, addition agents for lubricants, etc., see (35) (36).]

[For behavior of \bar{C} with resins derived from indene, coumarone, or dicyclopentadiene see (37). — For addition of \bar{C} to alkynes in pres. of a condensing agent such as AlCl₃, ZnCl₂, etc., see (38) cf. (39).]

With alcohols. \bar{C} with alcohols gives in general the corresp. alkyl stearates. [E.g., \bar{C} with MeOH gives methyl stearate (1:2095), m.p. 38.8°; \bar{C} with EtOH gives ethyl stearate (1:2078), α-form, m.p. 30.9°, β-form, m.p. 33.5°. — \bar{C} with benzyl alc. (1:6480) gives (40) benzyl stearate, m.p. 45.8°; \bar{C} with menthol (1:5940) gives (41) menthyl stearate, m.p. 38–39°.]

C has also been much employed in the prepn. of mixed glycerides, but this topic cannot be expanded in detail in this text.

With phenols. [\bar{C} on htg. with phenols splits out HCl yielding the corresp. esters: e.g., \bar{C} with phenol (1:1420) gives (1) phenyl stearate, m.p. 52° (1), 51.5-53.0 (44), b.p. 267° at 15 mm. (1); \bar{C} with p-cresol (1:1410) gives (1) p-tolyl stearate, m.p. 54°, b.p. 276° at 15 mm.]

[\bar{C} (2 moles) with pyrocatechol (1:1520) at 100° gives (42) (43) pyrocatechol distearate, m.p. 83-85° (43), 68° (42); \bar{C} (2 moles) with hydroquinone (1:1590) at 130° gives (42) hydroquinone distearate, m.p. 97°.]

[\tilde{C} with phenol (1:1420) + AlCl₃ in sym.-tetrachloroethane (3:5750) as solvent, however, gives (45) (44) (46) a mixt. of the corresp. hydroxystearophenones: viz., 27.8% yield o-hydroxyphenyl heptadecyl ketone, m.p. 64-66° (corresp. 2,4-dinitrophenylhydrazone, m.p. 96-97° (45)); and 28% yield p-hydroxyphenyl heptadecyl ketone, m.p. 87-89° corresp. 2,4-dinitrophenylhydrazone, m.p. 139.5-140° (45)); for study of influence upon o/p ratio of use of nitrobenzene or of CS₂ as solvents see (46).]

With salts of organic acids. [C with Ag stearate at 100° for 10 min. gives (47) stearic anhydride (1:4915), m.p. $71-72^{\circ}$ (48), $71-71.5^{\circ}$ (49), 70.7° (50), 70.5° (47), $70-71^{\circ}$ (51), but the latter is usually prepd. from stearic acid (1:0660) by htg. with Ac₂O (48) (49) (50) (51).

With esters. [Č with ethyl sodio-acetoacetate refluxed 1 hr. under N_2 gives (68% yield (52)) ethyl α -stearoylacetoacetate, m.p. 42°; note that this prod. with aq. NaOH splits off its acetyl group giving (74% yield (52)) ethyl stearoylacetate, m.p. 46.5° (corresp. copper enolate, m.p. 111-112°).]

With Grignard reagents. [C with ter-BuMgBr gives (28.5% yield (8)) ter-butyl n-hep-tadecyl ketone, m.p. 44.8-45.1° (corresp. semicarbazone, m.p. 78.0-78.2°); note that low yield suggests probability that the RMgBr also acted as a reducing agent cf. corresp. behavior of lauroyl chloride (3:9858), but no study of such effect for this combination is reported. — C with cyclohexyl MgBr gives (8) cyclohexyl n-heptadecyl ketone.]

[\bar{C} with EtMgBr + CdCl₂ (53) or \bar{C} with ZnEt₂ (54) gives (65% yield (53)) ethyl n-heptadecyl ketone (eikosanone-3) [Beil. I-719, I₁-(374), I₂-(774)], m.p. 60-61° (54), 59.5-60° (55), 57° (28), 54-55° (53) (corresp. oxime, m.p. 55.5-56.5° (54), semicarbazone, m.p. 89-91° (53)).]

With diazomethane. [\bar{C} with CH₂N₂ (2.2 moles) as directed gives (88.5% yield (15)) 1-diazononadecanone-2, m.p. 69°, which in AcOH loses N₂ and esterifies giving (89% yield (15)) nonadecanon-2-yl-l acetate, m.p. 72°.]

With amines. \bar{C} with org. prim. amines yields the corresp. amides [e.g., \bar{C} with p-cymidine (2-methyl-5-isopropylaniline) gives (56) stearo-(2-methyl-5-isopropyl)anilide, m.p. 93-94°; \bar{C} with vanillylamine (4-hydroxy-3-methoxybenzylamine) gives (5) N-(vanillyl)-stearamide, α -form, m.p. 94 5-95°, β -form, m.p. 90.0-90.5°].

 \bar{C} on hydrolysis yields stearic acid (1:0660), m.p. 69-70°; for the amide, anilide, p-toluidide, and other derivatives corresp. to \bar{C} see stearic acid (1:0660).

3:9960 (1) Krafft, Bürger, Ber. 17, 1379-1380 (1884). (2) Gault, Ehrmann, Bull. soc. chim.
 (4) 39, 876 (1926). (3) Ralston, Selby, J. Am. Chem. Soc. 61, 1019-1020 (1939). (4) Ott.
 Zimmermann, Ann. 425, 337 (1921). (5) Ford-Moore, Phillips, Rec. trav. chim. 53, 858 (1934).
 (6) Kabashima, Ber. 71, 1072 (1938). (7) Robinson, Roche, King, J. Am. Chem. Soc. 54, 707 (1932).
 (8) Strating, Backer, Rec. trav. chim. 55, 904, 914 (1936). (9) Fischer, Bergmann, Barwind, Ber. 53, 1597 (1920). (10) Fierz-David, Kuster, Helv. Chim. Acta 22, 89 (1939).

(11) Averill, Roche, King, J. Am. Chem. Soc. 51, 868 (1929). (12) Naegeli, Gruntuch, Lendorff, Helv. Chim. Acta 12, 236-238 (1929). (13) Ralston, McCorkle, Vander Wal (to Armour and Co.), U.S. 2,262,431, Nov. 11, 1941; C A 36, 1513 (1942). (14) Bückel, Ger. 281,364, Jan. 2, 1915; Cent. 1915, I 230; (C.A. 9, 2130 (1915)]. (15) Grundmann, Ann. 524, 31-32, 36-37 (1936). (16) Izard, Biochem. Z. 40, 403 (1912). (17) Escher, Helv. Chim. Acta 12, 37-38, 44-45 (1929). (18) Mikesa, Smith, Lieber, J. Ory. Chem. 2, 500-504 (1938). (19) Prat. Étienne, Bull. soc. chim. (5) 11, 30-34 (1944); C A. 38, 6274 (1944). (20) Rosenmund, Ber. 51, 592 (1918); Ger. 333,154, Feb. 18, 1921; Cent. 1921, II 737; not in C.A.

(21) Feulgen, Behrens, Z. physiol. Chem. 177, 221-230 (1928). (22) Aschan, Ber. 45, 1918 (1912). (23) Schroeter, Ber. 42, 3359 (1909). (24) Piggott, Statham (to Imp. Chem. Ind. Ltd.), Brit. 485,761, Nov. 24, 1937; Cent. 1938, II 1676; [C.A. 32, 7926 (1938)]. (25) Seidel, Engelfried, Ber. 69, 2569, 2578-1579 (1936). (26) Adam, Proc. Roy. Soc. (London) A-103, 684 (1923). (27) Claus, Häfelin, J. prakt. Chem. (2) 54, 399 (1896). (28) Ryan, Nolan, Proc. Irish Acad. 30-B, 1-7 (1912); Cent. 1913, II 2050; C.A. 7, 1712 (1913). (29) Williams, Dickert, Krynitsky, J. Am. Chem. Soc. 63, 2510-2511 (1941). (30) Gilman, Turck, J. Am. Chem. Soc. 61, 478-479 (1939).

(31) Ralston, Christensen (to Armour and Co.), U.S. 2,039,837, May 5, 1936; Cent. 1937, I 678; C.A. 30, 4239 (1936). (32) Ralston (to Armour and Co.), U.S. 2,089,154, Aug. 3, 1937; Cent. 1937, II 4240; C.A. 31, 6769 (1937). (33) Ralston, Christensen (to Armour and Co.), U.S. 2,162,970, June 26, 1939; Cent. 1939, II 3883; C.A. 33, 7815 (1939). (34) Kraft, Ber. 21, 2268 (1888). (35) Ralston, Christensen, Ind. Eng. Chem. 29, 194-196 (1937). (36) Ralston, Christensen (to Armour and Co.), U.S. 2,033,544, March 10, 1936; Cent. 1936, II 897; [C.A. 36, 3134 (1936)]. (37) Ralston, Vander Wal, Bauer, Segebrecht, Ind. Eng. Chem. 32, 99-100 (1940). (38) Nelles, Bayer (to I.G.), Ger. 642,147, Feb. 25, 1937; Cent. 1937, II 2597; C.A. 31, 3502 (1937): Brit. 461,080, March 11, 1937; Cent. 1937, II 2597; C.A. 31, 4676 (1937). (39) Kroeger, Sowa, Nieuwland, J. Org. Chem. 1, 163-169 (1936). (40) Shonle, Row, J. Am. Chem. Soc. 43, 363 (1921).

(41) Brauns, J. Am. Chem. Soc. 42, 1479 (1920). (42) Marangoni, Atti ist. Veneto sci., Pt. 2. Sci. mat. nat. 97, 209-218 (1937/8); Cent. 1939, I 95-96; C.A. 34, 6934 (1940), (43) Rosenmund,

Lohfert, Ber. 61, 2605 (1928). (44) Ralston, McCorkle, Bauer, J. Org. Chem. 5, 658 (1940). (45) Ralston, Bauer, J. Org. Chem. 5, 165-170 (1940). (46) Ralston, Ingle, McCorkle, J. Org. Chem. 7, 457-461 (1942). (47) Whitby, J. Chem. Soc. 1926, 1462. (48) Holde, Ripper, Zadek, Ber. 57, 104 (1924). (49) Holde, Gentner, Ber. 58, 1424 (1925). (50) Wallace, Copenhaver, J. Am. Chem. Soc. 63, 699 (1941).

(51) Autenrieth, Thomae, Ber. 57, 429 (1924).
(52) Bergel, Jacob, Todd, Work, J. Chem. Soc. 1938, 1378.
(53) Gilman, Nelson, Rec. trav. chim. 55, 528-530 (1936).
(54) Ponsio, de Gaspari, Gazz. chim. ital. 29, I 474 (1899).
(55) Saville, Shearer, J. Chem. Soc. 127, 593 (1925).
(56) Hann, Jamieson, J. Am. Chem. Soc. 50, 1443 (1928).

CHAPTER XXIII

I. INDEX OF COMPOUNDS ACCORDING TO EMPIRICAL FORMULA

This Empirical Formula Index comprises four parts as follows:

- A. Compounds containing only carbon and chlorine.
- B. Compounds containing only carbon, oxygen, and chlorine.
- C. Compounds containing only carbon, hydrogen, and chlorine.
- D. Compounds containing only carbon, hydrogen, oxygen, and chlorine.

Within each section the component individuals are arranged in groups according to increasing number of carbon atoms. Within each group of isomeric compounds the order of listing follows the sequence of the eight units comprising the Chemical Type Index.

A. COMPOUNDS CONTAINING ONLY CARBON AND CHLORINE

CCl ₄ Carbon tetrack	C ₁ GROUP M W. = 153.8 aloride	Cl=92.2% 3:5100	C ₄ Cl ₂ 1,4-Dichlorob	C ₄ GROUP M.W. = 119.0 ntadi-yne-1,3	Cl=59.6% 3:1
C ₂ Cl ₂ Dichloroacetyl	C ₂ GROUP M.W.=94.9 ene	Cl=74.7% 3:5010	C ₄ Cl ₆ Hexachlorobu	M.W. = 260.8 tadiene-1,3	Cl=81.6% 3:6425
C ₂ Cl ₄ Tetrachloroeth	M.W. = 165.8 ylene	C1=85.5% 3:5460	C _b Cl ₈ Octachlorocyc	C ₅ GROUP M.W.=343.7 lopentene	Cl=82.5% 3:0422
C ₂ Cl ₆ Hexachloroeth	M.W. = 236.8 ane	Cl=89.9% 3:4835	0.01	C ₆ GROUP	CI BARO
C ₅ Cl ₅ Hexachloropro	C ₃ GROUP M.W.=248.8 pene	Cl=85.5% 3:6370	C ₆ Cl ₆ Hexachlorober	$M.W. = 284.8$ nzene . C_{10} GROUP	Cl=74.7% 3:4939
C ₃ Cl ₈ Octachloroprop	M.W.=319.7	Cl=88.7% 3:4450	C ₁₀ Cl ₈ Octachloronar	M.W.=403.8 ohthalene	Cl=70.3% 3:4893

B. COMPOUNDS CONTAINING ONLY CARBON, OXYGEN, AND CHLORINE

COCl ₂ Carbonyl chlor	C ₁ GROUP M.W. = 98.9 ride (phosgene)	Cl=71.7% 3:5000	C ₂ O ₂ Cl ₂ Oxalyl (di)chl	M.W. = 126.9 oride	Cl=55.9% 3:5060
C2OCl4	C ₂ GROUP M.W. = 181.8	Cl=78.0% 3:5420	C ₂ O ₂ Cl ₄ Trichlorometh (diphosgene	M.W. = 197.8 ayl chloroformate)	Cl=71.7% 3:5515

C ₈ OCl ₄ Trichloroacrylo	C ₈ GROUP M.W. = 193.9 byl chloride	Cl=73.2% 3:5845	C ₄ O ₂ Cl ₆ Trichloroacetic	M.W.=308.8 acid anhydride C ₆ GROUP	Cl=68.9% 3:6575
Hexachloroace	M.W.=124.1 tone opionyl chloride	Cl=58.1% 3:6312 3:0470	C ₆ OCl ₆ "Hexachlorop	M.W. = 300.8 henol"	Cl=70.0% 3:3180
C ₈ O ₂ Cl ₆ Trichloromethy	M.W.=280.8 yl trichloroacetate	Cl=75.8% 3:0290		M.W. = 245.9 nzoquinone-1,2 nzoquinone-1,4	Cl=57.7% 3:3965
C ₃ O ₃ Cl ₆ Di-(trichlorom		Cl=71.7%	(chloranil)		3:49 78
carbonate (t	riphosgene) C4 GROUP	3:1915	C ₆ O ₂ Cl ₆ 2,3,5,5,6,6-Hex cyclohexen-		Cl=67.2% 3:3260
C ₄ OCl ₆ Dı-(trichlorovi	M.W. = 276.8 nyl) ether	Cl=76.9% 3:6373	"Hexachlorore		3:3470
C4OCl ₁₀	M.W.=418.6	Cl=84.7%		C7 GROUP	
Decachlorodiet		3:1676	C ₇ OCl ₆ Pentachlorobe	M.W.=312.8 nzoyl chloride	Cl=68.0% 3:2295
C ₄ O ₂ Cl ₄ Dichloromaley	M.W.=221.9 l (di)chloride	Cl=63.9% 3:6197		C ₈ GROUP	
C ₄ O ₈ Cl ₂ Dichloromaleic	M.W.=167.0 anhydride	Cl=42.5% 3:3635	C ₈ O ₃ Cl ₄ Tetrachloroph	M.W. = 285.9 thalic anhydride	Cl=49.6% 3:4947

C. COMPOUNDS CONTAINING ONLY CARBON, HYDROGEN, AND CHLORIDE

CHCl ₃	C ₁ GROUP M.W.=119.4	Cl=89.1%	C₂H₃Cl Vinyl chloride		Cl=56.7% 3:7010
Chloroform CH ₂ Cl ₂ Methylene (di	M.W.=84.9)chloride	3:5050 C1=83.5% 3:5020	$C_2H_3Cl_8$ 1,1,1-Trichloro 1,1,2-Trichloro		Cl=79.7% 3:5085 3:5330
CH ₂ Cl Methyl chloric		C1=70.2% 3:7005	C ₂ H ₄ Cl ₂ 1,1-Dichloroet 1,2-Dichloroet	hane	Cl=71.7% 3:5035 3:5130
C ₂ HCl Chloroacetyler	C ₂ GROUP M.W. = 60.5	C1=58.6% 3:7000	C ₂ H ₅ Cl Ethyl chloride	M.W.=64.5	Cl=55.1% 3:7015
C ₂ HCl ₃ Trichloroethyl	M.W. = 131.4 ene	Cl=81.0% 3:5170	C ₃ HCl ₅ 1,1,2,3,3-Petac	C ₃ GROUP M.W.=214.3 hloropropene-1	Cl=82.7% 3:6975
C ₂ HCl ₅ Pentachloroeth	M.W. = 202.3 nane	C1=87.6% 3:5880		M.W. = 285.2 eptachloropropane	
C ₂ H ₂ Cl ₂ 1.1-Dichloroet	M.W.=97.0 hylene	Cl = 73.1%	1,1,1,2,3,3,3-H CaH2Cla	eptachloropropane	3:6860 Cl=78.8%
(vinylidene	(di)chloride) hylene (cis form)	3:5005 3:5042	1,2,3,3-Tetrach		3:5920
1,2-Dichloroet 1,2-Dichloroet	hylene (<i>trans</i> form) hylene (ord. mixt.)	3:5030	1,1,1,2,3,3-Hex	M.W.=250.8 achloropropane achloropropane	Cl=84.8% 3:6460 3:6525
C ₂ H ₂ Cl ₄ 1,1,1,2-Tetrach 1,1,2,2-Tetrach	M.W. = 167.9 doroethane doroethane	Cl = 84.5% 3:5555 3:5756	C ₈ H ₈ Cl 3-Chloropropy	M.W.=74.5	Cl=47.6% 3:7100

CaHaCla	M.W. = 145.4	Cl = 73.1%	C4H2Cla	M.W. = 333.8	Cl = 85.0%
1,1,2-Trichlord	propene-1	3:5395	1.1.2.2.3.3.4.4	-Octachlorobutane	3:2000
1,2,3-Trichlord		3:5650	_,_,_,_,_,_,_,_	• • • • • • • • • • • • • • • • • • • •	
3,3,3-Trichloro		3:5345	C ₄ H ₃ Cl	M.W. = 86.5	Cl = 41.0%
0,0,0-1110111010	properte-r	0.0020	1-Chlorobuter		3:7070
CaHaCla	M.W. = 216.3	Cl=82.0%	1-CIMOTODU GE	1-0-y11 0- 1	5. IVIV
			O TT 01	NE XV - 157 4	C1 - 07 001
	chloropropane	3:4740	C ₄ H ₃ Cl ₃	M.W. = 157.4	Cl = 67.6%
1,1,2,3,3-Penta	achloropropane	3:6280	1,2,3-Trichlor	obutadiene-1,3	3:96 52
			~ ~ ~		~ ~~
$C_3H_4Cl_2$	M.W. = 111.0	Cl = 63.9%	C ₄ H ₈ Cl ₅	M.W. = 228.4	Cl = 77.6%
1,1-Dichloropr	opene-1	3:5120	1,1,1,4,4-Pent	achlorobutene-2	3:9 6 54
1,2-Dichloropr					
Higher-boili		3:5150	C ₄ H ₂ Cl ₇	M.W. = 299.3	Cl = 82.9%
1,2-Dichloropr			1.1.2.2.3.4.4-F	Ieptachlorobutane	3:9056
Lower-boiling		3:5110		•	
1,3-Dichloropr		3:5280	C4H4Cl2	M.W. = 123.0	Cl = 57.7%
2.3-Dichloropr		3:5190	1.2-Dichlorob		3:9957
		3:5140	2,3-Dichlorob		3:5220
3,3-Dichloropr	opene-1	3:3140	2,5 Dicinoron	diadiene-1,5	3. 3 2 2 2 3 3 3 3 3 3 3 3 3 3
		~ ~~	CaHaCla	M.W. = 193.9	Cl=73.1%
$C_3H_4Cl_4$	M.W. = 181.9	Cl = 78.0%			3:9058
1,1,1,2-Tetrac	hloropropane	3:5785		hlorobutene-1	
1,1,2,2-Tetrac	hloropropane	3:5825	2,3,3,4-Tetrac	hlorobutene-1	3:9060
1,1,2,3-Tetrac	hloropropane	3:6035			
1.2,2,3-Tetrac		3:5895	$C_4H_4Cl_6$	M.W. = 264.8	Cl = 80.3%
-,-,-,-			1,1,2,3,4,4-He	xachlorobutane	3:3155
CaHaCl	M.W. = 76.5	Cl = 46.3%			
1-Chloroprope		3:7030	C ₄ H ₅ Cl	M.W. = 88.5	Cl = 40.1%
2-Chloroprope		3:7020	4-Chlorobuta	diene-1.2	3:7225
			1-Chlorobuta		3:7210
3-Chioroprope	ne-1 (allyl chloride	9) 9:1099	2-Chlorobuta		3:7080
	36377 1477 4	CI #0.107	(Chloropre		000
$C_8H_5Cl_3$	M.W = 147.4	Cl = 72.1%	1-Chlorobuty		3:7175
1,1,1-Trichlore		3:5270	1-Cmorobuty.	110-2	3.7170
1,1,2-Trichlore		3:5630	~ ** ~*		~ ~ ~~
1,1,3-Trichlore	propane	3:5660	$C_4H_5Cl_3$	M.W. = 159.5	Cl = 66.7%
1,2,2-Trichlore	propane	3:5475	1,2,4-Trichlor		3:9062
1,2,3-Trichlore	propane	3:5840	2,3,4-Trichlor	obutene-2	3:9064
-,-,-	• •		1,1,3-Trichlor	o-2-methylpropene	-1 3:5025
$C_2H_6Cl_2$	M.W. = 113.0	Cl = 62.8%	3,3,3-Trichlor	o-2-methylpropene	-1 3:5605
1.1-Dichloropa		3:7230	1,3-Dichloro-	2-(chloromethyl)-	
1,2-Dichloropa		3:5200	propene-1		3:9066
1.3-Dichloropa		3:5450			
2.2-Dichloropa		3:7140	$C_4H_5Cl_5$	M.W. = 230.4	Cl = 77.0%
Z,Z-Dicmoropi	Opario	0.0110		achlorobutane	01-11.070
O TT 01	M W - 70 F	Cl = 45.1%	Solid isome		3:0750
C ₈ H ₇ Cl	M.W. = 78.5	3:7040	Liquid isome		3:9968
1-Chloropropa					
2-Chloropropa	ne	3:7025		achlorobutane	3:9970
			1,1,1,2,3-Pent		
	C ₄ GROUP		methylprop		3:1265
CAHCla	M.W. = 226.3	C1 = 78.3%		hloro-2-(chloro-	
	achlorobutadiene-1	.3 3:9044	methyl)pro	pane	3:9072
,,_,_,					
C ₄ H ₂ Cl ₄	M.W. = 191.9	Cl = 73.9%	$C_4H_6Cl_2$	M.W. = 125.0	Cl = 56.7%
1 2 3 4-Tetrac	hlorobutadiene-1,3		1,3-Dichlorob	utene-1	3:7650
Solid isome	•	3:0870	2,3-Dichlorob	utene-1	3:9074
Liquid isom		3:6150	3,4-Dichlorob		3:5350
Tudara mom		• •			
C ₄ H ₂ Cl ₅	M.W. = 262.8	Cl = 81.0%	1,1-Dichlorob	utene-2	3:7685
119944-11	kachlorobutene-2		1,2-Dichlorob		
Solid isome		3:1945	Higher-boil		3:5615
		3:9046	Lower-boil		3:5360
Liquid isom		3:9048	1.3-Dichlorob		3:5550
Hexachlorobu		3:9050	1.4-Dichlorob		3:5725
Hexachlorobu	tene- X	9 : 200U	1,4-Dicinolog	и <i>ю</i> н <i>0-2</i>	ø:9/79

2,3-Dichlorobutene-2 Higher-boiling isomer (trans) Lower-boiling isomer (cis)	3 : 7395 3 : 55 90	C_4H_9Cl M.W.=92.6 1-Chlorobutane 2-Chlorobutane	Cl=38.3% 3:7160 3:7125
1,1-Dichloro-2-methylpropene-1 1,3-Dichloro-2-methylpropene-1 3,3-Dichloro-2-methylpropene-1	3 : 5300 3 : 5590 3 : 748 0	1-Chloro-2-methylpropane 2-Chloro-2-methylpropane	3:7135 3:7 04 5
3-Chloro-2-(chloromethyl)- propene-1	3:5633	C_{δ} GROUP $C_{\delta}H_{\delta}Cl_{2}$ M.W. = 137.0	Cl=51.8%
C ₄ H ₆ Cl ₄ M.W.=195.9	Cl=72.4%	1-Chloro-2-(chloromethyl)- butadiene-1.3	3:9195
1,1,1,2-Tetrachlorobutane	3:5622		
1,2,2,3-Tetrachlorobutane 1,2,3,3-Tetrachlorobutane	3:9078 3:9080	C_5H_7Cl M.W.=102.6 1-Chloro-3-methylbutadiene-1,2	Cl=34.6% 3:7390
1,2,3,4-Tetrachlorobutane		1-Chioro-3-methylodtadiene-1,2	9:1080
Solid isomer	3:1760 3:9082	3-Chloropentadiene-1,3	3:7360
Liquid isomer	9:800%	1-Chloro-2-methylbutadiene-1,3 3-Chloro-2-methylbutadiene-1,3	3:9200 3:7290
1,1,1,2-Tetrachloro-2-		1-Chloro-3-methylbutadiene-1,3	3:7355
methylpropane 1,1,2,3-Tetrachloro-2-	3:4725	2 Chlore 2 mathadhatana 1	0.7177
methylpropane	3:6165	3-Chloro-3-methylbutyne-1	3:7155
1,1,3-Trichloro-2-(chloro-	0.0004	$C_{\delta}H_{7}Cl_{3}$ M.W. = 173.5	Cl = 61.3%
methyl) propane 1,2,3-Trichloro-2-(chloro-	3:908 4	1,3-Dichloro-2-(chloro- methyl)butene-1	3:9201
methyl)propane	3:6335	methyl)butene-i	0:92VI
C_4H_7Cl $M.W. = 90.6$	Cl=39.2%	$C_{b}H_{1}Cl_{b}$ M.W.=244.4	Cl = 72.5%
1-Chlorobutene-1	3:7110	3,3,4,4,4-Pentachloro-2- methylbutane	3:6725
2-Chlorobutene-1	3:7075		
3-Chlorobutene-1 4-Chlorobutene-1	3:7 090 3:7151	$C_5H_8Cl_2$ M.W.=139.0 2,5-Dichloropentene-2	Cl=51.0%
2-0mor 05q00m0-2		3,4-Dichloropentene-2	3:9202 3:8045
1-Chlorobutene-2	3:7205		
2-Chlorobutene-2	3:7105	3,3-Dichloro-2-methylbutene-1 3-Chloro-2-(chloromethyl)-	3:7690
1-Chloro-2-methylpropene-1 (isocrotyl chloride)	3:7120	butene-1	3:9206
3-Chloro-2-methylpropene-1		1,3-Dichloro-2-methylbutene-2	3:8170
(methallyl chloride)	3:7145	1,4-Dichloro-2-methylbutene-2	3:9204
$C_4H_7Cl_3$ M.W. = 161.5	Cl = 65.9%	$C_5H_8Cl_4$ M.W. = 209.9	Cl = 67.6%
1,1,3-Trichlorobutane	3:9086	1,2,3-Trichloro-2-(chloro- methyl)butane	9 . 5990
1,2,3-Trichlorobutane 2,2,3-Trichlorobutane	3:5935 3:5680	1,3-Dichloro-2,2-bis-(chloro-	3:5230
2,2,3-1 Hemorobutane	9.000	methyl)propane	3:2675
1,1,2-Trichloro-2-methylpropane	3:5710	C ₆ H ₉ Cl M.W. = 104.6	Cl=33.9%
1,2,3-Trichloro-2-methylpropane	3:5885	1-Chloropentene-1	3:7420
C4HaCle M.W.=127.0	Cl = 55.8%	2-Chloropentene-1	3:7280
1.1-Dichlorobutane	3:7550	3-Chloropentene-1 4-Chloropentene-1	3:7260
1,2-Dichlorobutane	3:7680	5-Chloropentene-1	3:7350 3:7410
1,3-Dichlerobutane	3:7925	b-Cimor openiene-1	0:1710
1,4-Dichlorobutane	-: 5835	1-Chloropentene-2	3:7470
2,2-Dichlorobutane	: 7415	2-Chloropentene-2	3:7285
2,3-Dichlorobutane	: 7615	3-Chloropentene-2	3:7240
d,l (racemic) isomer meso isomer	:7580	4-Chloropentene-2 5-Chloropentene-2	3:7 400
		o openiones	8:7455
1,1-Dichloro-2-methylpropane	8:7425	1-Chloro-2-methylbutene-1	3:7303
1,2-Dichloro-2-methylpropane	3:7430 3:7960	2-(Chloromethyl)butene-1 3-Chloro-2-methylbutene-1	3:9214
1,3-Dichloro-2-methylpropane	0.1000	O-Candi O-2-Intellity IDU/CHO-1	8:7300

1-Chloro-3-methylbutene-1	3:7215	1.2-Dichlorobenzene	3:6055
_		1,3-Dichlorobenzene	3:5960
1-Chloro-2-methylbutene-2	3:7485	1,4-Dichlorobenzene	3:0980
3-Chloro-2-methylbutene-2	3:7835	-,	0.000
4-Chloro-2-methylbutene-2	3:7465	C_6H_5Cl M.W. = 112.6	Cl = 31.5%
	0.1.200	3-Chlorohexatetraene-1,3,4,5	3:7735
Chlorocyclopentane	3:7545	0 Chioronozaven aene-1,0,2,0	0.7700
Candiday diopenional	0.1020	Chlorobenzene	3:7963
$C_8H_9Cl_8$ $M.W. = 175.5$	Cl = 60.6%	Chiorobenzene	0.1340
1.2.3-Trichloro-2-methylbutane	3:6100	$C_6H_5Cl_3$ M.W. = 183.5	C1 _ E0 000
2.3.3-Trichloro-2-methylbutane	3:4755		C1 = 58.0%
		3,4,6-Trichlorohexatriene-1,2,4	3: 936 2
4,4,4-Trichloro-2-methylbutane	3:9216	CITICI MATERIAL	~
1,3-Dichloro-2-(chloro-		$C_6H_6Cl_2$ M.W = 149.0	Cl = 47.6%
methyl)butane	3:9218	3,6-Dichlorohexatriene-1,3,4	3:93 01
	~ = = = = =		
$C_6H_{10}Cl_2$ M.W. = 141.0	Cl = 50.3%	$C_6H_6Cl_4$ M.W. = 219.9	Cl = 64.5%
1,1-Dichloropentane	3:8015	1,3,4,6-Tetrachlorohexadiene-2,	4 3:9306
1,2-Dichloropentane	3:81 40		
1,3-Dichloropentane	3:9220	$C_6H_6Cl_6$ $M.W. = 290.8$	Cl = 73.1%
1,4-Dichloropentane	3:9224	1,2,3,4,5,6-Hexachlorohexene-3	3:1220
1,5-Dichloropentane	3:8575	1,2,3,4,5,6-Hexachlorocyclohexa	
2,2-Dichloropentane	3:7755	Higher-melting isomer (trans)	
2,3-Dichloropentane	3:8010	Lower-melting isomer (cis)	3:4410
2.4-Dichloropentane	3:8120	nower merang nomer (ca)	0.2210
3,3-Dichloropentane	3:7895	$C_6H_7Cl_8$ M.W. = 185.5	Cl=57.4%
e,e zionorepontune	0	3,3,6-Trichlorohexadiene-1,4	
1.2-Dichloro-2-methylbutane	3:7920	3,3,0-1 richioronexaciene-1,4	3:930 8
1.3-Dichloro-2-methylbutane	3:9228	CHC WW-1710	C1 45.00
1.4-Dichloro-2-methylbutane	3:8360	$C_0H_0Cl_2$ M.W.=151.0	Cl = 47.0%
2,3-Dichloro-2-methylbutane	3:7975	1,3-Dichlorohexadiene-2,4	3:9310
2,4-Dichloro-2-methylbutane	3:8105		
3,3-Dichloro-2-methylbutane	3:9230	C_6H_9Cl $M.W.=116.6$	Cl = 30.4%
3,4-Dichloro-2-methylbutane	3:8075	3-Chlorohexadiene-1,3	3:9312
4,4-Dichloro-2-methylbutane	3:7885		
4,4-Dichioro-2-methylodiane	9:1000	1-Chloro-3-methylpentadiene-1,	2 3:9314
$C_6H_{11}Cl$ M.W. = 106.6	Cl = 33.3%	1-Chloro-3-methylpentadiene-1,	3 3:9316
1-Chloropentane	3:7460	2-Chloro-3-methylpentadiene-1,	
2-Chloropentane	3:7325		
3-Chloropentane	3:7330	1-Chlorohexvne-1	3:9320
5-Chloropentane	9.1990	3-Chloro-3-methylpentyne-1	3:9322
1-Chloro-2-methylbutane	3:7345	4-Chloro-4-methylpentyne-2	3:9324
2-Chloro-2-methylbutane	3:7220	1 Chair 1 mond pond no 2	0.00NZ
3-Chloro-2-methylbutane	3:7275	$C_aH_oCl_s$ $M.W.=187.5$	Cl = 56.7%
4-Chloro-2-methylbutane	3:7365	1.1.2-Trichlorohexene-1	3:9326
4-Cittoro-2-memyrodcane	0.7000	1,1,2-111CHOFOHEXEHE-1	0:50/0
1 Chloro 2 2 dimethylmana	3:7200	$C_6H_6Cl_5$ $M.W.=258.4$	C1_00 00
1-Chloro-2,2-dimethylpropane	9:1 <i>H</i> 00		Cl = 68.6%
C CROTTE		1,1,1,2,2-Pentachlorohexane	3:9328
C ₆ GROUP		A ** A1 ***	
C_6HCl_5 M.W. = 250.4	Cl = 70.8%	$C_6H_{10}Cl_2$ M.W. = 153.1	Cl = 46.3%
Pentachlorobenzene	3:2290	1,2-Dichlorohexene-1	3:9330
$C_6H_2Cl_4$ M.W. = 215.9	Cl = 65.7%	$C_6H_{10}Cl_4$ $M.W. = 224.0$	Cl = 63.3%
1,2,3,4-Tetrachlorobenzene	3:0655	1,1,2,2-Tetrachlorohexane	3:9832
1,2,3,5-Tetrachlorobensene	3:0915		
1,2,4,5-Tetrachlorobenzene	3:4115	$C_6H_{11}Cl$ M.W. = 118.6	Cl = 29.9%
,,_,		1-Chlorohexene-1	3:7630
$C_6H_3Cl_8$	Cl = 58.6%	2-Chlorohexene-1	3:7530
1,2,3-Trichlorobensene	3:0990	3-Chlorohexene-1	3:9334
1,2,4-Trichlorobensene	3:6420	4-Chlorohexene-1	8:7655
1,3,5-Trichlorobensene	3:1400	5-Chlorohexene-1	3:7665
1,0,0-110moronemente			
$C_0H_4Cl_2$ M.W. = 147.0	Cl = 48.2%	1-Chlorohexene-2	3:7620
		4-Chlorohexene-2	3:7675
3.4-Dichlorohexatetraene-1,2,4,5			

1-Chlorohexene-3	3:9336	2,3,4,6-Tetrachlorobensal	0.0000
3-Chlorohexene-3	3:7535	(di)chloride	3:69 80
		2,3,5,6-Tetrachlorobenzal	
3-Chloro-2-methylpentene-1	3:7660	(di)chloride	3:6980
4-Chloro-4-methylpentene-1	8:7500	C7H2Cl5 M.W. = 264.4	Cl = 67.1%
5-Chloro-2-methylpentene-2	3:7915	2,3,4,5,6-Pentachlorotoluene	3:4937
4-Chloro-3-methylpentene-2	3:9338	2,3,4-Trichlorobenzal (di)chloride	a 3:2212
4-Chloro-a-methy pentene-2	0.5000		
2 CT 1	9.7946	2,3,6-Trichlorobenzal (di)chloride	
2-Chloro-3,3-dimethylbutene-1	3:7340	2,4,5-Trichlorobenzal (di)chloride	
1-Chloro-2,3-dimethylbutene-2	3:7520	2,4,6-Trichlorobenzal (di)chloride	3:01 4 2
		$C_7H_4Cl_4$ M.W. = 230.0	Cl = 61.7%
Chlorocyclohexane	3:80 4 0		3:2710
•		2,3,4,5-Tetrachlorotoluene	3:2480
$C_6H_{12}Cl_2$ M.W. = 155.1	Cl = 45.7%	2,3,4,6-Tetrachlorotoluene	
1.2-Dichlorohexane	3:8380	2,3,5,6-Tetrachlorotoluene	3:2575
1,5-Dichlorohexane	3:9340	0.4 Disklasskassal (di) sklasida	3:9399
1,6-Dichlorohexane	3:8720	2,4-Dichlorobenzal (di)chloride	3:0490
2.2-Dichlorohexane	3:9342	2,5-Dichlorobenzal (di)chloride	
	3:8300	2,6-Dichlorobenzal (dı)chloride	3:9398
2,3-Dichlorohexane		3,4-Dichlorobenzal (di)chloride	3:6876
2,5-Dichlorohexane	3:8525	3,5-Dichlorobenzal (di)chloride	3:0370
3,4-Dichlorohexane	3:9344		
		2-Chlorobenzotrichloride	3:6880
2.3-Dichloro-2-methylpentane	3:9346	3-Chlorobenzotrichloride	3:6845
2.5-Dichloro-2-methylpentane	3:8540	4-Chlorobenzotrichloride	3:6825
2,0 21012111			
3.3-Dichloro-2,2-dimethylbutane	3:4325	$C_7H_5Cl_8$ M.W. = 195.5	Cl = 54.4%
3,3-Dichioro-2,2-dimeniyibulane	0.2040	2.3.4-Trichlorotoluene	3:0425
4.4 Di 11 O.O. Novemberlierten e	3:8132	2.3.5-Trichlorotoluene	3:0610
4,4-Dichloro-2,2-dimethylbutane	9:0108	2,3,6-Trichlorotoluene	3:0625
		2.4.5-Trichlorotoluene	3:2100
2,3-Dichloro-2,3-dimethylbutane	3:4520	2,4,6-Trichlorotoluene	3:0380
			3:0580
$C_6H_{18}Cl$ M.W. = 120.6	Cl = 29.4%	3,4,5-Trichlorotoluene	9:0000
1-Chlorohexane	3:7955		
2-Chlorohexane	3:7715	2,6-Dichlorobenzyl chloride	3:0410
3-Chlorohexane	3:7670	3,4-Dichlorobenzyl chloride	3:6795
0 02001022	•	3,5-Dichlorobenzyl chloride	3:0350
1-Chloro-2-methylpentane	3:7563		
2-Chloro-2-methylpentane	3:7490	2-Chlorobenzal (di)chloride	3:6625
	3:7565	3-Chlorobenzal (di)chloride	8:6710
3-Chloro-2-methylpentane	3:7495	4-Chlorobenzal (di)chloride	3:6700
4-Chloro-2-methylpentane		2 Chiorosoman (di)omoraco	0.0.00
5-Chloro-2-methylpentane	3:7695	Benzotrichloride	3:6540
	9.0040	TOTAL SOLITOR AND	₩. ₩ ₩ ₹₩
1-Chloro-3-methylpentane	3:9348	$C_7H_6Cl_2$ M.W.=161.0	Cl = 44.0%
2-Chloro-3-methylpentane	3:9350	2,3-Dichlorotoluene	
3-Chloro-3-methylpentane	3:7585		3:6345
3-(Chloromethyl)pentane	3:77 20	2,4-Dichlorotoluene	3:6290
* ***		2,5-Dichlorotoluene	3:62 <u>4</u> 5
1-Chloro-2,2-dimethylbutane	3:7590	2,6-Dichlorotoluene	3:6270
3-Chloro-2,2-dimethylbutane	3:7475	3,4-Dichlorotoluene	3:6355
4-Chloro-2,2-dimethylbutane	3:7555	3,5-Dichlorotoluene	3:6310
4-CHIOLO-2,2-dimeniyibulano	0		
2-Chloro-2,3-dimethylbutane	3:7600	2-Chlorobenzyl chloride	3:6400
2-CHOIO-2,0-CHICOMYIDGERIC	0.1000	3-Chlorobenzyl chloride	8:6445
		4-Chlorobenzyl chloride	3:0220
C ₇ GROUP			0.000
C ₂ HCl ₂ M.W. = 333.3	Cl = 74.5%	Bensal (di)chloride	3:6327
Pentachlorobenzal (di)chloride	3:3590	20220 (0)01101100	U. W.
Lentwomoroneman (or)emorida	J. 90 7 4	C_7H_7Cl M.W. = 126.6	C1 = 28.0%
O IT OI 34 TIT 000 0	C) 71 907	2-Chlorotoluene	
C ₇ H ₂ Cl ₆ M.W. = 298.8	Cl = 71.2%		3:8245
2,3,4,5-Tetrachlorobensal		3-Chlorotoluene	3:8275
(di)chloride	3:9397	4-Chlorotoluene	8:5287

Benzyl chloride	3:8535	4-Chloro-2,2-dimethylpentane	3:9440
C_7H_9Cl M.W. = 128.6 5-Chloro-5-methylhexen-1-yne-3	Cl=27.6% 3:9492	2-Chloro-2,3-dimethylpentane 3-Chloro-2,3-dimethylpentane	3:9442 3:7970
OH O MW -120 4	CI 07 107	5-Chloro-2,3-dimethylpentane	3:8153
$C_7H_{11}Cl$ M.W. = 130.6 4-Chloroheptadiene-1,6	Cl = 27.1% 3:8085	2-Chloro-2,4-dimethylpentane	3:7750
1-Chloro-3-ethylpentadiene-1,2	3:9406	3-Chloro-2,2,3-trimethylbutane	3: 4920
1-Chloroheptyne-1	3:8032	C ₈ GROUP	
1-Chloro-3-ethylpentyne-1	3:9410	C_8H_8Cl M.W. = 136.6 ω -Chlorophenylacetylene	Cl=25.1% 3:9494
$C_7H_{13}Cl$ M.W.= 132.6	Cl = 26.7%	o-Chlorophenylacetylene	3:9497
1-Chloroheptene-1	3:8219	m-Chlorophenylacetylene	3:9500
2-Chloroheptene-1	3:7988	p-Chlorophenylacetylene	3:0590
3-Chloroheptene-1	3: 94 12		
4-Chloroheptene-2	3:8050	C_8H_7Cl M.W. = 138.6 α -Chlorovinylbenzene	Cl=25.6% 3:8715
4-Chloroheptene-3	3:8023	β -Chlorobinylbenzene	3:8717
4-Chloroneptene-3	⊍. 0 ₩ ₽⊌	O H Ol W W 175 1	C1 - 40 FC
4-Chloro-5-methylhexene-1	3:7730	$C_8H_8Cl_2$ M.W.=175.1 Styrene dichloride	Cl=40.5% 3:6685
4-Chloro-3-methylhexene-2	3:9414	o-Xylylene (di)chloride	3:1040
4-Chloro-5-methylhexene-2	3:7890	m-Xylylene (di)chloride	3:1 010 3:0310
4-Chloro-2,4-dimethylpentene-1	3:7725	p-Xylylene (di)chloride	3:2825
3-Chloro-2,4-dimethylpentene-2	3:7605	C_8H_9Cl M W. = 140.6	Cl=25.2%
4-Chloro-2,4-dimethylpentene-2		3-Chloro-1,2-dimethylbenzene 4-Chloro-1,2-dimethylbenzene	3:8645 3:8675
$C_7H_{14}Cl_2$ M.W. = 169.1	Cl = 41.9%	4-Choro-1,2-dimensyrbenzene	9.0019
1,1-Dichloroheptane	3:8650	2-Chloro-1,3-dimethylbenzene	3:8590
1,2-Dichloroheptane	3:9420		3:8665
1,7-Dichloroheptane	3:9422	4-Chloro-1,3-dimethylbenzene	3:8640
2,2-Dichloroheptane	3:9424	5-Chloro-1,3-dimethylbenzene	9:9040
4,4-Dichloroheptane	3:9426	O Chlana 1.4 dimethodhannan	
	0.0540	2-Chloro-1,4-dimethylbenzene	3:8600
4,5-Dichloro-2,2-dimethylpentane	3:8516	O Chlamathulhanaana	3:8550
0.4.70'.11 0.4.154b	3:9428	2-Chloroethylbenzene 4-Chloroethylbenzene	3:8570
2,4-Dichloro-2,4-dimethylpentane		4-Chloroethylbenzene	0:00/0
3,3-Dichloro-2,4-dimethylpentane	9:7010	O Mathedhammed (a moded)	
4 % D' 11 . 0 0 1!	0.0400	2-Methylbenzyl (o-xylyl) chloride	3:8710
1,5-Dichloro-3,3-dimethylpentane	3:9430	3-Methylbenzyl (m-xylyl)	A:011A
O.T. OL' M.W1947	Cl = 26.3%	chloride	3:8700
$C_7H_{15}C1$ M.W.=134.7	3:8250	4-Methylbenzyl (p-xylyl)	4.0.44
1-Chloroheptane	3:9432	chloride	3:8660
2-Chloroheptane	3:8080	α-Chloroethylbenzene	3:8667
3-Chloroheptane 4-Chloroheptane	3:8095	β -Chloroethylbenzene	3:8712
4-Chioroneptane	0.0000	p ====================================	0.002.0
2-Chloro-2-methylhexane	3:7945	$C_8H_{12}Cl_2$ M.W. = 179.1	Cl = 39.6%
5-Chloro-2-methylnexane	3:7985	2,5-Dichloro-2,5-dimethylhexyne	
0-Omoro-2-memymexane			
1-Chloro-3-methylhexane	3:8155	$C_8H_{18}C1$ M.W. = 144.6	Cl = 24.5%
2-Chloro-3-methylhexane	3:9434	3-Chloro-octadiene-1,3	3: 9566
3-Chloro-3-methylhexane	3:7950		
4-Chloro-3-methylhexane	3:9436	1-Chloro-octyne-1 1-Chloro-octyne-2	3:9510 3:9514
2-Chloro-3-ethylpentane 3-Chloro-3-ethylpentane	3:9438 3:8955	3-Chloro-3-methylheptyne-4	3:9516

C ₈ H ₁₈ Cl M.W.=146.7 2-Chloro-octene-1 3-Chloro-octene-1	Cl=24.2% 3:8346 3:9518	2-Chloro-3,4-dimethylhexane 4-(Chloromethyl)-3-methylhexan	3:9558 ae 3:9560
3-Chioro-occene-1	9.9010	3-Chloro-3-ethyl-2-methylpentar	e 3:8210
2-Chloro-octene-2 4-Chloro-octene-2	3:8345 3:8185	4-Chloro-2,2,4-trimethylpentane	3:8113
4-Chloro-octene-4	3:8230	1-Chloro-2,2,3,3-tetramethyl- butane	3: 094 5
4-Chloro-6-methylheptene-1	3:8205		0.0020
CONTRACTOR OF THE STREET	9.0790	C, GROUP	
6-Chloro-2-methylheptene-2	3:9520	C ₉ H ₉ Cl M.W. = 152.6	Cl=23.2% 3:9604
4-Chloro-3-methylheptene-2	3:9524	1-Chloro-1-phenylpropene-1 2-Chloro-1-phenylpropene-1 3-Chloro-1-phenylpropene-1	3:9606 3:0010
4-Chloro-6-methylheptene-2	3:9525	0-Omoro-1-phonyspropono-1	
5-Chloro-4-methylheptene-3	3:9526	1-Chloro-2-phenylpropene-1	3:8742
4-Chloro-2,5-dimethylhexene-2	3:9529	1-Chloro-3-phenylpropene-1 2-Chloro-3-phenylpropene-1	3:8737 3:9608
4-Chloro-3,5-dimethylhexene-2	3:9528	$C_9H_{11}Cl$ $M.W. = 154.6$	Cl=22.9%
2-Chloro-2,5-dimethylhexene-3	3:9527	γ -Phenyl- n -propyl chloride	3:8777
1-Chloro-4-ethylhexene-3	3:8510	4-Chloro-isopropylbenzene α-Chloro-isopropylbenzene	3:87 0 5 3:9610
2-Chloro-3-ethyl-3-methyl-	0.0112	2-Chloro-1,3,5-trimethylbenzene	3:8725
pentene-1	3:8115	$C_9H_{15}Cl$ $M.W. = 158.7$	Cl=22.4%
$C_8H_{16}Cl_2$ M.W. = 183.1 1,6-Dichloro-octane	Cl=38.7% 3:9530	2-Chloro-6-methyl-5-methyl-	,,,
1,7-Dichloro-octane	3:9532	eneheptene-2	3:9614
1,8-Dichloro-octane	3:8805	1-Chlorononyne-1	3:9618
2,2-Dichloro-octane	3:8670	2-Chloro-2-methyloctyne-3	3:9622
4-Chloro-3-(chloromethyl)heptane	e 3:9534	$C_0H_{17}Cl$ M.W. = 160.7	Cl=22.1%
2,5-Dichloro-2,5-dimethylhexane	3:1550	4-Chloro-7-methyloctene-2	3:9628
3,4-Dichloro-3,4-dimethylhexane	3:8315	5-Chloro-4-methyloctene-3	3:9624
3,3-Dichloro-2,2,4-trimethylpenta	ne 3:9536	4-Chloro-3,6-dimethylheptene-2	3:9630
$C_8H_{17}Cl$ M.W. = 148.7	Cl = 23.9%	$C_9H_{18}Cl_2$ M.W. = 197.1	Cl = 36.0%
1-Chloro-octane	3:8585	1,2-Dichlorononane	3:9632
2-Chloro-octane	3:8378	1,9-Dichlorononane	3:8880
4-Chloro-octane	3:9538	2,6-Dichloro-2,6-dimethylheptan	e 3:0455
2-Chloro-2-methylheptane	3:8100	$C_9H_{19}Cl$ $M.W. = 162.7$	Cl=21.8%
6-Chloro-2-methylheptane	3:9540	1-Chlorononane	3:8719
3-Chloro-3-methylheptane	3:9544	2-Chlorononane	3:8635
3-(Chloromethyl)heptane	3:8370	3-Chlorononane	3:9638
8-(OHO! OHIemy!)heptane	0.00.0	5-Chlorononane	3: 964 0
8-Chloro-4-methylheptane 4-Chloro-4-methylheptane	3:9548 3:9550	3-Chloro-3-methyloctane	3:9642
1-Chloro-3-ethylhexane 3-Chloro-3-ethylhexane	3:9552 3:8223	4-Chloro-4-methyloctane	8:9644
•		3-Chloro-3-ethylheptane	3:9646
3-Chloro-2,3-dimethylhexane 2-Chloro-2,5-dimethylhexane	3 : 9554 3 : 9556	4-Chloro-4-ethylheptane	3:9648

3-Chloro-2,3-dimethylheptane	3:9650	$C_{10}H_{17}Cl$ M.W.=172.7	Cl = 20.5%
Chlore 0.5 dimethallontone	9.0070	3-Chloro-3-methylnonyne-4	3:9710
5-Chloro-2,5-dimethylheptane	3:9652	$C_{10}H_{19}Cl$ M.W.=174.7	Cl=20.3%
3-Chloro-2,2,3-trimethylhexane	3:9654	5-Chlorodecene-5	3:9712
3-Chloro-2,2-dimethyl-3-		4-Chloro-3,7-dimethyloctene-2	3:9714
ethylpentane	3:9656	4601 04 11 11 0	0.0740
C ₁₀ GROUP		4-Chloro-3,4-diethylhexene-2	3:9716
		$C_{10}H_{20}Cl_2$ M.W. = 211.2	Cl = 33.6%
$C_{10}H_5Cl_8$ M.W. = 231.5	Cl = 46.0%	1,10-Dichlorodecane	3:9720
1,2,3-Trichloronaphthalene	3:2125		
1,2,4-Trichloronaphthalene	3:2490	2,7-Dichloro-2,7-dimethyloctane	3:0840
1,2,5-Trichloronaphthalene	3:1930 3:2515		
1,2,6-Trichloronaphthalene 1,2,7-Trichloronaphthalene	3:2325	3,4-Dichloro-3,4-diethylhexane	3:9724
1,2,8-Trichloronaphthalene	3:2220	O 77 OI	
1,2,8-1 richioronaphthatene	3 . AAAU	$C_{10}H_{21}Cl$ M.W. = 176.7	Cl=20.1%
1,3,5-Trichloronaphthalene	3:3015	1-Chlorodecane	3:8785
1,3,6-Trichloronaphthalene	3:1975	A Chlora A mothedomore	0.0700
1,3,7-Trichloronaphthalene	3:3400	4-Chloro-4-methylnonane	3:9730
1.3.8-Trichloronaphthalene	3:2420	5-Chloro-5-methylnonane	3:9732
,,_	· · · · · · · · ·	5-Omoro-5-methymonane	0.810%
1,4,5-Trichloronaphthalene	3:4005	3-Chloro-3-ethyloctane	3:9734
1,4,6-Trichloronaphthalene	3:1625	s smore s singressime	0.0.01
		4-Chloro-4-ethyloctane	3:9736
2,3,5-Trichloronaphthalene	3:3300	•	
2,3,6-Trichloronaphthalene	3:2455	3-Chloro-2,3-dimethyloctane	3:9738
$C_{10}H_6Cl_2$ M.W. = 197.1	Cl = 36.0%		
	3:0320	8-Chloro-2,6-dimethyloctane	3:9740
1,2-Dichloronaphthalene 1,3-Dichloronaphthalene	3: 0320 3: 1310	4.001	
1,4-Dichloronaphthalene	3:1655	4-Chloro-4-n-propylheptane	3:9742
1,5-Dichloronaphthalene	3:3200	4 (1) 1 0 4 0 4 1 41 11 4	0.0044
1,6-Dichloronaphthalene	3:0810	4-Chloro-2,4,6-trimethylheptane	3:9744
1,7-Dichloronaphthalene	3:1385		
1,8-Dichloronaphthalene	3:2435	C ₁₁ GROUP	
<u></u>		$C_{11}H_9Cl$ M.W. = 176.6	Cl = 20.1%
2,3-Dichloronaphthalene	3:3665	1-(Chloromethyl)naphthalene	3:0250
2,6-Dichloronaphthalene	3:4040	2-(Chloromethyl)naphthalene	3:0747
2,7-Dichloronaphthalene	3:3 44 5		
		$C_{11}H_{23}Cl$ M.W. = 190.8	Cl = 18.6%
$C_{10}H_7Cl$ M.W. = 162.6	Cl = 21.8%	1-Chloroundecane	3:8803
1-Chloronaphthalene	3:6878		
2-Chloronaphthalene	3:1285	C ₁₂ GROUP	
	~! * 0 * 0	$C_{12}H_8Cl_2$ M.W. = 223.1	Cl=31.8%
$C_{10}H_8Cl_4$ M.W. = 270.0	C1 = 52.5%	2,2'-Dichlorobiphenyl	3:1325
Naphthalene tetrachloride	3:4750	2,3-Dichlorobiphenyl	3:9850
Tetrachlorotetralin	3:4703	2.4'-Dichlorobiphenyl	3:0670
G 77 G1 35 W 100 W	C1 01 0C7	2,5-Dichlorobiphenyl	3:9854
$C_{10}H_{13}Cl$ M.W. = 168.7	Cl = 21.0%		
2,3,6-Trimethylbenzyl chloride	3:9701 3:9702	3,3'-Dichlorobiphenyl	3:0180
2,4,5-Trimethylbenzyl chloride 2,4,6-Trimethylbenzyl chloride	3:9702 3:0372	3,4-Dichlorobiphenyl	3:0685
2,2,0-1 rimethytoenzyt chioride	9. V91 A	3,5-Dichlorobiphenyl	3:0360
2-Chloro-p-cymene	3:8775	4.4/ Diellenslichen	0.4000
3-Chloro-p-cymene	3:8770	4,4'-Dichlorobiphenyl	3:4300
P. O	2.3	C ₁₂ H ₂ Cl M.W. = 188.7	Cl=18.8%
4-Isopropylbenzyl chloride	3:8795	2-Chlorobiphenyl	3:0300
		3-Chlorobiphenyl	3:8940
β-Chloro-ter-butylbenzene	3:8780	4-Chlorobiphenyl	3:1912

C12H25Cl	M.W.=204.8	Cl=17.3%	1,1,2,2-Tetrachloro-1,2-	
1-Chlorododec		3:8810	diphenylethane 1,1-Dichloro-2-(o-chlorophenyl)-	3:4496
	C ₁₃ GROUP		ethane	3:1890
C12H10Cl2	M.W. = 237.1	Cl = 29.9%	1,1-Dichloro-2,2-bis-(p-chloro- phenyl)ethane	3:3320
Benzophenone	dichloride iphenylmethane	3:6960 3:1057	phenyi/echane	0.0000
,	-		$C_{14}H_{11}Cl_3$ M.W. = 285.6 1,1,1-Trichloro-2,2-diphenylethan	Cl = 37.2% ne 3:1420
C ₁₂ H ₁₁ Cl Benzohydryl c	M.W. = 202.7	Cl = 17.5% 3:0060	1,1,1-1 richioro-2,2-diphenylethal	16 9.12.00
			$C_{14}H_{12}Cl_2$ M.W. = 251.2	Cl = 28.3% 3:0995
C ₁₃ H ₂₇ Cl 1-Chlorotridec	M.W. = 218.8	Cl = 16.2% 3:9859	1,1-Di- $(p$ -chlorophenyl) ethane	a: 0999
1-01101011100		0.000	1,1-Dichloro-2,2-diphenylethane	3:1940
	C ₁₄ GROUP		d,l-1,2-Dichloro-1,2-	
C ₁₄ H ₈ Cl ₂	M.W. = 247.1	Cl = 28.7% 3:4916	diphenylethane	3:2570
9,10-Dichloros	munacene	9: 5810	meso-1,2-Dichloro-1,2-	0.4074
C14H8CL	M.W. = 318.0	Cl = 44.6%	diphenylethane	3:4854
1,1-Dichloro-2	-(o-chlorophenyl)- henyl)ethylene	3:19250	$C_{14}H_{13}Cl$ M.W. = 216.7	Cl = 11.7%
			1,1-Diphenylethyl chloride 2,2-Diphenylethyl chloride	3:9870 3:9871
	-(m-chlorophenyl)- henyl)ethylene	3:9863	2,2-Diphenylethyl chloride	9.9071
2-(p-cmore)	menyi)emyiene	9.9009	$C_{14}H_{29}Cl$ M W. = 232.8	Cl = 15.2%
	,2-bis-(p-chloro-	0.0400	1-Chlorotetradecane	3:9874
phenyl)ethy	iene	3:2438	C ₁₅ GROUP	
C14H8Cl6	M.W. = 388.9	Cl = 54.7%	$C_{15}H_{31}Cl$ M.W. = 246.9	Cl = 14.4%
1,1,1,2-Tetracl (p-chlorophe		3:2477	1-Chloropentadecane	3:9890
	-		C ₁₆ GROUP	
C ₁₄ H ₉ Cl ₃	M.W. = 283.6 is-(p-chlorophenyl	Cl = 37.5%	$C_{16}H_{33}Cl$ M.W. = 260.9	Cl=13.6%
ethylene	a-(p-cinoropheny)	3:1430	1-Chlorohexadecane	3:0015
C 17 C1	M W 254 5	C1 - 50 007	C ₁₇ GROUP	
C ₁₄ H ₉ Cl ₅ " o,o'-DDT "	M.W. = 354.5	C1 = 50.0% 3:9865	$C_{17}H_{85}Cl$ $M.W. = 274.9$	Cl = 12.9%
" o,p'-DDT "		3:1820	1-Chloroheptadecane	3:0100
"m,p'-DDT"	(ordinary DDT)	3:9867 3:3298	C ₁₈ GROUP	
p,p -DD1	(ordinary DD1)	9 : 9/80	$C_{18}H_{87}Cl$ $M.W. = 288.9$	Cl=12.3%
C14H10Cl2	M.W. = 249.1	Cl = 28.5%	1-Chloro-octadecane	3:0095
	,2-diphenylethylen rophenyl)ethylene	e 3:1938 3:2475	a anom	
		01,0210	C_{19} GROUP $C_{19}H_{15}Cl$ M.W. = 278.8	C1 10 FC
cis-1,2-Dichlor diphenyleth		3:1380	Triphenylchloromethane	Cl=12.7% 3:3410
trans-1,2-Dich		9:1904		0.0110
diphenyleth		3: 4210	C ₂₀ GROUP	
$C_{14}H_{10}Cl_4$	M.W. = 320.1	Cl = 44.3%	$C_{20}H_{16}Cl$ M.W. = 290.8 1-Chloro-1,2,2-triphenylethylene	Cl = 12.2% 3:3560
D COMPO	ייאראט ארמווני	NING ONIV	CARBON, HYDROGEN, OXYG	TORE A TREE
D. COMPC	CIPO CONTAI	TITLO OUT!	CARDON, MIDROGEN, UXIG	EN, AND

D. COMPOUNDS CONTAINING ONLY CARBON, HYDROGEN, OXYGEN, AND CHLORINE

C ₂ GROUP		Dichloromethyl chloroformate	3:5315
C ₂ HOCl ₃ M.W. = 147.4	Cl=72.2%	$C_2H_2OCl_2$ M.W. = 112.9	Cl=62.8%
Trichloroacetaldehyde (chloral)	3:5210	Dichloroacetaldehyde	3:5180
Dichloroscetyl chloride	3:5290	Chloroacetyl chloride	3:5235
C ₂ HO ₂ Cl ₂ M.W.=163.4	Cl=65.1%	$C_2H_2O_2Cl_2$ M.W. = 128.9	Cl=55.0%
Trichloroacetic acid	3:1150	Dichloroacetic acid	3:6208

Chloromethyl chloroformate	3:5275	C ₂ H ₃ OCl ₂ M.W. = 161.4	C1 05 000
•		α, α, β -Trichloropropionaldehyde	Cl = 65.9% 3:9033
C_2H_3OCl M.W.=78.5 Chloroacetaldehyde	Cl=45.2% 3:7212	α, α, α -Trichloroacetone	3:5620
•		α, α, γ -Trichloroacetone	3:5957
Acetyl chloride	3:7065	α,α-Dichloropropionyl chloride	3:5372
$C_2H_2OCl_3$ M.W. = 149.4 2,2,2-Trichloroethanol-1	Cl=71.2% 3:5775	α,β -Dichloropropionyl chloride β,β -Dichloropropionyl chloride	3 : 9032 3 : 9032-A
$C_2H_3O_2Cl$ M.W=94.5 Chloroacetic acid	Cl = 37.5% 3:1370	3,3,3-Trichloro-1,2-epoxypropan	
Methyl chloroformate	3:5075	$C_8H_8O_2Cl$ M.W. = 106.5 α -Chloroacrylic acid	Cl=33.3% 3:1445
$C_2H_3O_2Cl_8$ M.W. = 165.4	Cl = 64.3%	β-Chloroacrylic acid	3:2240
Choral hydrate	3:1270	$C_8H_8O_2Cl_8$ M W. = 177.4 α,α,β -Trichloropropionic acid	Cl=56.0% 3:1275
$C_2H_4OCl_2$ M.W.=115.0 2,2-Dichloroethanol-1	Cl=61.7% 3:5745	Methyl trichloroacetate	3:5800
symDichlorodimethyl ether	3:5245	•	
•		$C_3H_4OCl_2$ M.W. = 127.0 α, α -Dichloropropional dehyde	Cl = 55.9% 3:9033-A
$C_2H_4O_2Cl_2$ M.W. = 131 0 Dichloroacetaldehyde hydrate	Cl = 54.2% 3:1085	α,β -Dichloropropionaldehyde	3:9034
C_2H_bOCl M.W. = 80.5	Cl = 44.0%	symDichloroacetone unsymDichloroacetone	3:0563 3:5430
Ethylene chlorohydrin	3:5552	•	
Chloromethyl methyl ether	3:7085	α -Chloropropionyl chloride β -Chloropropionyl chloride	3 : 5320 3 : 5690
Ethyl hypochlorite	3:7022	$C_8H_4OCl_4$ M.W.=197.9	Cl=71.7%
C ₃ GROUP		1,1,1,3-Tetrachloropropanol-2 1,1,3,3-Tetrachloropropanol-2	3:9036 3:9037
C ₈ HOCl ₅ M.W.=230.3 Pentachloroacetone	Cl=77.0% 3:6205	$C_3H_4O_2Cl_2$ M.W. = 143.0	Cl=49.6%
rentacmoroacetone		α,α-Dichloropropionic acid α,β-Dichloropropionic acid	3:6162 3:0855
C ₈ HO ₂ Cl M.W. = 104.5 Chloropropiolic acid	Cl=33.9% 3:1685	β,β -Dichloropropionic acid	3:1058
$C_8HO_2Cl_8$ M.W. = 175.4 α,β,β -Trichloroacrylic acid	Cl=60.6% 3:1840	Methyl dichloroacetate β -Chloroethyl chloroformate	3:5655 3:5780
C ₂ HO ₂ Cl ₅ M.W. = 246.3	Cl = 72.0%	C_3H_5OC1 M.W. = 92.5	C1 = 38.3%
Pentachloropropionic acid	3:4895	β-Chloroallyl alcohol γ-Chloroallyl alcohol	3 : 5635 3 : 58 20
$C_2H_2OCl_4$ M.W. = 195.9	Cl=72.4%	α-Chloropropionaldehyde	3:5160
symTetrachloroacetone unsymTetrachloroacetone	3 : 6050 3 : 6085	β -Chloropropionaldehyde β -Chloropropionaldehyde	3:5576
unsym1 etracmoroacetone		Chlanacatana	3:5425
$C_8H_2O_2Cl_2$ M.W. = 141.0 α,β -Dichloroacrylic acid	C1 = 50.3% 3:2265	Chloroacetone	3:09.60
·		Propionyl chloride	3:7170
β , β -Dichloroacrylic acid	3:1875	3-Chloro-1,2-epoxypropane	
Malonyl (di)chloride	3:9030	(Epichlorohydrin)	3:5358
$C_2H_2O_2Cl_4$ M.W. = 211.9 $\alpha,\alpha,\beta,\beta$ -Tetrachloropropionic aci	Cl=66.9% d 3:1850	C ₂ H ₈ OCl ₈ M.W. = 163.4 1,1,1-Trichloropropanol-2	Cl=64.5% 3:0646
C ₈ H ₄ OCl M.W. = 90.5 α-Chloroacrolein Acryloyl chloride	Cl=39.2% 3:9031 3:7153	C ₈ H ₆ O ₂ Cl M.W.=108.5 α-Chloropropionic acid β-Chloropropionic acid	Cl = 32.7% 3:6125 3:0460

Methoxyacetyl chloride	3:5225	Diglycoloyl dichloride	1=41.5% 3:9092 3:0730
Chloromethyl acetate Methyl chloroacetate Ethyl chloroformate	3 : 5356 3 : 5585 3 : 7295	Chloroacetic acid anhydride C ₄ H ₄ O ₄ Cl ₂ M.W. = 187.0 Cl	1=37.9%
C ₈ H ₆ OCl ₂ M.W. = 129.0	Cl=55.0%	$d.l,\alpha,\alpha'$ -Dichlorosuccinic acid $meso,\alpha,\alpha'$ -Dichlorosuccinic acid	3:4711 3:4930
2,3-Dichloropropanol-1 1,1-Dichloropropanol-2 1,3-Dichloropropanol-2	3:6060 3:5755 3:5985	C_4H_4OCl M.W. = 104.5 Cl α -Chlorocrotonaldehyde α -Crotonoyl chloride	3:8117 3:7693
C ₈ H ₇ OCl M.W. = 94.5 2-Chloropropanol-1 3-Chloropropanol-1 1-Chloropropanol-2	Cl=37.5% 3:7917 3:8285 3:7747	$C_4H_5OCl_3$ M.W.=175.5 Cl α,α,β -Trichloro- n -butyraldehyde α,α,γ -Trichloro- n -butyraldehyde	= 60.6% 3:5910 3:9094
Chloromethyl ethyl ether	3:7195	α-Chlorocrotonic acid	= 29.4% 3:2760
α -Chloroethyl methyl ether β -Chloroethyl methyl ether	3:7150 3:7265	α-Chlorosocrotonic acid β-Chlorocrotonic acid β-Chlorosocrotonic acid	3:1615 3:2625 3:1300
$C_3H_7O_2Cl$ M.W. = 110.5 3-Chloropropanediol-1,2 2-Chloropropanediol-1,3	Cl=32.1% 3:9038 3:9039	γ -Chlorocrotonic acid Acetoacetyl chloride	3:2170 3:9098
C ₄ GROUP	6 1 66	Methyl α -chloroacrylate Allyl chloroformate	3: 9096 3:7487
C ₄ HO ₂ Cl ₈ M.W.= 187.4 Chlorofumaryl (di)chloride Chloromaleyl (di)chloride	Cl = 56.8% 3:6105 3:6158		3:7358 = 55.6%
C ₄ HO ₃ Cl M.W.=132.5 Chloromaleic acid anhydride	Cl = 26.8% 3:0280	α, α, β -Trichloro- n -butyric acid α, α, γ -Trichloro- n -butyric acid α, β, β -Trichloro- n -butyric acid	3:1280 3:1831 3:0925
$C_4H_2OCl_8$ M.W. = 349 8 $\alpha, \alpha', \beta, \beta, \beta, \beta', \beta', \beta'$ -Octachlorodiet	Cl=81.1% hyl	γ, γ, γ -Trichloro- n -butyric acid Ethyl trichloroacetate	3:1000 3:5950
ether	3:0738 Cl=46.4%	$C_4H_6O_3Cl$ M.W. = 136.5 Cl Ethoxalyl chloride	= 26.0% 3:5625
$C_4H_2O_2Cl_2$ M.W. = 153.0 Fumaryl (di)chloride	3:5875		3:3025 3:9098-A
$C_4H_2O_2Cl_4$ M.W. = 223.9 d,l- α , α' -Dichlorosuccinyl (di)chl meso- α , α' -Dichlorosuccinyl	Cl = 63.3% oride 3:0395	$C_4H_6O_3Cl_3$ M.W = 207.5 Cl β -Hydroxyethyl trichloro- acetate	=51.3% 3:9099
(di)chloride	3:9087		=50.3%
C ₄ H ₂ O ₃ Cl ₄ M.W. = 239 9 Dichloroacetic acid anhydride	C1=59.2% 3:6430	α-Chloro-n-butyryl chloride β-Chloro-n-butyryl chloride γ-Chloro-n-butyryl chloride	3:5570 3:9100 3:5970
$C_4H_2O_4Cl_2$ M.W. = 185.0 Dichloromaleic acid	Cl=38 3% 3:3634	α-Chloroisobutyryl chloride β-Chloroisobutyryl chloride	3:5385 3:9101
$C_4H_3O_4Cl$ M.W. = 150.5 Chlorofumaric acid Chloromaleic acid	Cl = 23.6% 3:4853 3:3432	α,β -Dichloro- n -butyraldehyde	3:9102
$C_4H_4O_2Cl_2$ M.W.=155.0 Succinyl (di)chloride	Cl=45.7% 3:6200	1,3-Dichlorobutanone-2 α,β -Dichlorovinyl ethyl ether	3:5900 3:5540
γ-Chloroacetoacetyl chloride	3:9088	C ₄ H ₆ O ₂ Cl ₂ M.W. = 157.0 Cl	=45.2%
C ₄ H ₄ O ₂ Cl ₄ M.W. = 225.9 6 -Chloroethyl trichloroacetate	C1=62.8% 3:6510	 α,β-Dichloro-n-butyric acid High-melting isomer Low-melting isomer 	3:1903 3:1375

2,3-Dichlorodioxane-1,4	3:9105	Methyl α -chloropropionate Methyl β -chloropropionate	3:7 90 8 3:57 6 5
β-Chloroethyl chloroacetate Ethyl dichloroacetate Methyl α,β-dichloropropionate	3:6230 3:5850 3:9103	n-Propyl chloroformate Isopropyl chloroformate	8:7540 3:7405
γ-Chloro-n-propyl chloro- formate	3: 910 3 3:6010	$C_4H_7O_2Cl_3$ M W. = 193.5 Chloral ethylalcoholate	Cl=55.0% 3:0860
$C_4H_6O_3Cl_2$ M.W. = 173.0 β , β -Dichloro- α -hydroxy-iso-	Cl=41.0%	α,α,β-Trichloro-n-butyr- aldehyde hydrate	3:1905
butyric acid β,β' -Dichloro- α -hydroxy-iso-	3:2145	$C_4H_7O_3Cl$ M.W. = 138.6 β -Hydroxyethyl chloroacetate	Cl = 25.6% 3:6780
butyric acid	3:2565	β-Methoxyethyl chloroformate	3:91 40
β-Hydroxyethyl dichloroacetate	3:9107	$C_4H_8OCl_2$ M.W. = 143.0 1,3-Dichlorobutanol-2	Cl=49.6% 3:9145
C_4H_7OCl M.W. = 106.6 2-Chlorobuten-2-ol-1	Cl=33.3% 3:8240	1,1-Dichloro-2-methylpropanol-2 1,3-Dichloro-2-methylpropanol-2	
3-Chlorobuten-2-ol-1 4-Chlorobuten-2-ol-1	3:8270 3:911 4	α, α' -Dichlorodiethyl ether	3:7595
2-Chlorobuten-3-ol-1	3:9113	α,β -Dichlorodiethyl ether	3:5640
1-Chlorobuten-3-ol-2	3:8110	α, β' -Dichlorodiethyl ether	3:9150
3-Chlorobuten-3-ol-2	3:9115	β,β' -Dichlorodiethyl ether	3:6025
3-Chloro-2-methylpropen-2-ol-1	3:8340	$C_4H_8O_2Cl_2$ M.W. = 159.0 Dichloroacetaldehyde ethyl	Cl=44.6%
α-Chloro-n-butyraldehyde	3:9109	alcoholate	3:5310
β-Chloro-n-butyraldehyde	3:9110 3:9111	C_4H_9OCl M.W. = 108.6	Cl = 32.7%
γ -Chloro- n -butyraldehyde	9.9111	2-Chlorobutanol-1	3:9160
α-Chloroisobutyraldehyde	3:7235	3-Chlorobutanol-1	3:9165
β -Chloroisobutyraldehyde	3:9112	4-Chlorobutanol-1	3:9170
	0.0040	1-Chlorobutanol-2	3:8025
1-Chlorobutanone-2	3:8012 3:7598	3-Chlorobutanol-2	3:8000
3-Chlorobutanone-2 4-Chlorobutanone-2	3:7640	d,l-threo-3-Chlorobutanol-2	3:8002
		d,l-erythro-3-Chlorobutanol-2 4-Chlorobutanol-2	3:8004 3:9175
n-Butyryl chloride	3:7370	0.001	
Isobutyryl chloride	3:7270	2-Chloro-2-methylpropanol-1 3-Chloro-2-methylpropanol-1	3:7905 3:9180
3-Chloro-2-methyl-1,2-		1-Chloro-2-methylpropanol-2	3:7752
epoxypropane	3:7657		
β -Chloroethyl vinyl ether	3:7464	ter-Butyl hypochlorite	3:7165
$C_4H_7OCl_3$ M.W. = 177.5	Cl = 59.9%	α-Chloroethyl ethyl ether β-Chloroethyl ethyl ether	3:7305 3:7463
2,2,3-Trichlorobutanol-1	3:1336	p-Chioroedhyr ethyr ether	0.1200
1,1,1-Trichlorobutanol-2	3:5 9 55	$C_4H_9O_2Cl$ M.W. = 124.6	Cl = 28.5%
1,1,1-Trichloro-2-methyl- propanol-2	3:2662	2-(β-Chloroethoxy)ethanol-1	3:9185
propanoi-2	0.2002	3-Chloro-2-methylpropanediol-1,	2 3:9190
$C_4H_7O_2Cl$ M.W. = 122.6	Cl = 28.9%	C₅ GROUP	
α -Chloro- n -butyric acid	3:9130	$C_5H_2O_3Cl_6$ M.W. = 322.8	Cl = 65.9%
β-Chloro-n-butyric acid	3:0035	Chloralide	3:3510
γ -Chloro- n -butyric acid	3:0020		
α-Chloroisobutyric acid β-Chloroisobutyric acid	3:0235 3:9132	$C_6H_3O_2Cl$ M.W. = 130.5 Furoyl chloride	Cl=27.2% 3:8515
Ethoxyacetyl chloride	3:7745	$C_5H_6O_2Cl_2$ M.W. = 169.0 Glutaryl (di)chloride	Cl=42.0% 3:6500
α -Chloroethyl acetate β -Chloroethyl acetate	3:7625 3:5735	C ₆ H ₇ OCl M.W.=118.6	Cl=29.9%
Ethyl chloroacetate	3:5700	Tiglyl chloride	3:9240

O TT O OL 34 TT 1010			
$C_6H_7O_2Cl$ $M.W. = 134.6$	Cl = 26.4%	β -Chloro- n -valeric acid	3:0270
Ethyl α-chloroacrylate	3:9242	γ -Chloro-n-valeric acid	3:9270
	3:5870	δ-Chloro-n-valeric acid	3:0075
Methyl α-chlorocrotonate		o-Chioro-n-valerie acid	9.4414
Methyl β -chlorocrotonate	3:92 <u>44</u>		0.0840
Methyl β -chloroisocrotonate	3:8028	α -Chloro- α -methyl- n -butyric acid	3:8718
		α -Chloro- β -methyl- n -butyric acid	3:0050
$C_5H_7O_2Cl_3$ M.W. = 205.5	Cl = 51.8%		
n-Propyl trichloroacetate	3:6135	Chloropivalic acid	3:0440
Isopropyl trichloroacetate	3:5975	Ozzotopił wie word	
250ptop31 tricinoroaccusto		β -Chloro- n -propyl acetate	3:8180
C TT O CI M TTT - 150 6	O1 00 FM		3:8310
$C_8H_7O_8C1$ M.W. = 150.6	Cl = 23.5%	γ-Chloro-n-propyl acetate	
Carbethoxyacetyl chloride	3:9246	β-Chloroisopropyl acetate	3:81 50
β -(Carbomethoxy) propionyl chlo	oride 3:9247		
		n-Propyl chloroacetate	3:8295
$C_5H_7O_2Cl_3$ M.W. = 221.5	Cl = 48.0%	Isopropyl chloroacetate	3:8160
β-Methoxyethyl trichloroacetate		zoopi opji omorouotuto	
p-intentoxyemyi urichiotoaceaae	0.000	Ethyl α-chloropropionate	3:8125
CLTLOCK NEW 1880	O1 45 507		
$C_8H_8OCl_2$ M.W. = 155.0	Cl = 45.7%	Ethyl β -chloropropionate	3:8290
α-Chloro-n-valeryl chloride	3:5860		
γ-Chloro-n-valeryl chloride	3:9260	Methyl α -chloro- n -butyrate	3:8103
δ-Chloro-n-valeryl chloride	3:9264	Methyl β -chloro-n-butyrate	3:8224
		Methyl γ-chloro-n-butyrate	3:8517
α -Chloro- α -methyl- n -butyryl		Medity1 y-citio10-%-buty1208	U
	9. 5000	36.41.1	9.7010
chloride	3:5670	Methyl α -chloroisobutyrate	3:7918
α -Chloro- β -methyl- n -butyryl			
chloride	3:81 44	n-Butyl chloroformate	3:7980
		Isobutyl chloroformate	3:7760
Chloropivalyl chloride	3:9266		
Candiopivalji dindrido	0.000	C ₅ H ₉ O ₂ Cl M.W. = 152.6 C	1=23.2%
O TI O OL 34 W 171 O	O1 41 FO7		
$C_5H_8O_2Cl_2$ M.W. = 171.0	Cl = 41.5%	Glycerol α -chlorohydrin α' -acetate	3:6775
β, γ -Dichloro- n -propyl acetate	3:6220	Glycerol α -chlorohydrin β -acetate	3:6517
β, β' -Dichloroisopropyl acetate	3:6318	Glycerol β -chlorohydrin α -acetate	3:6648
		- · · -	
n-Propyl dichloroscetate	3:6000	8-Methovyethyl chlorogetate	3 · 9285
n-Propyl dichloroacetate	3:6000 3:5800	β-Methoxyethyl chloroacetate	3:9285
n-Propyl dichloroacetate Isopropyl dichloroacetate	3:6000 3:5890	eta-Methoxyethyl chloroacetate eta -Ethoxyethyl chloroformate	3:9285 3:9280
Isopropyl dichloroacetate	3:5890	β -Ethoxyethyl chloroformate	3:9280
		β -Ethoxyethyl chloroformate $C_{\delta}H_{11}OCl$ $M.W.=122.6$ $C_{\delta}H_{12}OCl$	3:9280 1=28.9%
Isopropyl dichloroacetate Ethyl α,β -dichloropropionate	3:5890 3:6090	β -Ethoxyethyl chloroformate	3:9280
Isopropyl dichloroacetate	3:5890	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1	3:9280 1=28.9%
Isopropyl dichloroacetate Ethyl α,β -dichloropropionate $C_bH_8O_2Cl_2$ M.W. = 187.0	3:5890 3:6090	β-Ethoxyethyl chloroformate C _b H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1 1-Chloropentanol-2	3:9280 3:9280 3:9295 3:8225
Isopropyl dichloroacetate Ethyl α,β -dichloropropionate	3:5890 3:6090 Cl=37.9%	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1	3:9280 21=28.9% 3:9295
Isopropyl dichloroacetate Ethyl α,β -dichloropropionate $C_bH_8O_3Cl_2$ M.W. = 187.0 Di-(β -chloroethyl) carbonate	3:5890 3:6090 Cl=37.9% 3:6790	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloropentanol-3	3:9280 21=28.9% 3:9295 3:8225 3:8500
Isopropyl dichloroacetate Ethyl α,β -dichloropropionate $C_bH_8O_9Cl_2$ M.W. = 187.0 Di- $(\beta$ -chloroethyl) carbonate C_bH_9OCl M.W. = 120.6	3:5890 3:6090 Cl=37.9% 3:6790 Cl=29.4%	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloropentanol-3 1-Chloro-2-methylbutanol-2	3:9280 21=28.9% 3:9295 3:8225 3:8500 3:8175
Isopropyl dichloroacetate Ethyl α,β -dichloropropionate $C_bH_8O_2Cl_2$ M.W. = 187.0 Di- $(\beta$ -chloroethyl) carbonate C_bH_9OCl M.W. = 120.6 1-Chloropentanone-2	3:5890 3:6090 Cl=37.9% 3:6790 Cl=29.4% 3:8217	β-Ethoxyethyl chloroformate C _b H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloropentanol-3 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2	3:9280 21=28.9% 3:9295 3:8225 3:8500 3:8175 3:8030
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _k H ₈ O ₂ Cl ₂ M.W.=187.0 Di-(β-chloroethyl) carbonate C _k H ₉ OCl M.W.=120.6 1-Chloropentanone-2 3-Chloropentanone-2	3:5890 3:6090 Cl=37.9% 3:6790 Cl=29.4% 3:8217 3:7893	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloropentanol-3 1-Chloro-2-methylbutanol-2	3:9280 21=28.9% 3:9295 3:8225 3:8500 3:8175
Isopropyl dichloroacetate Ethyl α,β -dichloropropionate $C_4H_4O_3Cl_2$ M.W.=187.0 Di- $(\beta$ -chloroethyl) carbonate C_4H_9OCl M.W.=120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243	β-Ethoxyethyl chloroformate C _b H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloropentanol-3 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2	3:9280 21=28.9% 3:9295 3:8225 3:8500 3:8175 3:8030
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _k H ₈ O ₂ Cl ₂ M.W.=187.0 Di-(β-chloroethyl) carbonate C _k H ₉ OCl M.W.=120.6 1-Chloropentanone-2 3-Chloropentanone-2	3:5890 3:6090 Cl=37.9% 3:6790 Cl=29.4% 3:8217 3:7893	β-Ethoxyethyl chloroformate C _b H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloropentanol-3 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2	3:9280 21=28.9% 3:9295 3:8225 3:8500 3:8175 3:8030
Isopropyl dichloroacetate Ethyl α,β -dichloropropionate $C_4H_4O_3Cl_2$ M.W.=187.0 Di- $(\beta$ -chloroethyl) carbonate C_4H_9OCl M.W.=120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloropentanol-3 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2	3:9280 3:9285 3:9295 3:8225 3:8500 3:8175 3:8030 3:8335
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _b H ₈ O ₈ Cl ₂ M.W. = 187.0 Di-(β-chloroethyl) carbonate C _b H ₉ OCl M.W. = 120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2 5-Chloropentanone-2	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243 3:9267	β-Ethoxyethyl chloroformate C _b H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2	3:9280 3:9285 3:9295 3:8225 3:8500 3:8175 3:8030 3:8335
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C ₈ H ₈ O ₃ Cl ₂ M.W. = 187.0 Di-(β-chloroethyl) carbonate C ₈ H ₉ OCl M.W. = 120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2 5-Chloropentanone-2 1-Chloropentanone-3	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243 3:9267 3:9268	β-Ethoxyethyl chloroformate C _b H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloropentanol-3 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2	3:9280 3:9285 3:9295 3:8225 3:8500 3:8175 3:8030 3:8335 3:9290
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _b H ₈ O ₈ Cl ₂ M.W. = 187.0 Di-(β-chloroethyl) carbonate C _b H ₉ OCl M.W. = 120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2 5-Chloropentanone-2	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243 3:9267	β-Ethoxyethyl chloroformate C _b H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2	3:9280 3:9285 3:9295 3:8225 3:8500 3:8175 3:8030 3:8335
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _b H ₈ O ₃ Cl ₂ M.W.=187.0 Di-(β-chloroethyl) carbonate C _b H ₉ OCl M.W.=120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2 5-Chloropentanone-2 1-Chloropentanone-3 2-Chloropentanone-3	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:8243 3:8243 3:9267 3:9268 3:7935	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 G 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2 α-Chloro-thylbutanol-2 α-Chloro-thylbutanol-2 α-Chloro-thylbutanol-2	3:9280 3:9285 3:9295 3:8225 3:8500 3:8175 3:8030 3:8335 3:9290
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _b H ₈ O ₂ Cl ₂ M.W. = 187.0 Di-(β-chloroethyl) carbonate C _b H ₉ OCl M.W. = 120.6 1-Chloropentanone-2 3-Chloropentanone-2 5-Chloropentanone-2 1-Chloropentanone-3 2-Chloropentanone-3 1-Chloro-2-methylbutanone-3	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243 3:9267 3:9268 3:7935	β-Ethoxyethyl chloroformate C _b H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloropentanol-3 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2	3:9280 3:9285 3:9295 3:8225 3:8500 3:8175 3:8030 3:8335 3:9290
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _b H ₈ O ₃ Cl ₂ M.W.=187.0 Di-(β-chloroethyl) carbonate C _b H ₉ OCl M.W.=120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2 5-Chloropentanone-2 1-Chloropentanone-3 2-Chloropentanone-3	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:8243 3:8243 3:9267 3:9268 3:7935	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2 α-Chloro-thyl n-propyl ether ter-Amyl hypochlorite C ₆ GROUP	3:9280 3:9285 3:9285 3:8225 3:8225 3:8175 3:8030 3:8335 3:9290 3:7525 3:9287
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _b H ₈ O ₂ Cl ₂ M.W. = 187.0 Di-(β-chloroethyl) carbonate C _b H ₉ OCl M.W. = 120.6 1-Chloropentanone-2 3-Chloropentanone-2 5-Chloropentanone-2 1-Chloropentanone-3 2-Chloropentanone-3 1-Chloro-2-methylbutanone-3	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243 3:9267 3:9268 3:7935	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2 α-Chloro-thyl n-propyl ether ter-Amyl hypochlorite C ₆ GROUP C ₆ HOCl ₅ M.W.=266.4	3:9280 3:9285 3:9295 3:8225 3:8500 3:8175 3:8030 3:8335 3:7525 3:9287
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _b H ₈ O ₂ Cl ₂ M.W. = 187.0 Di-(β-chloroethyl) carbonate C _b H ₉ OCl M.W. = 120.6 1-Chloropentanone-2 3-Chloropentanone-2 5-Chloropentanone-2 1-Chloropentanone-3 2-Chloropentanone-3 1-Chloro-2-methylbutanone-3	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243 3:9267 3:9268 3:7935	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2 α-Chloro-thyl n-propyl ether ter-Amyl hypochlorite C ₆ GROUP	3:9280 3:9285 3:9285 3:8225 3:8225 3:8175 3:8030 3:8335 3:9290 3:7525 3:9287
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _b H ₈ O ₃ Cl ₂ M.W. = 187.0 Di-(β-chloroethyl) carbonate C _b H ₉ OCl M.W. = 120.6 1-Chloropentanone-2 3-Chloropentanone-2 5-Chloropentanone-2 1-Chloropentanone-3 2-Chloropentanone-3 2-Chloro-2-methylbutanone-3 n-Valeryl chloride	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:8243 3:8243 3:9267 3:9268 3:7935 3:9269 3:7597 3:7740	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 Control of the control of t	3:9280 3:9295 3:9295 3:8225 3:8500 3:8175 3:8030 3:8335 3:9290 3:7525 3:9287
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _b H _B O ₂ Cl ₂ M.W.=187.0 Di-(β-chloroethyl) carbonate C _b H _B OCl M.W.=120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2 1-Chloropentanone-3 2-Chloropentanone-3 1-Chloro-2-methylbutanone-3 2-Chloro-2-methylbutanone-3 n-Valeryl chloride α-Methyl-n-butyryl chloride	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243 3:9267 3:9268 3:7935 3:9269 3:7597 3:740 3:7603	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 G-Chloropentanol-1 1-Chloropentanol-2 1-Chloropentanol-3 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2 α-Chloroethyl n-propyl ether ter-Amyl hypochlorite C ₆ GROUP C ₆ HOCl ₅ M.W.=286.4 Pentachlorophenol C ₆ HO ₂ Cl ₅ M.W.=211.4	3:9280 3:9295 3:9295 3:8225 3:8500 3:8175 3:8030 3:8335 3:9290 3:7525 3:9287
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _b H ₈ O ₅ Cl ₂ M.W. = 187.0 Di-(β-chloroethyl) carbonate C _b H ₉ OCl M.W. = 120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2 1-Chloropentanone-3 2-Chloropentanone-3 1-Chloro-2-methylbutanone-3 2-Chloro-2-methylbutanone-3 n-Valeryl chloride α-Methyl-n-butyryl chloride β-Methyl-n-butyryl chloride	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:8243 3:9267 3:9268 3:7935 3:9269 3:7597 3:7560	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 G-Chloropentanol-1 1-Chloropentanol-2 1-Chloropentanol-3 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2 α-Chloroethyl n-propyl ether ter-Amyl hypochlorite C ₆ GROUP C ₆ HOCl ₅ M.W.=286.4 Pentachlorophenol C ₆ HO ₂ Cl ₅ M.W.=211.4	3:9280 3:9285 3:9295 3:8225 3:8225 3:8175 3:8030 3:8335 3:7525 3:9287 41=66.6% 3:4850
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _b H _B O ₂ Cl ₂ M.W.=187.0 Di-(β-chloroethyl) carbonate C _b H _B OCl M.W.=120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2 1-Chloropentanone-3 2-Chloropentanone-3 1-Chloro-2-methylbutanone-3 2-Chloro-2-methylbutanone-3 n-Valeryl chloride α-Methyl-n-butyryl chloride	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243 3:9267 3:9268 3:7935 3:9269 3:7597 3:740 3:7603	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 Control of the control of t	3:9280 3:9295 3:9295 3:8225 3:8500 3:8175 3:8030 3:8335 3:9290 3:7525 3:9287
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _k H ₈ O ₂ Cl ₂ M.W. = 187.0 Di-(β-chloroethyl) carbonate C ₄ H ₉ OCl M.W. = 120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2 1-Chloropentanone-3 2-Chloropentanone-3 1-Chloro-2-methylbutanone-3 2-Chloro-2-methylbutanone-3 n-Valeryl chloride α-Methyl-n-butyryl chloride β-Methyl-n-butyryl chloride α,α-Dimethylpropionyl chloride	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243 3:9267 3:9268 3:7935 3:9269 3:7597 3:7603 3:7450	β-Ethoxyethyl chloroformate C _b H ₁₁ OCl M.W.=122.6 Conception of the conception o	3:9280 3:9295 3:9295 3:8225 3:8560 3:8175 3:8030 3:8335 3:7525 3:9287
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _b H ₈ O ₅ Cl ₂ M.W. = 187.0 Di-(β-chloroethyl) carbonate C _b H ₉ OCl M.W. = 120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2 1-Chloropentanone-3 2-Chloropentanone-3 1-Chloro-2-methylbutanone-3 2-Chloro-2-methylbutanone-3 n-Valeryl chloride α-Methyl-n-butyryl chloride β-Methyl-n-butyryl chloride	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:8243 3:9267 3:9268 3:7935 3:9269 3:7597 3:7560	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 G 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloropentanol-3 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2 α-Chloro-2-methylbutanol-2 α-Chloroethyl n-propyl ether ter-Amyl hypochlorite C ₆ GROUP C ₆ HOCl ₅ M.W.=286.4 C Pentachlorophenol C ₆ HO ₂ Cl ₈ M.W.=211.4 2,3,5-Trichlorobenzoquinone-1,4 C ₆ H ₂ OCl ₄ M.W.=231.9	3:9280 3:9295 3:9295 3:8225 3:8500 3:8175 3:8030 3:8335 3:9290 3:7525 3:9287
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C ₈ H ₈ O ₂ Cl ₂ M.W. = 187.0 Di-(β-chloroethyl) carbonate C ₈ H ₉ OCl M.W. = 120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2 5-Chloropentanone-3 2-Chloropentanone-3 2-Chloropentanone-3 1-Chloro-2-methylbutanone-3 n-Valeryl chloride α-Methyl-n-butyryl chloride β-Methyl-n-butyryl chloride α,α-Dimethylpropionyl chloride Tetrahydro-α-furfuryl chloride	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243 3:9267 3:9268 3:7935 3:9269 3:7597 3:7740 3:7603 3:7450 3:7450 3:8152	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 G 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2 α-Chloroethyl n-propyl ether ter-Amyl hypochlorite C ₆ GROUP C ₆ HOCl ₅ M.W.=286.4 C Pentachlorophenol C ₆ HO ₂ Cl ₈ M.W.=211.4 2,3,5-Trichlorobenzoquinone-1,4 C ₆ H ₃ OCl ₄ M.W.=231.9 C 2,3,4,5-Tetrachlorophenol	3:9280 3:9285 3:9295 3:8225 3:8225 3:8175 3:8030 3:8335 3:9290 3:7525 3:9287 41=66.6% 3:4850 41=50.3% 3:4672
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C _k H ₈ O ₂ Cl ₂ M.W. = 187.0 Di-(β-chloroethyl) carbonate C ₄ H ₉ OCl M.W. = 120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2 1-Chloropentanone-3 2-Chloropentanone-3 1-Chloro-2-methylbutanone-3 2-Chloro-2-methylbutanone-3 n-Valeryl chloride α-Methyl-n-butyryl chloride β-Methyl-n-butyryl chloride α,α-Dimethylpropionyl chloride Tetrahydro-α-furfuryl chloride C ₄ H ₉ O ₂ Cl M.W. = 136.6	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243 3:9267 3:9268 3:7935 3:9269 3:7597 3:7603 3:7450 3:8152 C1=26.0%	β-Ethoxyethyl chloroformate C _b H ₁₁ OCl M.W.=122.6 C 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloropentanol-3 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2 α-Chloro-2-methylbutanol-2 α-Chloroethyl n-propyl ether ter-Amyl hypochlorite C ₆ GROUP C ₆ HOCl ₅ M.W.=286.4 C Pentachlorophenol C ₆ HO ₂ Cl ₅ M.W.=211.4 C 2,3,5-Trichlorobenzoquinone-1,4 C ₆ H ₃ OCl ₄ M.W.=231.9 C 2,3,4,5-Tetrachlorophenol 2,3,4,5-Tetrachlorophenol	3:9280 3:9295 3:9295 3:8225 3:8500 3:8175 3:8030 3:8335 3:9290 3:7525 3:9287
Isopropyl dichloroacetate Ethyl α,β-dichloropropionate C ₈ H ₈ O ₂ Cl ₂ M.W. = 187.0 Di-(β-chloroethyl) carbonate C ₈ H ₉ OCl M.W. = 120.6 1-Chloropentanone-2 3-Chloropentanone-2 4-Chloropentanone-2 5-Chloropentanone-3 2-Chloropentanone-3 2-Chloropentanone-3 1-Chloro-2-methylbutanone-3 n-Valeryl chloride α-Methyl-n-butyryl chloride β-Methyl-n-butyryl chloride α,α-Dimethylpropionyl chloride Tetrahydro-α-furfuryl chloride	3:5890 3:6090 C1=37.9% 3:6790 C1=29.4% 3:8217 3:7893 3:8243 3:9267 3:9268 3:7935 3:9269 3:7597 3:7740 3:7603 3:7450 3:7450 3:8152	β-Ethoxyethyl chloroformate C ₆ H ₁₁ OCl M.W.=122.6 G 5-Chloropentanol-1 1-Chloropentanol-2 1-Chloro-2-methylbutanol-2 3-Chloro-2-methylbutanol-2 4-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2 2-Chloro-2-methylbutanol-2 α-Chloroethyl n-propyl ether ter-Amyl hypochlorite C ₆ GROUP C ₆ HOCl ₅ M.W.=286.4 C Pentachlorophenol C ₆ HO ₂ Cl ₈ M.W.=211.4 2,3,5-Trichlorobenzoquinone-1,4 C ₆ H ₃ OCl ₄ M.W.=231.9 C 2,3,4,5-Tetrachlorophenol	3:9280 3:9285 3:9295 3:8225 3:8225 3:8175 3:8030 3:8335 3:9290 3:7525 3:9287 41=66.6% 3:4850 41=50.3% 3:4672

$C_6H_2O_2Cl_2$ M.W. = 177.0	Cl=40.1%	2-Chlorohydroquinone	3:3139
2,3-Dichlorobenzoquinone-1,4 2,5-Dichlorobenzoquinone-1,4 2,6-Dichlorobenzoquinone-1,4	3:2855 3:4470 3:3750	C ₆ H ₇ O ₄ Cl M.W. = 178.6 Dimethyl chlorofumarate	Cl=19.9% 3:6582
$C_6H_2O_2Cl_4$ M.W. = 247.9 Tetrachloropyrocatechol	Cl=57.2% 3:4875	Dimethyl chloromaleate	3:9351
Tetrachlororesorcinol Tetrachlorohydroquinone	3:4135 3:4941	$C_6H_8O_2Cl_2$ M.W. = 183.0 Adipyl (di)chloride	Cl=38.7% 3:9352
$C_6H_2O_4Cl_2$ M.W. = 209.0 2,5-Dichloro-3,6-dihydroxy-	C1 = 33.9%	$C_6H_8O_4Cl_2$ M.W. = 215.0 Di-(β -chloroethyl) oxalate	Cl=33.0% 3:0572
benzoquinone-1,4	3:4970	Ethylene glycol bis-(chloroacetat	te) 3:0720
$C_6H_8OCl_3$ M.W. = 197.5 2,3,4-Trichlorophenol	Cl = 53.9% 3:2185	Dimethyl $d, l-\alpha, \alpha'$ -dichlorosuccin	ate 3:0485
2,3,5-Trichlorophenol 2,3,6-Trichlorophenol	3:1340 3:1160	Dimethyl $meso-\alpha,\alpha'$ -dichloro- succinate	3:0240
2,4,5-Trichlorophenol	3:1620	CaHaOCl M.W. = 132.6	Cl = 26.7%
2,4,6-Trichlorophenol 3,4,5-Trichlorophenol	3:1673 3:2885	2-Chlorocyclohexanone-1	3:0120
•		3-Chlorocyclohexanone-1	3:9360
$C_6H_3O_2Cl$ M.W.=142.5 2-Chlorobenzoquinone-1,4	Cl = 24.9% 3:1100	4-Chlorocyclohexanone-1	3:9364
$C_6H_3O_2Cl_3$ M.W.=213.5	Cl = 49.8%	C ₆ H ₉ O ₂ Cl M.W. = 148.6	Cl = 23.9%
3,4,5-Trichlorocatechol	3:3448	Ethyl α -chlorocrotonate Ethyl β -chlorocrotonate	3:8523 3:8538
2,4,6-Trichlororesorcinol 2,3,5-Trichlorohydroquinone	3:2174 3: 40 52	Ethyl γ -chlorocrotonate	3:8657
$C_6H_3O_3Cl_3$ M.W. = 229.5	Cl = 46.4%	Ethyl α -chloroisocrotonate	3:9368
4,5,6-Trichloropyrogallol 3,5,6-Trichloro-2-hydroxy-	3:4782	Ethyl β -chloroisocrotonate	3:8325
hydroquinone	3: 4444	$C_6H_9O_2Cl_3$ M.W. = 219.5	Cl = 48.6%
2,4,6-Trichlorophloroglucinol	3:4030	β,β,β -Trichloro-ter-butylacetate	3:6180
$C_6H_4OCl_2$ M.W.=163.0 2.3-Dichlorophenol	Cl=43.5% 3:1175	Ethyl α,α,β -trichloro-n-butyrate	3:6380
2,4-Dichlorophenol	3:0560	n-Butyl trichloroacetate	3:6315
2,5-Dichlorophenol	3:1190 3:1595	secButyl trichloroacetate	3:9372
2,6-Dichlorophenol 3,4-Dichlorophenol	3:1460	Isobutyl trichloroacetate ter-Butyl trichloroacetate	3:6140 3:0138
3,5-Dichlorophenol	3:1670	•	
$C_0H_4O_2Cl_2$ M.W. = 179.0	Cl = 39.6%	$C_6H_9O_3Cl$ M.W. = 164.6 γ -(Carbomethoxy)-n-butyryl	Cl = 21.5%
3,5-Dichlorocatechol 4,5-Dichlorocatechol	3:2192 3:3525	chloride	3:9373
4,6-Dichlororesorcinol	3:3380	Ethyl α -chloroacetoacetate	3:6207
2,3-Dichlorohydroquinone	3:4220	Ethyl γ -chloroacetoacetate	3:6375
2,5-Dichlorohydroquinone	3:4690	$C_6H_9O_3Cl_3$ M W. = 235.5	Cl = 45.2%
2,6-Dichlorohydroquinone	3: 4600	Trichloroparaldehyde	3:2300
C_6H_6OCl $M.W. = 128.6$	C1 = 27.6%	$C_6H_{11}OCl$ M.W. = 134.6	Cl=26.3%
o-Chlorophenol m-Chlorophenol	3 : 5980 3 : 0255	2-Chlorocyclohexanol-1	
p-Chlorophenol	3:0475	Liquid stereoisomer (cis) Solid stereoisomer (trans)	3:9374 3:0175
C ₆ H ₅ O ₂ Cl M.W. = 144.6	Cl = 24.5%	4-Chlorocyclohexanol-1	3:9376
3-Chlorocatechol	3:07 <u>45</u>	- C Nowida	3:8168
4-Chlorocatechol	3:2470	n-Caproyl chloride	9:9T#2
2-Chlororesorcinol	3:2690	α-Methyl-n-valeryl chloride	3:8020
4-Chlororesorcinol 5-Chlororesorcinol	3:31 99 3:353 0	β -Methyl- n -valeryl chloride γ -Methyl- n -valeryl chloride	3:8 93 5
A-CATTOL OF ODOL OFFICE	U. 0000	1-1-TONITATION A STORY I CHICKING	

α,α -Dimethyl-n-butyryl chloride	3:7900	C7 GROUP	
α,β -Dimethyl-n-butyryl chloride	3:7965	•	C1 00 FC
β , β -Dimethyl- n -butyryl chloride	3:7880	C ₇ HOCl ₅ M.W.=278.4 Pentachlorobenzaldehyde	Cl=63.7% 3:4892
α-Ethyl-n-butyryl chloride	3:7990	$C_7HO_2Cl_5$ M.W. = 294.4	Cl=60.2%
$C_6H_{11}O_2Cl$ M.W. = 150.6	Cl=23.5%	Pentachlorobenzoic acid	3:4910
n-Butyl chloroacetate	3:8530		
secButyl chloroacetate	3:8350	$C_7H_2OCl_4$ M.W. = 243.9	Cl = 58.1%
ter-Butyl chloroacetate	3:8220	2,3,4,5-Tetrachlorobenzaldehyde	
Isobutyl chloroacetate	3:8375	2,3,4,6-Tetrachlorobenzaldehyde 2,3,5,6-Tetrachlorobenzaldehyde	
n -Propyl α -chloropropionate	3:9384		
Isopropyl α -chloropropionate	3:8165	$C_7H_2O_2Cl_4$ M.W. = 259.9 2,3,4,5-Tetrachlorobenzoic acid	Cl=54.6% 3:4790
n-Propyl β-chloropropionate	3:8545		
Isopropyl β -chloropropionate	3:9388	$C_7H_3OCl_3$ M.W.=209.5 2,3,4-Trichlorobenzaldehyde	Cl=50.8% 3:2445
Ethyl α-chloro-n-butyrate	3:8307	2,3,5-Trichlorobenzaldehyde	3:1060
Ethyl β -chloro- n -butyrate	3:8373	2,3,6-Trichlorobenzaldehyde	3:2287
Ethyl γ-chloro-n-butyrate	3:8597	2,4,5-Trichlorobenzaldehyde	3:3375
		2,4,6-Trichlorobenzaldehyde	3:1200
Ethyl α -chloroisobutyrate	3:8147	3,4,5-Trichlorobenzaldehyde	3:2440
Methyl α -chloro- n -valerate	3:8264	C ₇ H ₈ O ₂ Cl ₃ M.W. = 225.4 2,4,6-Trichloro-3-hydroxy-	Cl=47.2%
n-Amyl chloroformate	3:9380	benzaldehyde	3:3520
Isoamyl chloroformate	3:8215	,	
250ming 1 cittor or or intactor	0.0020	2,3,4-Trichlorobenzoic acid	3:4810
$C_6H_{11}O_2Cl_8$ M.W. = 221.5	Cl = 48.0%	2,3,5-Trichlorobenzoic acid	3:4485
Chloral diethylacetal	3:6317	2,3,6-Trichlorobenzoic acid	3:4500
Chloral n-butylalcoholate	3:0843	2.4.5-Trichlorobenzoic acid	3:4630
Chiorai n-butylaiconolate	U. UOZU	2.4.6-Trichlorobenzoic acid	3:4545
$C_6H_{11}O_4Cl$ M.W. = 182.6 Diethylene glycol mono-	Cl=19.4%	3,4,5-Trichlorobenzoic acid	3:4920
(chloroacetate)	3:9390	CHOC MI 1870	OI 40 FO
(emoroacetate)	0.0000	$C_7H_4OCl_2$ M.W. = 175.0	Cl = 40.5%
C II OCI W W 181 1	C1 - 41 007	2,3-Dichlorobenzaldehyde	3:1480
$C_6H_{12}OCl_2$ M.W. = 171.1	Cl=41.6%	2,4-Dichlorobenzaldehyde	3:1800
β,β'-Dichloro-di-n-propyl ether	3:8610 3:8745	2,5-Dichlorobenzaldehyde	3:1145
γ, γ' -Dichloro-di-n-propyl ether	3:8605	2,6-Dichlorobenzaldehyde	3:1690
β,β'-Dichloro-di-isopropyl ether		3,4-Dichlorobenzaldehyde 3,5-Dichlorobenzaldehyde	3:0550 3:1475
$C_6H_{12}O_2Cl_2$ M.W. = 187.1	Cl = 37.9%		
Formaldehyde β , β' -dichloro-		o-Chlorobenzoyl chloride	3:6640
isopropyl ethylacetal	3:9394	m-Chlorobenzoyl chloride	3:6590
		p-Chlorobenzoyl chloride	3:65 50
Acetaldehyde bis -(β -chloroethyl)			
acetal	3:6210	$C_7H_4O_2Cl_2$ M.W. = 191.0	Cl = 37.1%
Dichloroacetaldehyde diethylacet	al 3:6110	3,5-Dichloro-2-hydroxy- benzaldehyde	3:2637
		- -	, .
Ethylene glycol bis- $(\beta$ -chloroethyl		2,4-Dichloro-3-hydroxy-	
ether	3:6655	benzaldehyde	3:4140
G TT G G L 3 C TT 100 C	C1 00.00	2,6-Dichloro-3-hydroxybenz-	O. HIEU
$C_6H_{18}OCl$ M.W.= 136.6	Cl=26.0%	aldehyde	3:4160
6-Chlorohexanol-1	3:9395	4,6-Dichloro-3-hydroxybenz-	O. X.100
n -Butyl α -chloroethyl ether	3:9396	aldehyde	3:3952
CaH12O2Cl M.W.=152.6	Cl=23.2%	3,5-Dichloro-4-hydroxybenz-	
C ₆ H ₁₈ O ₂ Cl M.W.=152.6 Chloroacetaldehyde diethylacetal		aldehyde	3:4400

2.3-Dichlorobenzoic acid	3:4650	2.6-Dichloro-4-methylphenol 3:0400
2,4-Dichlorobenzoic acid	3:4560	2,0 2.0moro 2-morny phonor 0.0200
		C 77 C C
2,5-Dichlorobenzoic acid	3: 4340	C_7H_7OCl M.W. = 142.6 $Cl = 24.9\%$
2,6-Dichlorobenzoic acid	3:4200	3-Chloro-2-methylphenol 3:2280
3,4-Dichlorobenzoic acid	3:4925	4-Chloro-2-methylphenol 3:6789
3,5-Dichlorobenzoic acid	3:4840	5-Chloro-2-methylphenol 3:1815
5,5-1310HOLOBEH2010 acid	O. TOTO	
		6-Chloro-2-methylphenol 3:8615
	=34.3%	
3.5-Dichloro-2-hydroxybenzoic acid	3:4935	2-Chloro-3-methylphenol 3:1055
• •		4-Chloro-3-methylphenol 3:1535
3.5-Dichloro-4-hydroxybenzoic acid	9.4050	
5,5-Dichioro-4-nyuroxybenzoic acid	0 . Z000	6-Chloro-3-methylphenol 3:6766
C_7H_5OCl M.W. = 140.6 Cl =	25.2%	2-Chloro-4-methylphenol 3:6215
o-Chlorobenzaldehyde	3:6410	3-Chloro-4-methylphenol 3:1025
m-Chlorobenzaldehyde	3:6475	3-Cinoro-1-methylphenol 5:1925
<i>p</i> -Chlorobenzaldehyde	3:0765	Phenoxymethyl chloride 3:9448
		• • • • • • • • • • • • • • • • • • • •
Benzoyl chloride	3:6240	. (11)
		o-Chloroanisole 3:6255
CITOCI MW-011 F C	- E0 907	m-Chloroanisole 3:6195
	=50.3%	p-Chloroanisole 3:6300
2,4,6-Trichloro-3-methylphenol	3: 061 8	
		$C_7H_{10}O_2Cl_2$ M.W.=197.1 $Cl=36.0\%$
$C_7H_5O_2Cl$ M.W. = 156.5 Cl	=22.7%	
	3:1010	Pimelyl (di)chloride 3:9450
3-Chloro-2-hydroxybenzaldehyde		
4-Chloro-2-hydroxybenzaldehyde	3: 096 0	$C_7H_{11}OCl$ M.W. = 146.6 $Cl = 24.2\%$
5-Chloro-2-hydroxybenzaldehyde	3:2800	
• • • • • • • • • • • • • • • • • • • •		Hexahydrobenzoyl chloride 3:8580
2-Chloro-3-hydroxybenzaldehyde	3:4085	
		$C_7H_{11}O_2Cl$ M.W. = 162.6 $Cl = 21.8\%$
4-Chloro-3-hydroxybenzaldehyde	3:3780	Cyclohexyl chloroformate 3:5770
6-Chloro-3-hydroxybenzaldehyde	3:3350	Cy did to the control of the control
		O II O OL 14 M OO F OL 4 F ACC
2-Chloro-4-hydroxybenzaldehyde	3:4280	$C_7H_{11}O_2Cl_8$ M.W. = 233.5 $Cl = 45.6\%$
		n-Amyl trichloroacetate 3:6560
3-Chloro-4-hydroxybenzaldehyde	3: 40 65	Isoamyl trichloroacetate 3:6490
		ter-Amyl trichloroacetate 3:6185
o-Chlorobenzoic acid	3:4150	er-Amyr bricinoroacetate 9:0100
m-Chlorobenzoic acid	3:4392	
		$C_7H_{11}O_4Cl$ M.W. = 194.6 $Cl = 18.2\%$
p-Chlorobenzoic acid	3: 494 0	3-Chloropropanediol-1,2 diacetate 3:6840
o-Hydroxybenzoyl chloride	3:0085	$C_7H_{12}O_3Cl_2$ M.W. = 215.1 $Cl = 33.0\%$
m-Hydroxybenzoyl chloride	3:9446	
	3:9447	Di- $(\gamma$ -chloro- n -propyl) carbonate 3:6895
p-Hydroxybenzoyl chloride	J. GER!	
		$C_7H_{18}OCl$ M.W. = 148.6 $Cl = 23.9\%$
$C_7H_5O_3Cl$ M.W. = 172.6 Cl	=20.6%	n-Heptanoyl chloride 3:8520
3-Chloro-2-hydroxybenzoic acid	3:4745	"-IIchmioline 9:9956
	3:4908	
4-Chloro-2-hydroxybenzoic acid		α -Methyl- n -caproyl chloride 3:9452
5-Chloro-2-hydroxybenzoic acid	3:4705	β -Methyl- n -caproyl chloride 3:8305
6-Chloro-2-hydroxybenzoic acid	3: 4610	γ-Methyl-n-caproyl chloride 3:8355
• •		
O Chloro 2 hardrough	3:4395	δ -Methyl- n -caproyl chloride 3:8365
2-Chloro-3-hydroxybenzoic acid		
4-Chloro-3-hydroxybenzoic acid	3: 493 3	α, α -Dimethyl-n-valeryl chloride 3:9456
6-Chloro-3-hydroxybenzoic acid	3:4720	α,β -Dimethyl-n-valeryl chloride 3:9458
• • •		$\gamma_{,\gamma}$ -Dimethyl- n -valeryl chloride 3:9460
O Chlore 4 buduomshamasis - 23	9.4490	1.1-Timenthi-16-Agree At Cittoure
2-Chloro-4-hydroxybenzoic acid	3:4430	
3-Chloro-4-hydroxybenzoic acid	3: 46 75	α -Ethyl- n -valeryl chloride 3:8235
$C_7H_6OCl_2$ M.W. = 177.0 Cl	=40.1%	α,α,β-Trimethyl-n-butyryl chloride 3:8145
4,5-Dichloro-2-methylphenol	3:2910	α -Ethyl- β -methyl- n -butyryl
4,6-Dichloro-2-methylphenol	3:1020	chloride 3:9462
• •		
2.4-Dichloro-3-methylphenol	3:1205	$C_7H_{18}O_2Cl$ M.W. = 164.6 $Cl = 21.5\%$
2,6-Dichloro-3-methylphneol	3:0150	n -Butyl α -chloropropionate 3:8595
4,6-Dichloro-3-methylphenol	3:17 4 5	Isobutyl α -chloropropionate 3:3470
•		

n-Butyl β -chloropropionate Isobutyl β -chloropropionate Ethyl α -chloro-n-valerate	3:9474 3:8655 3:8596	C ₈ H ₈ O ₄ Cl M.W.=200.6 3-Chlorophthalic acid 4-Chlorophthalic acid	Cl = 17.7% 3:4820 3:4390
Ethyl β-chloro-n-valerate Ethyl β-chloro-n-valerate Ethyl δ-chloro-n-valerate Ethyl δ-chloro-n-valerate	3:8629 3:8703 3:8727	4-Chloroisophthalic acid 5-Chloroisophthalic acid	3:4980 3:4960
Ethyl α-chloroisovalerate	3:8528	Chloroterephthalic acid	3:4995
Ethyl α-chloro-α-methyl-n- butyrate	3:8518	$C_8H_6OCl_2$ M.W. = 189.0 ω , ω -Dichloroacetophenone	Cl=37.5% 3:6835
$C_7H_{16}OCl$ M.W. = 150.7	Cl=23.5%	p-Chlorophenacyl chloride	3:2990
7-Chloroheptanol-1 n-Amyl α-chloroethyl ether	3:0013 3:9480	$C_8H_8O_3Cl_2$ M.W. = 221.0 2,4-Dichlorophenoxyacetic acid	Cl=32.1% 3:4095
C ₇ H ₁₈ O ₃ Cl M.W.=166.7 \$-Chloropropionaldehyde diethylacetal	Cl=21.3% 3:9490	C ₈ H ₇ OCl M.W.=154.6 ω-Chloroacetophenone o-Chloroacetophenone m-Chloroacetophenone	Cl = 22.9% 3:1212 3:6615 3:6815
C ₈ GROUP		p-Chloroacetophenone	3:6735
C ₈ H ₂ O ₃ Cl ₂ M.W.=217.0 3,4-Dichlorophthalic anhydride	C1=32.7% 3:3695	Phenylacetyl chloride	3:9567
3,5-Dichlorophthalic anhydride 3,6-Dichlorophthalic anhydride 4,5-Dichlorophthalic anhydride	3 : 2375 3 : 4860 3 : 4830	o-Toluyl chloride m-Toluyl chloride p-Toluyl chloride	3:8740 3:6535
$C_8H_2O_4Cl_4$ M.W.=303.9 Tetrachlorophthalic acid	Cl=46.7% 3:4946	$C_8H_7OCl_8$ M.W. = 225.5 4,5,6-Trichloro-2,3-dimethylphen 3,5,6-Trichloro-2,4-dimethylphen	
$C_8H_8O_8Cl$ M.W. = 182.6 3-Chlorophthalic anhydride	Cl=19.4% 3:3900	3,4,6-Trichloro-2,5-dimethylphen	ol 3:4709
4-Chlorophthalic anhydride	3:2725	2,5,6-Trichloro-3,4-dimethylphen 2,4,6-Trichloro-3,5-dimethylphen	
$C_8H_4O_2Cl_2$ M.W. = 203.0	Cl = 34.9%	C ₈ H ₇ O ₂ Cl M.W. = 170.6	Cl=20.8%
Phthalyl (di)chloride (sym.) Phthalyl (di)chloride (unsym.)	3 : 6900 3 : 2395	3-Chloro-2-methylbenzoic acid	3:4435
		4-Chloro-2-methylbenzoic acid 5-Chloro-2-methylbenzoic acid	3:4700 3:4670
Isophthalyl (di)chloride	3:0520	6-Chloro-2-methylbenzoic acid	3:3275
Terephthalyl (di)chloride	3:2205	4-Chloro-3-methylbenzoic acid 5-Chloro-3-methylbenzoic acid	3:4915 3:4715
$C_8H_4O_4Cl_2$ M.W. = 235.0 3.4-Dichlorophthalic acid	Cl=30.2% 3:4880	6-Chloro-3-methylbenzoic acid	3:4615
3,5-Dichlorophthalic acid	3:4580	2-Chloro-4-methylbenzoic acid	3:4355
3,6-Dichlorophthalic acid 4,5-Dichlorophthalic acid	3:4870 3:4890	3-Chloro-4-methylbenzoic acid	3:4900
4,5-Demorophunane acid	9 . 20 9 0	2-Chlorophenylacetic acid	. 3:2640
4,6-Dichloroisophthalic acid	3:4965	3-Chlorophenylacetic acid 4-Chlorophenylacetic acid	3:1910 3:3135
2,5-Dichloroterephthalic acid	3: 49 85	Dhanara actual ablacida	
$C_8H_6OCl_8$ M.W. = 223.5	Cl=47.6%	Phenoxyacetyl chloride	3:87 90
ω,ω,ω-Trichloroscetophenone	3:6874	2-Methoxybenzoyl chloride	8:6870
C ₂ H ₅ O ₂ Cl M.W. = 184.6 Piperonyl chloride	Cl=19.2% 3:1960	3-Methoxybenzoyl chloride 4-Methoxybenzoyl chloride	3 : 6797 3 : 6890
		Phenyl chloroacetate	3:0565
C ₂ H ₄ O ₂ Cl ₂ M.W.=255.5 2,4,5-Trichlorophenoxyacetic aci	Cl=41.6% id 3:4335	Bensyl chloroformate	3:9565

C _A H ₁ OCl M.W. = 186.6 Cl = 19.0% S-Chloro-phenoxyacetic acid 3:4326 P-Chlorophenoxyacetic acid 3:4326 P-Chlorophenoxyacetic acid 3:4325 P-Chlorophenoxyacetic acid 3:2426 P-Chlorophenoxyacetic acid 3:2426 P-Chlorophenoxyacetic acid 3:2426 P-Chlorophenyl-propiolic acid P-Chloroph	Methyl o-chlorobenzoate Methyl m-chlorobenzoate Methyl p-chlorobenzoate	3 : 6695 3 : 6670 3 : 0535	C ₈ H ₁₈ O ₅ Cl M.W. = 226.7 Triethylene glycol mono- (chloroscetate)	Cl=15.6% 3:9588
-Chlorophenoxyacetic acid mechlorophenoxyacetic acid 3:4256 p-Chlorophenoxyacetic acid 3:4375 p-Chlorophenoxyacetic acid 3:4385 p-Chlorophenoxyacetic acid 3:4386 p-Chlorophenoxyacetic acid 3:4385 p-Chlorophenoxyacetic acid 3:4386 p-Chlorophenoxyacetic acid 3:4386 p-Chlorophenoxyacetic acid 3:4386 p-Chlorophenoxyacetic acid 3:4385 p-Chloropheno	mondy's p-unorodonadado	0.000	(cmoroacetate)	9:3000
p-Chlorophenoxyacetic acid C ₁ H ₁ OCl ₂ M.W. = 191.1 C ₁ =37.1% S ₆ -Dichloro-2,3-dimethylphenol 2,5-Dichloro-3,4-dimethylphenol 3:2442 C ₂ H ₂ OCl ₂ M.W. = 164.6 C ₃ -Dichloro-3,4-dimethylphenol 3:245 S ₆ -Dichloro-3,4-dimethylphenol 3:245 S ₆ -Dichloro-3,4-dimethylphenol 3:245 S ₆ -Dichloro-3,4-dimethylphenol 3:246 S ₆ -Dichloro-3,5-dimethylphenol 3:2482 C ₆ -Dichloro-3,5-dimethylphenol 3:2483 C ₆ -Dichloro-3,5-dimethylphenol 3:2483 C ₆ -Dichloro-3,4-dimethylphenol 3:2483 C ₆ -Dichloro-3,4-dimethylphenol 3:2484 C ₆ -Dichloro-3,4-dimethylphenol 3:2485 C ₆ -Dichloro-2,4-dimethylphenol 3:2486 C ₆ -Chlorophenylpropiolic acid p-Chlorophenylpropiolic acid p-Chlorophenylpropi	o-Chlorophenoxyacetic acid	3:4260		
CaHq.OCls M.W. = 191.1 Cl = 37.1% disthylacetal 3:9594				Cl = 19.6%
2.4-Dichloro-3.4-dimethylphenol 3:0935 5.6-Dichloro-3.4-dimethylphenol 3:3905 5.6-Dichloro-3.4-dimethylphenol 3:3905 2.4-Dichloro-3.5-dimethylphenol 3:3905 C _A H ₀ OCl M.W. = 166.6 C _A H ₀ OCl M.W. = 244.6 C _A H ₀ O _C M.W. = 244.6 C _A H ₀ O _C M.W. = 244.6 C _A H ₁ O _C O _C M.W. = 180.6 C _A H ₁ O _C O _C M.W. = 180.6 C _A H ₁ O _C O _C M.W. = 180.6 C _A H ₁ O _C O _C M.W. = 180.6 C _A H ₁ O _C O _C M.W. = 180.6 C _A H ₁ O _C O _C M.W. = 180.6 C _A H ₁ O _C O _C M.W. = 180.6 C _A H ₁ O _C O _C M.W. = 180.6 C _A H ₁ O _C O _C M.W. = 180.6 C _A H ₁ O _C O _C M.W. = 180.6 C _A H ₁ O _C O _C M.W. = 180.6 C _A H ₁ O _C O _C M.W. = 180.6 C _A H ₁ O _C O _C M.W. = 206.6 C _A H ₁ O _C O _C M.W. = 206.6 C _A H ₁ O _C O _C M.W. = 206.6 C _A H ₁ O _C O _C M.W. = 206.6 C _A H ₁ O _C O _C M.W. = 223.1 C _A H ₁ O _C O _C M.W. = 224.1 C _A H ₁ O _C O _C M.W. = 224.1 C _A H ₁ O _C O _C M.W. = 224.1 C _A H ₁ O _C O _C M.W. = 224.1 C _A H ₁ O _C O _C M.W. = 224.1 C _A H ₁ O _C O _C M.W. = 224.1 C _A H ₁ O _C O _C M.W. = 180.7 C _A H ₁ O _C O _C M.W. = 180			diethylacetal	3:9594
2.6-Dichloro-3,4-dimethylphenol 3:0935 5,6-Dichloro-3,4-dimethylphenol 3:3095 2.4-Dichloro-3,5-dimethylphenol 3:2838 2.6-Dichloro-3,5-dimethylphenol 3:2838 C ₆ -H ₆ OCl M.W. = 156.6 Cl = 22.6% Chloromethyl-phenyl-carbinol 3:9570 4-Chloro-2,3-dimethylphenol 3:2818 5-Chloro-2,3-dimethylphenol 3:2818 5-Chloro-2,4-dimethylphenol 3:2818 6-Chloro-2,4-dimethylphenol 3:2818 6-Chloro-2,5-dimethylphenol 3:2858 4-Chloro-2,5-dimethylphenol 3:2868 4-Chloro-2,5-dimethylphenol 3:2868 4-Chloro-2,5-dimethylphenol 3:2868 4-Chloro-3,4-dimethylphenol 3:2868 6-Chloro-3,4-dimethylphenol 3:2868 6-Chloro-3,4-dimethylphenol 3:2705 6-Chloro-3,4-dimethylphenol 3:2705 6-Chloro-3,4-dimethylphenol 3:2705 6-Chloro-3,5-dimethylphenol 3:2705 6-Chloro-3,5-dimethylphenol 3:2864 4-Chloro-3,5-dimethylphenol 3:3565 β-Phenoxyethyl chloride 3:0165 β-Phenoxyethyl chloride 3:0165 β-Phenoxyethyl chloride 3:0165 β-Phenoxyethyl chloride 3:0165 β-Chloro-1,6-dimethylphenol 3:3684 β-Chloro-1,6-dimethylphenol 3:2864 β-Chloro-1,6-dimethylphenol 3:2864 β-Chloro-1,6-dimethylphenol 3:2864 β-Chloro-2,6-dimethylphenol 3:2864 β-Chloro-3,6-dimethylphenol 3:2864 β-Chloro-1,6-dimethylphenol 3:2864 β-Chloro-1,6-dimethylphenol 3:2864 β-Chloro-1,6-dimethylphenol 3:2864 β-Chloro-1,6-dimethylphenol 3:2868 β-Chloro-1,6-dimethylphenol 3:2868 β-Chloro-3,6-dimethylphenol 3:2868 β-Chloro-3,6			<u> </u>	
2.4-Dichloro-3,5-dimethylphenol 3:2182	2,6-Dichloro-3,4-dimethylphenol	3:0935		
CaHaOC M.W. = 156.6 Cl = 22.6% Chloromethyl-phenyl-carbinol 3:9579 CaHaOc M.W. = 244.6 Cl = 14.4% S-Chloro-2,3-dimethylphenol 3:218 S-Chloro-2,3-dimethylphenol 3:218 S-Chloro-2,4-dimethylphenol 3:218 S-Chloro-2,4-dimethylphenol 3:289 CaHaOc M.W. = 166.6 Cl = 21.3% CaHaOc M.W. = 186.6 Cl = 21.3% CaHaOc M.W. = 184.6 Cl = 21.6% CaHaOc M.W. = 243.1 Cl = 29.6% CaHaOc M.W. = 255.1 Cl = 31.5% CaHaOc M.W. = 178.7 Cl = 20.8% CaHaOc M.W. = 178.7 Cl = 20.8% CaHaOc M.W. = 178.7 Cl = 21.8% CaHaOc M.W. = 178.7 Cl = 20.8% CaHaOc M.W. = 178.7 Cl = 20.8% CaHaOc M.W. = 191.6 CaHaOc M.W. =			o-Chlorophenylpropiolic acid	3:3956
Chloromethyl-phenyl-carbinol 3:9576 Chloro-2,3-dimethylphenol 3:2118 5-Chloro-2,3-dimethylphenol 3:2118 5-Chloro-2,3-dimethylphenol 3:2118 5-Chloro-2,4-dimethylphenol 3:3734 2-Chlorobenzenetricarboxylic acid-1,3,5 3:4855				3:4265
4-Chloro-2,3-dimethylphenol 3:2118 5-Chloro-2,4-dimethylphenol 3:2116 5-Chloro-2,4-dimethylphenol 3:8784 4-Chloro-2,5-dimethylphenol 3:8784 4-Chloro-2,5-dimethylphenol 3:1822 4-Chloro-2,6-dimethylphenol 3:2189 4-Chloro-2,6-dimethylphenol 3:2189 4-Chloro-3,4-dimethylphenol 3:2189 5-Chloro-3,4-dimethylphenol 3:2189 5-Chloro-3,4-dimethylphenol 3:2705 5-Chloro-3,4-dimethylphenol 3:2705 5-Chloro-3,5-dimethylphenol 3:2754 4-Chloro-3,5-dimethylphenol 3:2754 5-Chloro-3,5-dimethylphenol 3:2755 6-Chloro-3,5-dimethylphenol 3:3505 6-Chloro-3,5-dimethylphenol 3:3505 6-Chloro-3,5-dimethylphenol 3:3505 6-Chloro-3,5-dimethylphenol 3:3505 6-Chloro-3,5-dimethylphenol 3:3505 6-Chlorophenetole 3:8735 6-Chlorophenetole 3:8735 6-Chlorophenetole 3:6323 6-Chlorophenole 3:6324 6-Chlorophenole 3				
4-Chloro-2,3-dimethylphenol 3:2456 5-Chloro-2,4-dimethylphenol 3:2450 6-Chloro-2,4-dimethylphenol 3:8784 4-Chloro-2,5-dimethylphenol 3:8784 4-Chloro-2,5-dimethylphenol 3:1822 4-Chloro-2,6-dimethylphenol 3:1822 4-Chloro-3,4-dimethylphenol 3:2180 6-Chloro-3,4-dimethylphenol 3:2754 6-Chloro-3,4-dimethylphenol 3:1754 6-Chloro-3,5-dimethylphenol 3:1754 4-Chloro-3,5-dimethylphenol 3:1754 6-Chloro-3,5-dimethylphenol 3:3844 4-Chloro-3,5-dimethylphenol 3:3505 6-Chloro-3,5-dimethylphenol 3:3505 6-Chloro-3,5-dimethylphenol 3:3505 6-Phenoxyethyl chloride 3:3505 6-Phenoxyethyl chloride 3:3632 6-Chlorophenetole 3:6323 6-Chloro	Chloromethyl-phenyl-carolhol			C1 = 14.4%
5-Chloro-2,4-dimethylphenol 3:2460 6-Chloro-2,4-dimethylphenol 3:8784 4-Chloro-2,5-dimethylphenol 3:1822 C ₂ H ₇ OCl M.W.=166.6 Cl=21.3% 4-Chloro-2,6-dimethylphenol 3:2180 2-Chloro-3,4-dimethylphenol 3:2180 6-Chloro-3,4-dimethylphenol 3:2765 6-Chloro-3,4-dimethylphenol 3:2765 6-Chloro-3,5-dimethylphenol 3:2765 6-Chloro-3,5-dimethylphenol 3:3505 4-Chloro-3,5-dimethylphenol 3:3505 6-Chloro-3,5-dimethylphenol 3:3505 6-Chloro-3,5-dimethylphenol 3:3505 6-Phenoxyethyl chloride 3:0165 6-Phenoxyethyl chloride 3:0165 6-Chlorophenetole 3:6323 6-Chlorophenetole 3:6323 6-Chlorophenotole 3:6324 6-Chlorophenotole 3:6324 6-Chlorophenotole 3:6324 6-Chlorophenotole 3:6325 6-Chlorophenotole 3:6326 6-Chlo				3:4855
5-Chloro-2,4-dimethylphenol 3:8460 6-Chloro-2,4-dimethylphenol 3:8784 4-Chloro-2,5-dimethylphenol 3:1822 4-Chloro-2,5-dimethylphenol 3:2180 2-Chloro-3,4-dimethylphenol 3:2705 6-Chloro-3,4-dimethylphenol 3:2705 6-Chloro-3,4-dimethylphenol 3:2705 6-Chloro-3,5-dimethylphenol 3:1754 4-Chloro-3,5-dimethylphenol 3:3754 4-Chloro-3,5-dimethylphenol 3:3505 6-Phenoxyethyl chloride 3:3505 6-Phenoxyethyl chloride 3:6532 6-Chlorophenetole 3:6332 6-Chlorophenetole 3:6333 6-Chlorophenetole 3:6340 6-Chlorophenetole 3:6333 6-Chlorophenetole 3:6340 6-Chlorophenetole 3:6333 6-Chlorophenetole 3:6340 6-Chlorophenetole 3:6333 6-Chlorophenetole 3:6333 6-Chlorophenetole 3:6340 6-Chlorophenetole 3:6333 6-Chlorophenetole 3:6340 6-Chlorophenetole 3:6333 6-Chlorophenetole 3:6340 6-Chlorophenyl ketone 3:9644 6	5-Chloro-2,3-dimethylphenol	3:2115		
6-Chloro-2,4-dimethylphenol 3:8784 4-Chloro-2,5-dimethylphenol 3:1822 Chloro-2,6-dimethylphenol 3:2180 4-Chloro-2,6-dimethylphenol 3:0158 5-Chloro-3,4-dimethylphenol 3:2705 6-Chloro-3,4-dimethylphenol 3:2705 6-Chloro-3,4-dimethylphenol 3:1754 2-Chloro-3,5-dimethylphenol 3:0844 4-Chloro-3,5-dimethylphenol 3:0844 4-Chloro-3,5-dimethylphenol 3:0844 4-Chloro-3,5-dimethylphenol 3:3505 β-Phenoxyethyl chloride 3:0165 β-Phenoxyethyl chlo	5-Chloro-2.4-dimethylphenol	3:2460		9.4075
4-Chloro-2,6-dimethylphenol 3:1822 4-Chloro-2,6-dimethylphenol 3:2180 4-Chloro-2,6-dimethylphenol 3:2180 5-Chloro-3,4-dimethylphenol 3:2705 6-Chloro-3,4-dimethylphenol 3:2705 6-Chloro-3,5-dimethylphenol 3:31754 4-Chloro-3,5-dimethylphenol 3:3505 4-Chloro-3,5-dimethylphenol 3:3505 4-Chloro-3,5-dimethylphenol 3:3505 4-Chloro-3,5-dimethylphenol 3:3505 4-Chloro-3,5-dimethylphenol 3:3505 4-Chloro-3,5-dimethylphenol 3:3505 6-Phenoxyethyl chloride 3:0165 6-Chlorophenetole 3:6323 6-Chlorophenetole 3:6324 6-Chlorophenetole 3:			acid-1,0,0	0.2510
2-Chloro-3,4-dimethylphenol 3:0168 5-Chloro-3,4-dimethylphenol 3:2705 6-Chloro-3,4-dimethylphenol 3:1754 2-Chloro-3,4-dimethylphenol 3:1754 2-Chloro-3,5-dimethylphenol 3:6844 4-Chloro-3,5-dimethylphenol 3:3565 6-Phenoxyethyl chloride 3:0165 6-Chlorophenetole 3:6323 6-Phenoxyethyl chloride 3:6323 6-Chlorophenetole 3:6324 6-Chlorophenyl ketone 3:9344	4-Chloro-2,5-dimethylphenol	3:1822		Cl=21.3% 3:0330
2-Chloro-3,4-dimethylphenol 3:2705 6-Chloro-3,4-dimethylphenol 3:2705 6-Chloro-3,4-dimethylphenol 3:1754 2-Chloro-3,5-dimethylphenol 3:6844 4-Chloro-3,5-dimethylphenol 3:3505 4-Chloro-3,5-dimethylphenol 3:3505 6-Phenoxyethyl chloride 3:0165 6-Phenoxyethyl chloride 3:6844 6-Chloro-3,5-dimethylphenol 3:3505 6-Phenoxyethyl chloride 3:0165 6-Phenoxyethyl chloride 3:0165 6-Chlorophenetole 3:6323 6-Chlorophenyl chlorophenetole 3:6323 6-Chlorophenyl chloride 3:6323 6-Chlorophenyl chloride 3:6324 6-Chlorophenyl chloride 3:632	4-Chloro-2,6-dimethylphenol	3:2180		
5-Chloro-3,4-dimethylphenol 6-Chloro-3,4-dimethylphenol 3:1754 2-Chloro-3,5-dimethylphenol 3:6844 4-Chloro-3,5-dimethylphenol 3:3565 β-Phenoxyethyl chloride 3:6845 ρ-Chlorophenetole 3:8735 μ-Chlorophenetole 3:6323 μ-Chlorophenyl ethyl ketone 3:6346	2-Chloro-3.4-dimethylphenol	3:0158		
2-Chloro-3,5-dimethylphenol 3:6844 4-Chloro-3,5-dimethylphenol 3:3505 4-Chloro-3,5-dimethylphenol 3:3505 6-Phenoxyethyl chloride 3:6165 α-Chlorophenetole 3:6735 α-Chlorophenetole 3:6735 α-Chlorophenetole 3:6323 α-Chlorophenyl ethyl ketone 3:6346 α-Chlorophyl ethyl ketone 3:6366 α-Chlorophyl ethyl ketone 3:6366 α-Chlorophyl ethyl ketone 3:6366 α-Chlorophyl ethyl ketone 4:6406 α-α-α-α-α-α-α-α-α-α-α-α-α-α-α-α-α-α-α-			w-Chief p-inesity laces optioned	0.1100
2-Chloro-3,5-dimethylphenol 3:6844 4-Chloro-3,5-dimethylphenol 3:3505 β-Phenoxyethyl chloride 3:0165 ο-Chlorophenetole 3:8735 m-Chlorophenetole 3:6323 p-Chlorophenetole 3:6323 p-Chlorophenyl ethyl ketone 3:8340 p-Chlorophenyl ethyl ketone 3:8360 p-Chlorophenyl ethyl ketone 3:8340 p-Chlorophenyl ethyl ketone 4:8450 p-Chlorophenyl ethyl ketone 3:8340 p-Chlorophenyl ethyl ketone 4:8450 p-Chlorophenyl ethyl ketone 4:8450 p-Chlorophenyl ethyl ketone 4:8450 p-Chlorophenyl ethyl ketone 4:8450 p-Chlorophenotole 3:8540 p-Chlorophenotole 3:8540 p-Chlorophenotole 3:6323 p-Chlorophenotole 3:6323 p-Chlorophenotole 3:6324 p-Chlorophenotole 3:6323 p-Chlorophenotole 3:6323 p-Chlorophenotole 3:6323 p-Chlorophenotole 3:6323 p-Chlorophenotole 3:6320 p-Chlorophenotole 3:6320 p-Chlorophenotole 3:6320 p-Chlorophenotole 3:6320 p-Ch	6-Chloro-3,4-dimethylphenol	3:1754		3:9664
4-Chloro-3,5-dimethylphenol 3:3505 β-Phenoxyethyl chloride 3:0165 σ-Chlorophenetole 3:8735 m-Chlorophenetole 3:6323 p-Chlorophenetole 3:6323 p-Chlorophenetole 3:6323 Ethyl σ-chlorobenzoate 3:6300 Ethyl σ-chlorobenzoate 3:6730 Ethyl p-chlorobenzoate 3:6750 Ethyl p-chlorobenzoate 3:6750 C ₂ H ₁₁ O ₄ Cl M.W. = 206.6 Cl = 17.2% Diethyl chlorofumarate 3:6864 Diethyl chloromaleate 3:6697 C ₂ H ₁₁ O ₄ Cl ₂ M.W. = 211.1 Cl = 33.6% Suberyl (di)chloride 3:9576 C ₂ H ₁₁ O ₄ Cl ₂ M.W. = 211.1 Cl = 33.6% Suberyl (di)chloride 3:9576 C ₂ H ₁₁ O ₄ Cl ₂ M.W. = 243.1 Cl = 29.6% Diethyl d ₁ l-α,α-dichlorosuccinate 3:9578 Diethyl d ₂ l-α,α-dichlorosuccinate 3:9578 Diethyl meso-α,α-dichlorosuccinate 3:1364 C ₂ H ₁₁ OCl M.W. = 176.7 Cl = 20.1% n-Octanoyl chloride 3:8680 C ₂ H ₁₂ O ₂ Cl M.W. = 178.7 Cl = 19.9% n-Octanoyl α-chloropropionate 3:2580 C ₂ H ₁₆ O ₂ Cl M.W. = 178.7 Cl = 19.9% Suberyl α-chloropropionate 3:2580 C ₂ H ₁₆ O ₂ Cl M.W. = 178.7 Cl = 19.9% Suberyl α-chloropropionate 3:2580 C ₂ H ₁₆ O ₂ Cl M.W. = 178.7 Cl = 19.9% Suberyl α-chloropropionate 3:2580 C ₂ H ₁₆ O ₂ Cl M.W. = 178.7 Cl = 19.9% Suberyl α-chloropropionate 3:2580 C ₂ H ₁₆ O ₂ Cl M.W. = 178.7 Cl = 19.9% Suberyl α-chloropropionate 3:2580 C ₂ H ₁₆ O ₂ Cl M.W. = 178.7 Cl = 19.9% Suberyl α-chloropropionate 3:2580 C ₂ H ₁₆ O ₂ Cl M.W. = 178.7 Cl = 19.9% Suberyl α-chloropropionate 3:2580 C ₂ H ₁₆ O ₂ Cl M.W. = 178.7 Cl = 19.9% Suberyl α-chloropropionate 3:2580	2-Chloro-3,5-dimethylphenol	3:0844	p-Cmoroethyl phenyl ketone	9:1119
β-Phenoxyethyl chloride 3:0165 C ₉ H ₉ O ₂ Cl M.W. = 184.6 Cl = 19.2% o-Chlorophenetole 3:8735 Ethyl o-chlorobenzoate 3:6860 m-Chlorophenetole 3:6323 Ethyl m-chlorobenzoate 3:6776 p-Chlorophenetole 3:0000 Ethyl p-chlorobenzoate 3:6756 C ₈ H ₁₁ O ₄ Cl M.W. = 206.6 Cl = 17.2% β-Chloroethyl benzoate 3:8860 Diethyl chlorofumarate 3:6864 C ₈ H ₁₁ OCl M.W. = 170.6 Cl = 20.8% Diethyl chloromaleate 3:6867 C ₉ H ₁₄ O ₂ Cl ₂ M.W. = 170.6 Cl = 20.8% Suberyl (di)chloride 3:6867 C ₉ H ₁₄ O ₂ Cl ₂ M.W. = 225.1 Cl = 31.5% Suberyl (di)chloride 3:9576 Azelayl (di)chloride 3:9580 C ₈ H ₁₉ O ₄ Cl ₂ M.W. = 243.1 Cl = 29.6% C ₉ H ₁₇ OCl M.W. = 176.7 Cl = 20.1% Diethyl d.l-α,α-dichlorosuccinate 3:9578 3:1364 C ₈ H ₁₉ OCl M.W. = 178.7 Cl = 21.8% n-Octanoyl chloride 3:8680 C ₁₀ GROUP C ₁₀ GROUP C ₁₀ H ₂ O ₂ Cl ₂ M.W. = 191.6 C ₁ Cl = 18	4-Chloro-3,5-dimethylphenol	3:3505	•	3:0340
c-Chlorophenetole 3:8735 Ethyl o-chlorobenzoate 3:6866 m-Chlorophenetole 3:6323 Ethyl m-chlorobenzoate 3:6776 p-Chlorophenetole 3:6323 Ethyl m-chlorobenzoate 3:6776 C ₈ H ₁₁ O ₄ Cl M.W. = 206.6 Cl = 17.2% β-Chloroethyl benzoate 3:8860 Diethyl chlorofumarate 3:6864 C ₈ H ₁₁ OCl M.W. = 170.6 Cl = 20.8% Diethyl chloromaleate 3:6697 C ₉ H ₁₁ OCl M.W. = 170.6 Cl = 20.8% Suberyl (di)chloride 3:6576 Agelayl (di)chloride 3:8520 C ₈ H ₁₂ O ₂ Cl ₂ M.W. = 223.1 Cl = 20.6% C ₉ H ₁₄ O ₂ Cl ₂ M.W. = 225.1 Cl = 31.5% Suberyl (di)chloride 3:9578 Agelayl (di)chloride 3:9580 C ₈ H ₁₂ O ₄ Cl ₂ M.W. = 243.1 Cl = 29.6% Pelargonyl chloride 3:8765 Diethyl d ₁ J-α,α-dichlorosuccinate 3:9578 Pelargonyl chloride 3:8765 C ₈ H ₁₂ OCl M.W. = 162.7 Cl = 21.8% 9-Chlorononanol-1 3:6176 C ₂ H ₁₆ OCl M.W. = 162.7 Cl = 21.8% 9-C	β -Phenoxyethyl chloride	3:0165		
## Chlorophenetole ## Sie676	en. 1 . 1	0.0007		
## Chlorophenetole				3:6770
C ₂ H ₁₁ O ₄ Cl M.W. = 206.6 Cl = 17.2% β-Chloroethyl benzoate 3:8866 Diethyl chlorofumarate 3:6864 Diethyl chloromaleate 3:6697 γ-Phenoxy-n-propyl chloride 3:8826 γ-Phenoxy-n-propyl chloride 3:8826 C ₂ H ₁₂ O ₂ Cl ₂ M.W. = 211.1 Cl = 33.6% C ₂ H ₁₄ O ₂ Cl ₂ M.W. = 225.1 Cl = 31.5% Suberyl (di) chloride 3:9576 Azelayl (di) chloride 3:9686 C ₂ H ₁₂ O ₄ Cl ₂ M.W. = 243.1 Cl = 29.6% Diethyl d, l-α,α-dichlorosuccinate 3:9578 Diethyl d, l-α,α-dichlorosuccinate 3:9578 Diethyl meso-α,α-dichlorosuccinate 3:1364 C ₂ H ₁₂ OCl M.W. = 176.7 Cl = 20.1% n-Octanoyl chloride 3:8686 C ₂ H ₁₂ OCl M.W. = 162.7 Cl = 21.8% n-Octanoyl chloride 3:8686 C ₂ H ₁₂ OCl M.W. = 178.7 Cl = 19.9% S-Chlorononanol-1 3:6176 Cl = 18.5% S-Chloropropionate 3:9586 S-Chloropropionate 3:9586 Cl = 19.9% S-Chloropro				3:6750
Diethyl chlorofumarate 3:6864 2:6697 C _b H ₁₁ OCl M.W. = 170.6 3:8820 C _c H ₁₂ O ₂ Cl ₂ M.W. = 211.1 Cl = 33.6% Suberyl (di) chloride 3:9576 Aselayl (di) chloride 3:9576 Aselayl (di) chloride 3:9630 C _c H ₁₂ O ₄ Cl ₂ M.W. = 243.1 Cl = 29.6% Diethyl d.l-α,α-dichlorosuccinate 3:9578 Diethyl meso-α,α-dichlorosuccinate 3:1364 C _c H ₁₂ OCl M.W. = 162.7 Cl = 21.8% n-Octanoyl chloride 3:8680 C _c H ₁₆ O ₂ Cl M.W. = 178.7 Cl = 19.9% C _c H ₁₆ O ₂ Cl M.W. = 178.7 Cl = 19.9% C _c H ₁₆ O ₂ Cl M.W. = 178.7 Cl = 19.9% C _c H ₁₆ O ₂ Cl M.W. = 178.7 Cl = 19.9% C _c H ₁₆ O ₂ Cl M.W. = 191.6 Cl = 18.5% Cl = 19.9% Cl =		Cl = 17 2%	β-Chloroethyl benzoate	3:8860
Diethyl chloromaleate 3:6697 γ -Phenoxy- n -propyl chloride 3:8830 C ₃ H ₁₂ O ₂ Cl ₂ M.W. = 211.1 Cl = 33.6% C ₉ H ₁₄ O ₂ Cl ₂ M.W. = 225.1 Cl = 31.5% Suberyl (di)chloride 3:9576 Aselayl (di)chloride 3:9680 C ₂ H ₁₂ O ₄ Cl ₂ M.W. = 243.1 Cl = 29.6% C ₉ H ₁₇ OCl M.W. = 176.7 Cl = 20.1% Diethyl d ₁ L-α,α-dichlorosuccinate 3:9578 Pelargonyl chloride 3:8765 Diethyl meso-α,α-dichlorosuccinate 3:1364 C ₉ H ₁₉ OCl M.W. = 178.7 Cl = 19.8% C ₂ H ₁₈ OCl M.W. = 162.7 Cl = 21.8% 9-Chlorononanol-1 3:0170 C ₂ H ₁₈ O ₂ Cl M.W. = 178.7 Cl = 19.9% C ₁₀ H ₄ O ₂ Cl ₂ M.W. = 191.6 Cl = 18.5% Isoamyl α-chloropropionate 3:9580 C ₁₀ H ₄ O ₂ Cl ₂ M.W. = 191.6 Cl = 18.5% 3.4-Dichloromaphthoquinone-1,2 3:4775			C H. OCI M W = 170 6	C1-20.80
Suberyl (di)chloride 3:9576 Aselayl (di)chloride 3:9680 $C_8H_{19}O_4Cl_3$ M.W. = 243.1 Diethyl d_1l - α,α -dichlorosuccinate Cl = 29.6% Signs of the policy of the polic				3:8820
Diethyl d,l-α,α-dichlorosuccinate Diethyl d,l-α,α-dichlorosuccinate Diethyl meso-α,α-dichlorosuccinate Diethyl me				Cl=31.5% 3:9680
Diethyl meso-α,α-dichlorosuccinate 3:1364 C ₂ H ₁₉ OCl M.W.=162.7 Cl=21.8% n-Octanoyl chloride 3:8680 C ₂ H ₁₉ OCl M.W.=178.7 Cl=19.8% 9-Chlorononanol-1 3:0170 C ₁₀ GROUP C ₂ H ₁₆ O ₂ Cl M.W.=178.7 Cl=19.9% Isoamyl α-chloropropionate 3:9580 3.4-Dichloronaphthoquinone-1,2 3:4775				Cl=20.1% 3:8765
C ₈ H ₁₈ OCl M.W.=162.7 Cl=21.8% n-Octanoyl chloride 3:8680 C ₁₀ GROUP C ₈ H ₁₈ O ₂ Cl M.W.=178.7 Cl=19.9% C ₁₀ H ₄ O ₂ Cl ₂ M.W.=191.6 Cl=18.5% Isoamyl a-chloropropionate 3:9580 3,4-Dichloronaphthoquinone-1,2 3:4737	Diethyl meso-a, a-dichlorosuccins	ate 3:1364	C ₆ H ₁₉ OCl M.W.=178.7	Cl=19.8%
n-Octanoyl chloride 3:8680 C ₁₀ GROUP C ₂ H ₁₆ O ₂ Cl M.W.=178.7 Cl=19.9% C ₁₀ H ₄ O ₂ Cl ₂ M.W.=191.6 Cl=18.5% Isoamyl α-chloropropionate 3:9580 3,4-Dichloronaphthoguinone-1,2 3:478	OH OOL WW 1897	C1=21 8%		3:0170
C ₂ H ₁₆ O ₂ Cl M.W.=178.7 Cl=19.9% C ₁₀ H ₄ O ₂ Cl ₂ M.W.=191.6 Cl=18.5% Isoamyl α-chloropropionate 3:9580 3,4-Diohloronaphthoquinone-1,2 3:478				
Isoamyl α-chloropropionate 3:9590 3,4-Dichloronaphthoquinone-1,2 3:4775				a
	Isoamyl α -chloropropionate	3:9580	3,4-Dichloronaphthoquinone-1,2	CI = 18.5% 3:4775 3:4857

$C_{10}H_5O_2Cl$ M.W. = 192.6			
	Cl = 18.4%	$C_{10}H_{16}O_{2}Cl_{2}$ M.W. = 239.1	Cl = 29.7%
3-Chloronaphthoquinone-1,2	3:4704	Sebacyl (di)chloride	3:9780
4-Chloronaphthoquinone-1,2	3:4000	Debacyi (di)oniorido	0.000
a-Omoromaphimodumono-1,2	0.2000	$C_{10}H_{19}OCl$ M.W. = 190.7	Cl=18.6%
0 Chlana - hab a 1 4	0.0700	n-Decanoyl chloride	3:8800
2-Chloronaphthoquinone-1,4	3:3580	n-Decanoyi emoride	0.0000
5-Chloronaphthoquinone-1,4	3:4492	C H OCI MW -1096	CI 19 407
6-Chloronaphthoquinone-1,4	3:3145	$C_{10}H_{21}OCl$ M.W.=192.6	Cl=18.4%
		10-Chlorodecanol-1	3:0014
$C_{10}H_6OCl_2$ M.W. = 213.1	C1 = 33.3%	G 77 CG1 15 777 100 6	~~
2,3-Dichloronaphthol-1	3:293 5	$C_{11}H_7OCl$ M.W. = 190.6	Cl = 18.6%
2,4-Dichloronaphthol-1	3:3250	α-Naphthoyl chloride	3:6930
5,7-Dichloronaphthol-1	3:3985	β-Naphthoyl chloride	3:0900
5.8-Dichloronaphthol-1	3:3420		
6,7-Dichloronaphthol-1	3:4315	$C_{11}H_7O_2Cl$ M.W. = 206.6	Cl = 17.2%
7,8-Dichloronaphthol-1	3:2635	2-Chloronaphthoic acid-1	3:4330
		4-Chloronaphthoic acid-1	3: 49 36
1,3-Dichloronaphthol-2	3:1990	5-Chloronaphthoic acid-1	3: 4944
1,4-Dichloronaphthol-2	3:3840	6-Chloronaphthoic acid-1	3:4845
1,6-Dichloronaphthol-2	3:3600	7-Chloronaphthoic acid-1	3:4942
		8-Chloronaphthoic acid-1	3:4680
3,4-Dichloronaphthol-2	3:3295		
4,8-Dichloronaphthol-2	3:4420	1-Chloronaphthoic acid-2	3:4885
5,8-Dichloronaphthol-2	3:4155	3-Chloronaphthoic acid-2	3:4928
		5-Chloronaphthoic acid-2	3:4952
$C_{10}H_7OCl$ M.W. = 178.6	Cl = 19.8%	8-Chloronaphthoic acid-2	3:4948
2-Chloronaphthol-1	3:1490	8-Chioronaphthole acid-2	0.1010
3-Chloronaphthol-1	3:4170	$C_{11}H_{19}O_{3}Cl$ M.W. = 234.7	C1 _ 15 107
4-Chloronaphthol-1	3:3720		Cl = 15.1%
5-Chloronaphthol-1	3:3960	ω-(Carbomethoxy)pelargonyl	
6-Chloronaphthol-1	3:2615	chloride	3:9792
7-Chloronaphthol-1	3:3810	A	
8-Chloronaphthol-1	3:1610	$C_{11}H_{21}OC1$ M.W. = 204.7	Cl = 17.3%
0-Cinorollapatonor 2	0.1010	Undecanoyl chloride	3:9800
1-Chloronaphthol-2	3:1700		
	3:2545	C ₁₂ GROUP	
3-Chioronaphthol-2	3:3045		O1 4800
4-Chloronaphthol-2		$C_{12}H_9OCl$ M.W. = 204.7	Cl = 17.3%
5-Chloronaphthol-2	3:3945	3-Chloro-2-hydroxybiphenyl	3:1757
6-Chloronaphthol-2	3:3500	5-Chloro-2-hydroxybiphenyl	3:8980
7-Chloronaphthol-2	3:3925		
8-Chloronaphthol-2	3:2965	3-Chloro-4-hydroxybiphenyl	3:1900
-	3:2965	3-Chloro-4-hydroxybiphenyl 4'-Chloro-4-hydroxybiphenyl	3:1900 3:4262
8-Chloronaphthol-2 C ₁₀ H ₁₁ OCl M.W. = 182.6		4'-Chloro-4-hydroxybiphenyl	
·	3:2965		
$C_{10}H_{11}OCl$ M.W. = 182.6	3:2965	4'-Chloro-4-hydroxybiphenyl	3:4262
$C_{10}H_{11}OCl$ M.W. = 182.6 ω -Chloro-2,4-dimethyl-	3:2965 Cl=19.4%	4'-Chloro-4-hydroxybiphenyl	3:4262
$C_{10}H_{11}OCl$ M.W. = 182.6 ω -Chloro-2,4-dimethyl- acetophenone ω -Chloro-2,5-dimethyl-	3:2965 Cl=19.4%	$4'$ -Chloro- 4 -hydroxybiphenyl α -Naphthylacetyl chloride	3:4262 3:9856
$C_{10}H_{11}OCl$ M.W. = 182.6 ω -Chloro-2,4-dimethyl- acetophenone ω -Chloro-2,5-dimethyl- acetophenone	3:2965 C1=19.4% 3:1355	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₅ Cl ₃ M.W.=319.7 Para-(β-chloro-n-butyraldehyde)	3:4262 3:9856 Cl=33.3% 3:2650
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-2,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl-	3:2965 Cl=19.4% 3:1355 3:0245	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₂ Cl ₃ M.W.=319.7	3:4262 3:9856 Cl=33.3% 3:2650
$C_{10}H_{11}OCl$ M.W. = 182.6 ω -Chloro-2,4-dimethyl- acetophenone ω -Chloro-2,5-dimethyl- acetophenone	3:2965 C1=19.4% 3:1355	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₃ Cl ₃ M.W.=319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde)	3:4262 3:9856 Cl=33.3% 3:2650 3:3220
$C_{10}H_{11}OCl$ M.W. = 182.6 ω -Chloro-2,4-dimethylacetophenone ω -Chloro-2,5-dimethylacetophenone ω -Chloro-3,4-dimethylacetophenone	3:2965 C1=19.4% 3:1355 3:0245 3:1775	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₂ Cl ₃ M.W.=319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₆ OCl M.W.=218.8	3:4262 3:9856 Cl=33.3% 3:2650 3:3220 Cl=16.2%
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-2,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl-	3:2965 Cl=19.4% 3:1355 3:0245	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₃ Cl ₃ M.W.=319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde)	3:4262 3:9856 Cl=33.3% 3:2650 3:3220
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-2,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl- acetophenone 2,4,6-Trimethylbenzoyl chloride	3:2965 C1=19.4% 3:1355 3:0245 3:1775 3:9750	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₅ Cl ₅ M.W. = 319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₅ OCl M.W. = 218.8 Lauroyl chloride	3:4262 3:9856 Cl=33.3% 3:2650 3:3220 Cl=16.2% 3:9858
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-2,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl- acetophenone 2,4,6-Trimethylbenzoyl chloride C ₁₀ H ₁₃ OCl M.W. = 184.7	3:2965 C1=19.4% 3:1355 3:0245 3:1775 3:9750 C1=19.2%	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₃ Cl ₃ M.W.=319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₅ OCl M.W.=218.8 Lauroyl chloride C ₁₂ H ₂₆ OCl M.W.=220.8	3:4262 3:9856 Cl=33.3% 3:2650 3:3220 Cl=16.2% 3:9858 Cl=16.1%
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-2,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl- acetophenone 2,4,6-Trimethylbenzoyl chloride	3:2965 C1=19.4% 3:1355 3:0245 3:1775 3:9750	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₅ Cl ₅ M.W. = 319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₅ OCl M.W. = 218.8 Lauroyl chloride	3:4262 3:9856 Cl=33.3% 3:2650 3:3220 Cl=16.2% 3:9858
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-2,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl- acetophenone 2,4,6-Trimethylbenzoyl chloride C ₁₀ H ₁₈ OCl M.W. = 184.7 2-Chloro-4-n-butylphenol	3:2965 C1=19.4% 3:1355 3:0245 3:1775 3:9750 C1=19.2% 3:8830	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₂ Cl ₃ M.W.=319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₆ OCl M.W.=218.8 Lauroyl chloride C ₁₂ H ₂₆ OCl M.W.=220.8 12-Chlorododecanol-1	3:4262 3:9856 Cl=33.3% 3:2650 3:3220 Cl=16.2% 3:9858 Cl=16.1%
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-2,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl- acetophenone 2,4,6-Trimethylbenzoyl chloride C ₁₀ H ₁₃ OCl M.W. = 184.7	3:2965 C1=19.4% 3:1355 3:0245 3:1775 3:9750 C1=19.2%	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₃ Cl ₃ M.W.=319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₅ OCl M.W.=218.8 Lauroyl chloride C ₁₂ H ₂₆ OCl M.W.=220.8	3:4262 3:9856 Cl=33.3% 3:2650 3:3220 Cl=16.2% 3:9858 Cl=16.1%
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-2,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl- acetophenone 2,4,6-Trimethylbenzoyl chloride C ₁₀ H ₁₈ OCl M.W. = 184.7 2-Chloro-4-n-butylphenol	3:2965 C1=19.4% 3:1355 3:0245 3:1775 3:9750 C1=19.2% 3:8830	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₃ Cl ₅ M.W.=319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₆ OCl M.W.=218.8 Lauroyl chloride C ₁₂ H ₂₆ OCl M.W.=220.8 12-Chlorododecanol-1 C ₁₃ GROUP	3:4262 3:9856 Cl=33.3% 3:2650 3:3220 Cl=16.2% 3:9858 Cl=16.1% 3:0172
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-3,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl- acetophenone 2,4,6-Trimethylbenzoyl chloride C ₁₀ H ₁₅ OCl M.W. = 184.7 2-Chloro-4-n-butylphenol	3:2965 C1=19.4% 3:1355 3:0245 3:1775 3:9750 C1=19.2% 3:8830	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₂ Cl ₃ M.W. = 319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₅ OCl M.W. = 218.8 Lauroyl chloride C ₁₂ H ₂₆ OCl M.W. = 220.8 12-Chlorododecanol-1 C ₁₃ GROUP C ₁₂ H ₃ OCl ₂ M.W. = 251.1	3:4262 3:9856 Cl=33.3% 3:2650 3:3220 Cl=16.2% 3:9858 Cl=16.1% 3:0172
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-2,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl- acetophenone 2,4,6-Trimethylbenzoyl chloride C ₁₀ H ₁₈ OCl M.W. = 184.7 2-Chloro-4-n-butylphenol	3:2965 C1=19.4% 3:1355 3:0245 3:1775 3:9750 C1=19.2% 3:8830 3:9760	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₃ Cl ₃ M.W.=319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₅ OCl M.W.=218.8 Lauroyl chloride C ₁₂ H ₂₆ OCl M.W.=220.8 12-Chlorododecanol-1 C ₁₃ GROUP C ₁₃ H ₃ OCl ₂ M.W.=251.1 2,2'-Dichlorobenzophenone	3:4262 3:9856 Cl=33.3% 3:2650 3:3220 Cl=16.2% 3:9858 Cl=16.1% 3:0172 Cl=28.2% 3:0717
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-3,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl- acetophenone 2,4,6-Trimethylbensoyl chloride C ₁₀ H ₁₈ OCl M.W. = 184.7 2-Chloro-4-n-butylphenol 2-Chloro-4-ter-butylphenol p-Chlorocarvacrol	3:2965 C1=19.4% 3:1355 3:9245 3:1775 3:9750 C1=19.2% 3:8830 3:9760 3:0480	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₃ Cl ₃ M.W.=319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₅ OCl M.W.=218.8 Lauroyl chloride C ₁₂ H ₂₆ OCl M.W.=220.8 12-Chlorododecanol-1 C ₁₃ GROUP C ₁₄ H ₃ OCl ₂ M.W.=251.1 2,2'-Dichlorobenzophenone 2,3'-Dichlorobenzophenone	3:4262 3:9856 Cl=33.3% 3:2650 3:3220 Cl=16.2% 3:9858 Cl=16.1% 3:0172 Cl=28.2% 3:6717 3:9859-A
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-3,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl- acetophenone 2,4,6-Trimethylbenzoyl chloride C ₁₀ H ₁₅ OCl M.W. = 184.7 2-Chloro-4-n-butylphenol	3:2965 C1=19.4% 3:1355 3:0245 3:1775 3:9750 C1=19.2% 3:8830 3:9760	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₃ Cl ₃ M.W.=319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₆ OCl M.W.=218.8 Lauroyl chloride C ₁₂ H ₂₆ OCl M.W.=220.8 12-Chlorododecanol-1 C ₁₃ GROUP C ₁₂ H ₃ OCl ₂ M.W.=251.1 2,2'-Dichlorobenzophenone 2,3'-Dichlorobenzophenone 2,4-Dichlorobenzophenone	3:4262 3:9856 Cl=33.3% 3:2650 3:3220 Cl=16.2% 3:9858 Cl=16.1% 3:0172 Cl=28.2% 3:9717 3:9859-A 3:9825
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-3,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl- acetophenone 2,4,6-Trimethylbenzoyl chloride C ₁₀ H ₁₃ OCl M.W. = 184.7 2-Chloro-4-n-butylphenol 2-Chloro-4-ier-butylphenol p-Chlorocarvacrol p-Chlorothymol	3:2965 C1=19.4% 3:1355 3:0245 3:1775 3:9750 C1=19.2% 3:8830 3:9760 3:0480 3:1293	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₅ Cl ₅ M.W. = 319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₅ OCl M.W. = 218.8 Lauroyl chloride C ₁₂ H ₂₆ OCl M.W. = 220.8 12-Chlorododecanol-1 C ₁₃ GROUP C ₁₅ H ₃ OCl ₅ M.W. = 251.1 2,2'-Dichlorobenzophenone 2,3'-Dichlorobenzophenone 2,4'-Dichlorobenzophenone	3:4262 3:9856 Cl=33.3% 3:2650 3:3220 Cl=16.2% 3:9858 Cl=16.1% 3:0172 Cl=28.2% 3:0717 3:9858-A 3:0825 3:1565
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-3,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl- acetophenone 2,4,6-Trimethylbensoyl chloride C ₁₀ H ₁₃ OCl M.W. = 184.7 2-Chloro-4-n-butylphenol 2-Chloro-4-ter-butylphenol p-Chlorocarvacrol p-Chlorothymol C ₁₀ H ₁₅ O ₃ Cl M.W. = 200.7	3:2965 C1=19.4% 3:1355 3:0245 3:1775 3:9750 C1=19.2% 3:8830 3:9760 3:0480 3:1293 C1=17.7%	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₃ Cl ₃ M.W.=319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₅ OCl M.W.=218.8 Lauroyl chloride C ₁₂ H ₂₆ OCl M.W.=220.8 12-Chlorododecanol-1 C ₁₃ GROUP C ₁₄ H ₃ OCl ₂ M.W.=251.1 2,2'-Dichlorobenzophenone 2,3'-Dichlorobenzophenone 2,4'-Dichlorobenzophenone 2,4'-Dichlorobenzophenone	3:4262 3:9856 C1=33.3% 3:2650 3:3220 C1=16.2% 3:9858 C1=16.1% 3:0172 C1=28.2% 3:6717 3:9859-A 3:0825 3:1565 3:2340
C ₁₀ H ₁₁ OCl M.W. = 182.6 ω-Chloro-2,4-dimethyl- acetophenone ω-Chloro-3,5-dimethyl- acetophenone ω-Chloro-3,4-dimethyl- acetophenone 2,4,6-Trimethylbenzoyl chloride C ₁₀ H ₁₃ OCl M.W. = 184.7 2-Chloro-4-n-butylphenol 2-Chloro-4-ier-butylphenol p-Chlorocarvacrol p-Chlorothymol	3:2965 C1=19.4% 3:1355 3:0245 3:1775 3:9750 C1=19.2% 3:8830 3:9760 3:0480 3:1293 C1=17.7%	4'-Chloro-4-hydroxybiphenyl α-Naphthylacetyl chloride C ₁₂ H ₂₁ O ₅ Cl ₅ M.W. = 319.7 Para-(β-chloro-n-butyraldehyde) Para-(α-chloro-isobutyraldehyde) C ₁₂ H ₂₅ OCl M.W. = 218.8 Lauroyl chloride C ₁₂ H ₂₆ OCl M.W. = 220.8 12-Chlorododecanol-1 C ₁₃ GROUP C ₁₅ H ₃ OCl ₅ M.W. = 251.1 2,2'-Dichlorobenzophenone 2,3'-Dichlorobenzophenone 2,4'-Dichlorobenzophenone	3:4262 3:9856 Cl=33.3% 3:2650 3:3220 Cl=16.2% 3:9858 Cl=16.1% 3:0172 Cl=28.2% 3:0717 3:9858-A 3:0825 3:1565

3,3'-Dichlorobenzophenone 3,4-Dichlorobenzophenone 3,4'-Dichlorobenzophenone	3:3860 3:3070 3:3415	$C_{14}H_{27}OCl$ M.W.=246.8 Myristoyl chloride	Cl=14.4% 3:9885
3,5-Dichlorobenzophenone 4,4'-Dichlorobenzophenone	3:1505 3:4270	$C_{14}H_{20}OCl$ M.W. = 248.8 14-Chlorotetradecanol-1	Cl=14.2% 3: 93 75
C ₁₈ H ₉ OCl M.W.=216.7 2-Chlorobenzophenone 3-Chlorobenzophenone 4-Chlorobenzophenone	Cl=16.4% 3:0715 3:2160 3:1914	C ₁₅ GROUP C ₁₅ H ₂₉ OCl M.W. = 260.8 Pentadecanoyl chloride	Cl=13.6% 3:9900
C ₁₄ H ₂₆ OCl M.W.=232.8 Tridecanoyl chloride	Cl=15.2% 3:9860	C_{16} GROUP $C_{16}H_{31}OCl$ M.W. = 274.9 Palmitoyl chloride	Cl=12.9% 3:9912
C_{14} GROUP $C_{14}H_7O_2Cl$ M.W. = 242.7 1-Chloroanthraquinone 2-Chloroanthraquinone	Cl=14.6% 3:4480 3:4922	C ₁₆ H ₃₈ OCl M.W. = 276.9 16-Chlorohexadecanol-1	Cl=12.8% 3:0525
C ₁₄ H ₉ O ₂ Cl M.W.=244.7 o-Benzoylbenzoyl chloride	Cl=14.5% 3:9880	C ₁₇ GROUP C ₁₇ H ₂₉ OCl M.W.=288.9 Heptadecanoyl chloride	Cl = 12.3% 3:9925
$C_{14}H_{10}OCl_2$ M.W. = 265.1 α -Chlorodiphenylacetyl chloride	C1 = 26.8% 3:0885	C ₁₈ GROUP	
$C_{14}H_{10}O_2Cl_2$ M.W. = 281.1 D ₁ -(p-chlorophenyl) acetic acid	Cl=25.2% 3:4613	C ₁₈ H ₃₈ OCl M.W. = 300.9 Elaidyl chloride Oleoyl chloride	Cl=11.8% 3:9950 3:9940
$C_{14}H_{11}OCl$ M.W. = 230.7 p-Phenylphenacyl chloride Desyl chloride	Cl=15.4% 3:3934 3:1618	$C_{18}H_{35}OC1$ M.W. = 302.9 Stearoyl chloride	Cl=11.7% 3:9960
$C_{14}H_{11}O_2Cl$ M.W. = 246.7 Diphenylchloroacetic acid	Cl=14.4% 3:3585	C ₁₈ H ₃₇ OCl M.W. = 304.9 18-Chloro-octadecanol-1	Cl=11.6% 3:0985

II. INDEX OF EMPIRICAL FORMULAS ACCORDING TO PERCENTAGE CHLORINE CONTENT

The empirical formulas for all groups of isomers listed in this book are represented below in diminishing order of their percentage chlorine. Note that there are numerous instances in which this value is the same for several different formulas. An analogous list of empirical formulas arranged according to their molecular weights comprises Index III (page 1383).

To ascertain which specific compounds corresponding to a given formula are described in the text of this volume, see the Empirical Formula Index (page 1359).

%		. %		%			
Chlorine	Formula	Chlorine	Formula	Chlorine	Formula		
92.2	CCL	76.9	C4OCl6	68.0	C7OCls		
89.9	C ₂ Cl ₆	75.8	C ₂ O ₂ Cl ₆	67.6	C ₄ H ₈ Cl ₈		
89.1	CHCl ₂	74.7	C_2Cl_2	67.6	C ₅ H ₈ Cl ₄		
88.7	C ₂ Cl ₈	74 .7	C ₆ Cl ₆	67.2	C6O2Cl6		
87.6	C ₂ HCl ₅	74.5	C7HCl7	67.1	C7H8Cl5		
87.0	C ₂ HCl ₇	73.9	C ₄ H ₂ Cl ₄	66.9	$C_3H_2O_2Cl_4$		
85.5	C ₂ Cl ₄	73.2	C ₈ OCl ₄	66.7	$C_4H_5Cl_3$		
85.5	C ₂ Cl ₆	73.1	$C_2H_2Cl_2$	66.6	C ₆ HOCl ₅		
85.0	$C_4H_2Cl_8$	73.1	$C_8H_3Cl_8$	65.9	C ₂ H ₃ OCl ₃		
84.8	C ₃ H ₂ Cl ₆	73.1	C ₄ H ₄ Cl ₄	65.9	$C_4H_7Cl_8$		
84.7	C4OCl10	73.1	C6H6Cl6	65.9	C ₅ H ₂ O ₃ Cl ₆		
84.5	$C_2H_2Cl_4$	72.5	C ₅ H ₇ Cl ₅	65.7	C ₆ H ₂ Cl ₄		
83.5	CH_2Cl_2	72.4	C ₃ H ₂ OCl ₄	65.1	C ₂ HO ₂ Cl ₃		
82.9	C ₄ H ₃ Cl ₇	72.4	C4H6Cl4	64.5	CaHoOCla		
82.7	C ₈ HCl ₅	72.2	C ₂ HOCl ₃	64.5	$C_6H_6Cl_4$		
82.5	C _b Cl ₈	72.1	C ₃ H ₅ Cl ₃	64.3	C ₂ H ₂ O ₂ Cl ₂		
82.0	$C_8H_8Cl_5$	72.0	$C_3HO_2Cl_5$	63.9	C ₂ H ₄ Cl ₂		
81.6	C ₄ Cl ₆	71.7	$COCl_2$	63.9	C ₄ O ₂ Cl ₄		
81.1	$C_4H_2OCl_8$	71.7	$C_2O_2Cl_4$	63.7	C7HOCl5		
81.0	C ₂ HCl ₃	71.7	$C_2H_4Cl_2$	63.3	C ₄ H ₂ O ₂ Cl ₄		
81.0	C4H2Cl6	71.7	C ₃ O ₃ Cl ₆	63.3	$C_6H_{10}Cl_4$		
80.3	C4H4Cl6	71.7	C ₈ H ₄ OCl ₄	62.8	C ₂ H ₂ OCl ₂		
79.7	C ₂ H ₃ Cl ₃	71.2	C ₂ H ₈ OCl ₈	62.8	C ₈ H ₆ Cl ₂		
78.8	C ₄ H ₂ Cl ₄	71.2	C7H2Cl6	62.8	C ₄ H ₄ O ₂ Cl ₄		
78.3	C4HCl5	70.8	C ₆ HCl ₅	61.7	$C_2H_4OCl_2$		
78.0	C2OCl4	70.7	C ₆ OCl ₆	61.7	C7H4Cl4		
78.0	C ₈ H ₄ Cl ₄	70.3	C ₁₀ Cl ₈	61.3	C ₅ H ₇ Cl ₂		
77.6	C4H3Cl5	70.2	CH ₂ Cl	61.2	C ₆ H ₂ OCl ₄		
77.0	C ₈ HOCl ₅	68.9	C ₄ O ₈ Cl ₆	60.6	C ₃ HO ₂ Cl ₃		
77.0	C ₄ H ₄ Cl ₅	68.6	C ₆ H ₉ Cl ₅	60.6	C ₄ H ₅ OCl ₃		
	1380						

%		%		%	
Chlorine	Formula .	Chlorine	Formula	Chlorine	Formula.
60.6	$C_5H_9Cl_8$	48.0	C ₅ H ₇ O ₈ Cl ₈	38.3	C ₄ H ₉ Cl
60.2	C7HO2Cl5	48.0	C ₆ H ₁₁ O ₂ Cl ₈	37.9	C4H4O4Cl2
59.9	C ₄ H ₇ OCl ₈	47.6	C ₈ H ₈ Cl	37.9	$C_6H_8O_8Cl_2$
59.6	C ₄ Cl ₂	47.6	C ₆ H ₆ Cl ₂	37.9	$C_6H_{12}O_2Cl_2$
59.2	C ₄ H ₂ O ₈ Cl ₄	47.6	C ₈ H ₅ OCl ₃	37.5	C ₂ H ₃ O ₂ Cl
58.6	C ₂ HCl	47.2	C7H3O2Cl3	37.5	CaH7OC1
58.6	$C_6H_3Cl_8$	47.2	C ₈ H ₇ OCl ₈	37.5	C ₈ H ₆ OCl ₂
58.1	C ₈ OCl ₆	47.0	$C_6H_8Cl_2$	37.5	C ₁₄ H ₉ Cl ₈
58.1	C7H2OCL	46.7	C ₈ H ₂ O ₄ Cl ₄	37.2	C ₁₄ H ₁₁ Cl ₄
58.0	$C_6H_5Cl_8$	46.4	$C_4H_2O_2Cl_2$	37.1	C7H4O2Cl2
57.7	$C_4H_4Cl_2$	46.4	$C_6H_3O_3Cl_3$	37.1	C ₈ H ₈ OCl ₂
57.7	$C_6O_2Cl_4$	46.3	C_8H_6Cl	36.0	C ₇ H ₁₀ O ₂ Cl ₂
57.4	C ₆ H ₇ Cl ₈	46.3	C ₆ H ₁₀ Cl ₂	36.0	C ₂ H ₁₈ Cl ₂
57.2	C ₆ H ₂ O ₂ Cl ₄	46.0	C10H6Cls	36.0	C ₁₀ H ₆ Cl ₂
56.8	C ₄ HO ₂ Cl ₃	45.7	$C_4H_4O_2Cl_2$	34.9	C ₈ H ₄ O ₂ Cl ₂
56.7	C ₂ H ₃ Cl	45.7	C ₆ H ₈ OCl ₂	34.6	C ₆ H ₇ Cl
56.7	C ₄ H ₆ Cl ₂	45.7	C ₆ H ₁₂ Cl ₂	34.3	C7H4O8Cl2
56.7	C ₆ H ₉ Cl ₈	45.6	C ₇ H ₁₁ O ₂ Cl ₃	33.9	C ₃ HO ₂ Cl
56.0	C ₈ H ₈ O ₂ Cl ₈	45.2 45.2	C ₂ H ₈ OCl C ₄ H ₆ O ₂ Cl ₂	33.9	C ₄ H ₅ OCl
55.9	$C_2O_2Cl_2$	40.2	C4H6O2CI2	33.9	C ₅ H ₉ Cl
55.9	$C_8H_4OCl_2$	45.2	$C_6H_9O_8Cl_8$	33.9	C ₆ H ₂ O ₄ Cl ₂
55.8	$C_4H_8Cl_2$	45.1	C ₈ H ₇ Cl	33.6	C ₈ H ₁₂ O ₂ Cl ₂
55.6	$C_4H_5O_2Cl_8$	44.6	$C_4H_8O_2Cl_2$	33.6	$C_{10}H_{20}Cl_2$
55.1	C_2H_5Cl	44.6	C ₁₄ H ₈ Cl ₄	33.3	C ₂ H ₃ O ₂ Cl
55.0	$C_2H_2O_2Cl_2$	44.3	$C_{14}H_{10}Cl_4$	33.3	C ₄ H ₇ OCl
55.0	CaH6OCl2	44.0	C ₂ H ₅ OCl	33.3	C ₅ H ₁₁ Cl
55.0	C ₄ H ₇ O ₂ Cl ₃	44.0	C7H6Cl2	33.3	C10H6OCl2
54.7	C14H8Cl6	43.5	C ₆ H ₄ OCl ₂	33.3	C12H21O2Cla
54.6	$C_7H_2O_2Cl_4$	42.5	$C_4O_8Cl_2$	33.0	C6H8O4Cl2
54.4	$C_7H_5Cl_3$	42.0	$C_6H_6O_2Cl_2$	33.0	C7H12O8Cl2
54.2	$C_2H_4O_2Cl_2$	41.9	$C_7H_{14}Cl_2$	32.7	C ₃ H ₅ O ₂ Cl
53.9	$C_6H_8OCl_8$	41.6	$C_6H_{12}OCl_2$	32.7	C ₄ H ₉ OCl
52.5	$C_{10}H_8Cl_4$	41.6	$C_8H_8O_8Cl_8$	32.7	$C_8H_2O_8Cl_2$
51.8	$C_5H_6Cl_2$	41.5	C ₄ H ₄ O ₃ Cl ₂	32.1	C ₈ H ₇ O ₂ Cl
51.8	$C_bH_7O_2Cl_8$	41.5	$C_5H_8O_2Cl_2$	32.1	$C_8H_6O_8Cl_2$
51.3	C4H5O3Cl3	41.0	C4H3Cl	31.8	$C_{12}H_8Cl_2$
51.0	$C_bH_8Cl_2$	41.0	C ₄ H ₆ O ₈ Cl ₂	31.5	C ₆ H ₆ Cl
50.8	C7H8OCl3	40.5	C7H4OCl2	31.5	C ₉ H ₁₄ O ₂ Cl ₂
50.3	C ₃ H ₂ O ₂ Cl ₂	40.5 40.1	$C_8H_8Cl_2$ C_4H_5Cl	30.4	C ₆ H ₉ Cl
50.3	$C_4H_6OCl_2$	40.1	Canto	30.2	C ₈ H ₄ O ₄ Cl ₂
50.3	$C_{\delta}H_{10}Cl_{2}$	40.1	C ₆ H ₂ O ₂ Cl ₂	29.9	C ₅ H ₇ OCl
50.3	$C_6HO_2Cl_8$	40.1	C7H6OCl2	29.9	C ₆ H ₁₁ Cl
50.3	C7H5OCl3	39.6	C ₆ H ₄ O ₂ Cl ₂	29.9	C ₁₈ H ₁₀ Cl ₂
50.0	C ₁₄ H ₉ Cl ₅	39.6	C ₈ H ₁₂ Cl ₂	29.7	C ₁₀ H ₁₆ O ₂ Cl ₂
49.8	$C_6H_8O_2Cl_8$	39.2	C ₃ H ₃ OCl	29.6	$C_8H_{12}O_4Cl_2$
49.6	C ₃ H ₄ O ₂ Cl ₂	39.2	C ₄ H ₇ Cl	29.4	C4H6O2Cl
49.6	C4H8OCl2	38.7	C ₆ H ₈ O ₂ Cl ₂	29.4	C _t H _t OCl
49.6	C ₈ O ₈ CL	38.7	C ₈ H ₁₆ Cl ₂	29.4	C ₆ H ₁₈ Cl
48.6	C ₆ H ₉ O ₂ Cl ₃	38.3	C ₃ H ₄ OCl	28.9	C ₄ H ₇ O ₂ Cl
48.2	$C_6H_4Cl_2$	38.3	$C_4H_2O_4Cl_3$	28.9	C ₅ H ₁₁ OCl

%		%		%	
Chlorine	Formula	Chlorine	Formula	Chlorine	Formula
28.7	C14HaCl2	22.6	C ₈ H ₉ OCl	17.7	$C_{10}H_{13}O_2Cl$
28.5	C ₄ H ₉ O ₂ Cl	22.4	C ₂ H ₁₅ Cl	17.5	C ₁₈ H ₁₁ Cl
28.5	C14H10Cl2	22.1	C ₂ H ₁₇ Cl	17.3	C ₁₁ H ₂₁ OCl
28.3	C ₁₄ H ₁₂ Cl ₂	21.8	C ₇ H ₁₁ O ₂ Cl	17.3	C ₁₂ H ₂ OCl
28.2	C ₁₂ H ₈ OCl ₂	21.8	C ₈ H ₁₅ OCl	17.3	$C_{12}H_{25}Cl$
	0,422,0004	22.0	,		- 13 20
28.0	C_7H_7Cl	21.8	C ₉ H ₁₉ Cl	17.2	$C_8H_{11}O_4Cl$
27.6	C ₆ H ₆ OCl	21.8	C ₁₀ H ₇ Cl	17.2	$C_{11}H_7O_2Cl$
27.6	C7H9Cl	21.5	C ₆ H ₉ O ₃ Cl	16.4	C ₁₈ H ₉ OCl
27.2	$C_5H_8O_2Cl$	21.5	$C_7H_{13}O_2Cl$	16.2	$C_{12}H_{23}OCl$
27.1	C7H11Cl	21.5	C ₈ H ₁₇ OCl	16.2	$C_{18}H_{27}Cl$
26.8	C4HO2Cl	21.5	C ₂ H ₅ OCl	16.1	C ₁₂ H ₂₅ OCl
26.8	C ₁₄ H ₁₀ OCl ₂	21.3 21.3	C ₇ H ₁₆ O ₂ Cl	15.6	
26.7	C ₆ H ₉ OCl	21.3 21.3	C ₉ H ₇ OCl	15.4	
26.7 26.7	C ₇ H ₁₈ Cl	21.0 21.0	C ₉ H ₉ OCl	15.2	C ₁₃ H ₂₅ OCl
26.4	C ₅ H ₇ O ₂ Cl	21.0	C ₁₀ H ₁₈ Cl	15.2	C ₁₄ H ₂₉ Cl
20.2	Childon	21.0	ClottisCi	10.2	014112901
26.3	C ₆ H ₁₁ OCl	20.8	C ₈ H ₇ O ₂ Cl	15.1	$C_{11}H_{19}O_3Cl$
26.3	C7H15Cl	20.8	C ₂ H ₁₁ OCl	14.6	C ₁₄ H ₇ O ₂ Cl
26.0	C ₄ H ₅ O ₃ Cl	20.6	C7H5O3Cl	14.5	C14H0O2Cl
26.0	C ₅ H ₉ O ₂ Cl	20.5	$C_{10}H_{17}Cl$	14.4	$C_9H_5O_6Cl$
26.0	C ₆ H ₁₃ OCl	20.3	$C_{10}H_{19}Cl$	14.4	$\mathrm{C}_{14}\mathrm{H}_{11}\mathrm{O}_{2}\mathrm{Cl}$
25.6	C ₄ H ₇ O ₃ Cl	20.1	C ₉ H ₁₇ OCl	14.4	C ₁₄ H ₂₇ OCl
25.6	C ₈ H ₇ Cl	20.1	$C_{10}H_{21}Cl$	14.4	$C_{15}H_{31}Cl$
25.2	C7H5OCl	20.1	C ₁₁ H ₉ Cl	14.2	C14H29OCl
25.2	C ₈ H ₉ Cl	19.9	C ₆ H ₇ O ₄ Cl	13.6	C ₁₅ H ₂₉ OCl
25.2	$\mathrm{C_{14}H_{10}O_{2}Cl_{2}}$	19.9	$C_8H_{15}O_2Cl$	13.6	$C_{16}H_{83}Cl$
25.1	CaHaCl	19.8	C ₉ H ₁₉ OCl	12.9	C ₁₆ H ₃₁ OCl
24.9	C ₆ H ₈ O ₂ Cl	19.8	C ₁₀ H ₇ OCl	12.9	C ₁₇ H ₃₅ Cl
24.9	C ₇ H ₇ OCl	19.6	C ₈ H ₁₇ O ₂ Cl	12.8	C ₁₆ H ₂₅ OCl
24.5	C ₆ H ₅ O ₂ Cl	19.6	C ₂ H ₅ O ₂ Cl	12.7	C ₁₉ H ₁₅ Cl
24.5	C ₈ H ₁₈ Cl	19.4	C ₆ H ₁₁ O ₄ Cl	12.3	C ₁₇ H ₈₈ OCl
24.2	C7H11OCl	19.4	C ₈ H ₃ O ₈ Cl	12.3	$C_{18}H_{87}Cl$
24.2	C ₈ H ₁₈ Cl	19.4	C ₁₀ H ₁₁ OCl	12.2	$C_{10}H_{15}Cl$
23.9	C ₆ H ₉ O ₂ Cl	19.2	C ₈ H ₆ O ₈ Cl	11.8	C ₁₈ H ₃₈ OCl
23.9	C ₇ H ₁₈ OCl	19.2	C ₂ H ₂ O ₂ Cl	11.7	C ₁₈ H ₈₅ OCl
23.9	C ₈ H ₁₇ Cl	19.2	$C_{10}H_{13}OCl$	11.7	$C_{14}H_{13}Cl$
23.6	C ₄ H ₈ O ₄ Cl	19.0	C ₈ H ₇ O ₈ Cl	11.6	C ₁₈ H ₈₇ OCl
23.5	C ₅ H ₇ O ₈ Cl	18.8	$\mathbf{C_{12}H_{9}Cl}$		
23.5	$C_6H_{11}O_2Cl$	18.6	$C_{10}H_{19}OCl$		
23.5	C7H15OCl	18.6	$\mathbf{C_{11}H_{28}Cl}$		
23. 2	C ₆ H ₉ O ₃ Cl	18.6	$C_{11}H_7OCl$		
23.2	C ₆ H ₁₂ O ₂ Cl	18.5	C ₁₀ H ₄ O ₂ Cl ₂		
23.2	C ₂ H ₂ Cl	18.4	C ₁₀ H ₅ O ₂ Cl		
22.9	CaHrOCl	18.4	C ₁₀ H ₂₁ OCl		
22.9	C ₂ H ₁₁ Cl	18.2	C7H11O4Cl		
22.7	C7H5O2Cl	17.7	C ₈ H ₅ O ₄ Cl		
	- -		-		

III. INDEX OF EMPIRICAL FORMULAS ACCORDING TO MOLECULAR WEIGHTS

The empirical formulas for all groups of isomers listed in this book are represented below in increasing order of their molecular weights. Note that there are numerous instances in which this value is the same for several different formulas. An analogous list of empirical formulas arranged according to their percentage chlorine comprises Index II (page 1380).

To ascertain which specific compounds corresponding to a given formula are described in the text of this volume see the Empirical Formula Index (page 1359).

M.W.	Formula	M.W.	Formula	M.W.	Formula
50.5	CH ₂ Cl	113.0	C ₂ H ₆ Cl ₂	136.5	$C_4H_5O_3Cl$
60.5	C ₂ HCl	115.0	C ₂ H ₄ OCl ₂	136.6	C ₅ H ₉ O ₂ Cl
62.5	C ₂ H ₂ Cl	116.6	C_6H_9Cl	136.6	C ₆ H ₁₈ OCl
64.5	C ₂ H ₅ Cl	118.6	C ₅ H ₇ OCl	136.6	C ₈ H ₅ Cl
74.5	C_3H_3Cl	118.6	$C_0H_{11}Cl$	137.0	$C_5H_6Cl_2$
76.5	C_3H_5Cl	119.0	C_4Cl_2	138.6	C ₄ H ₇ O ₈ Cl
78.5	C_2H_3OCI	119.4	CHCl ₃	138.6	C_8H_7Cl
78.5	C_3H_7Cl	120.5	$C_4H_6O_2Cl$	139.0	$C_5H_8Cl_2$
80.5	C ₂ H ₅ OCl	120.6	C_bH_9OCl	140.6	C7H5OCl
84.9	$\mathrm{CH_2Cl_2}$	120.6	$C_6H_{18}Cl$	140.6	C_8H_9Cl
86.5	C_4H_3Cl	122.6	$C_4H_7O_2Cl$	141.0	$C_8H_2O_2Cl_2$
88. 5	C₄H₅Cl	122.6	$C_5H_{11}OCl$	141.0	$C_4H_6OCl_2$
90.5	C_3H_3OCl	123.0	$C_4H_4Cl_2$	141.0	$C_6H_{10}Cl_2$
90.6	C ₄ H ₇ Cl	124.1	C_3OCl_6	142.5	$C_6H_3O_2Cl$
92.5	C_3H_5OCl	124.6	$C_4H_9O_2Cl$	142.6	C7H7OCl
92.6	C ₄ H ₉ Cl	125.0	$C_4H_6Cl_2$	143.0	$C_3H_4O_2Cl_2$
94.5	$C_2H_3O_2Cl$	126.6	C_7H_7Cl	143.0	$C_4H_8OCl_2$
94.5	C ₃ H ₇ OCl	126.9	$C_2O_2Cl_2$	1 44 .6	$C_6H_6O_2Cl$
94.9	C_2Cl_2	127.0	$C_3H_4OCl_2$	144.6	$C_8H_{18}Cl$
97.0	$C_2H_2Cl_2$	127.0	$C_4H_8Cl_2$	145.4	C ₈ H ₈ Cl ₈
98.9	COCl ₂ `	128.6	C_6H_5OCl	146.6	C7H11OCl
99.0	$C_2H_4Cl_2$	128.6	C7H9Cl	146.7	$C_8H_{16}Cl$
102.6	C_bH_7Cl	128.9	$C_2H_2O_2Cl_2$	147.0	$C_6H_4Cl_2$
104.5	C_8HO_2Cl	129.0	$C_3H_6OCl_2$	147.4	C ₂ HOCl ₈
104.5	C ₄ H ₅ OCl	130.5	$\mathrm{C_5H_3O_2Cl}$	147.4	$C_8H_5Cl_8$
104.6	C_bH_9Cl	130.6	$C_7H_{11}Cl$	148.6	$C_6H_9O_2C_1$
106.5	$C_8H_8O_2Cl$	131.0	$C_2H_4O_2Cl_2$	148.6	$C_7H_{13}OCl$
106.6	C ₄ H ₇ OCl	131.4	C_2HCl_3	148.7	$C_8H_{17}Cl$
106.6	C ₆ H ₁₁ Cl	132.5	C_4HO_3C1	149.0	$C_6H_6Cl_2$
108.5	C ₈ H ₅ O ₂ Cl	132.6	C_6H_9OCl	149.4	$C_2H_3OCl_3$
108.6	C ₄ H ₉ OCl	132.6	$C_7H_{18}Cl$	150.5	C4H4O4Cl
110.5	C ₈ H ₇ O ₂ Cl	133.4	$C_2H_3Cl_3$	150.6	$C_5H_7O_3C_1$
111.0	C ₈ H ₄ Cl ₂	134.6	C ₅ H ₇ O ₂ Cl	150.6	C ₆ H ₁₁ O ₂ Cl
112.6	C_6H_6Cl	134.6	C ₆ H ₁₁ OCl	150.7	C7H15OCl
112.9	$C_2H_2OCl_2$	134.7	C7H16Cl	151.0	C ₆ H ₈ Cl ₂
			1383		

M.W.	Formula	M.W.	Formula	M.W.	Formula
152.6				191.1	
	C ₆ H ₉ O ₃ Cl	173.0	C ₄ H ₆ O ₈ Cl ₂		C ₈ H ₈ OCl ₂
152.6	$C_6H_{13}O_2Cl$	173.5	C ₆ H ₇ Cl ₈	191.5	C ₄ H ₅ O ₂ Cl ₃
152.6	C ₉ H ₉ Cl	174.7	$C_{10}H_{19}Cl$	191.6	C ₁₀ H ₄ O ₂ Cl ₂
153.0	$C_4H_2O_2Cl_2$	175.0	C7H4OCl2	191.9	C ₄ H ₂ Cl ₄
153.1	$C_6H_{10}Cl_2$	175.1	$C_8H_8Cl_2$	192.6	$C_{10}H_4O_2Cl$
153.8	CCl ₄	175.4	C ₈ HO ₂ Cl ₈	192.6	C ₁₀ H ₂₁ OCl
154.6	C ₈ H ₇ OCl	175.5	C ₄ H ₅ OCl ₅	193.5	C ₄ H ₇ O ₂ Cl ₂
154.6	C ₂ H ₁₁ Cl	175.5	C ₆ H ₉ Cl ₈	193.9	C ₂ OCl ₄
155.0	C ₄ H ₄ O ₂ Cl ₂	176.6	C11H ₀ Cl	193.9	C4H4Cl4
155.0	C _b H ₈ OCl ₂	176.7	C ₂ H ₁₇ OCl	194.6	C7H11O4Cl
200.0	092260012	21011	Oprilloor	101.0	C/IIICECI
155.1	$C_6H_{12}Cl_2$	176.7	$C_{10}H_{21}Cl$	195.5	C7H5Cl8
156.6	C7HsO2Cl	177.0	C ₆ H ₂ O ₂ Cl ₂	195.9	C ₂ H ₂ OCl ₄
156.6	C ₈ H ₉ OCl	177.0	C ₇ H ₆ OCl ₂	195.9	CaHaCla
157.0	C ₄ H ₆ O ₂ Cl ₂	177.4	C ₄ H ₈ O ₂ Cl ₈	197.1	C7H10O2Cl2
157.4	C ₄ H ₈ Cl ₈	177.5	C ₄ H ₇ OCl ₃	197.1	$C_9H_{18}Cl_2$
158.7	C ₂ H ₁₅ Cl	178.6	C ₆ H ₇ O ₄ Cl	197.1	C10H6Cl2
159.0	C ₄ H ₈ O ₂ Cl ₂	178.6	C ₁₀ H ₇ OCl	197.5	C ₆ H ₂ OCl ₂
159.5	C4H5Cl3	178.7	C ₈ H ₁₅ O ₂ Cl	197.8	C ₂ O ₂ Cl ₄
160.7	C ₉ H ₁₇ Cl	178.7	C ₉ H ₁₉ OCl	197.9	C ₈ H ₄ OCl ₄
161.0	$C_7H_6Cl_2$	179.0	$C_6H_4O_2Cl_2$	200.6	C ₈ H ₅ O ₄ Cl
161.4	CaHaOCla	179.1	CaH12Cl2	200.7	C10H12O2Cl
161.5	C ₄ H ₇ Cl ₃	179.9	C ₂ H ₂ Cl ₄	202.3	C ₂ HCl ₅
162.6	C ₇ H ₁₁ O ₂ Cl	180.6	C ₂ H ₅ O ₂ Cl	202.7	C ₁₈ H ₁₁ Cl
162.6	C ₁₀ H ₇ Cl	180.7	C ₈ H ₁₇ O ₂ Cl	203.0	$C_8H_4O_2Cl_2$
162.7	C ₈ H ₁₈ OCl	181.5	$C_6H_3Cl_3$	204.7	$C_{11}H_{21}OCl$
162.7	C ₉ H ₁₉ Cl	181.8	C2OCl4	204.7	C ₁₂ H ₉ OCl
163.0	C ₆ H ₄ OCl ₂	181.9	C ₂ H ₄ Cl ₄	204.8	C ₁₂ H ₂₅ Cl
163.4	C ₂ HO ₂ Cl ₃	182.6	C ₆ H ₁₁ O ₄ Cl	205.5	
163.4	CaH6OCla	182.6	C ₈ H ₈ O ₈ Cl		C ₆ H ₇ O ₂ Cl ₈
164.6	C ₆ H ₉ O ₈ Cl	182.6	C ₁₀ H ₁₁ OCl	206.6	C ₈ H ₁₁ O ₄ Cl
104.0	Cenaca	182.0	Cioniioci	206.6	$C_{11}H_7O_2Cl$
164.6	$C_7H_{18}O_2Cl$	183.0	C ₆ H ₈ O ₂ Cl ₂	207.0	C7H4O3Cl2
164.6	C ₉ H ₆ OCl	183.1	C ₈ H ₁₆ Cl ₂	207.5	C ₄ H ₅ O ₂ Cl ₂
164.7	C ₆ H ₁₇ OCl	183.5	C ₆ H ₅ Cl ₈	209.0	C ₆ H ₂ O ₄ Cl ₂
165.4	C ₂ H ₂ O ₂ Cl ₂	184.6	CaHaOaCl	209.5	
165.8		184.6	C ₀ H ₀ O ₂ Cl		C7H2OCl3
100.8	C ₂ Cl ₄	104.0	Childosol	209.9	C ₅ H ₈ Cl ₄
166.6	C _p H ₇ OCl	184.7	C ₁₀ H ₁₂ OCl	211.1	CaH12O2Cl2
166.7	C ₇ H ₁₆ O ₂ Cl	185.0	C ₄ H ₂ O ₄ Cl ₂	211.2	C ₁₀ H ₂₀ Cl ₂
167.0	C ₄ O ₂ Cl ₂	185.5	C ₆ H ₇ Cl ₈	211.4	C ₆ HO ₂ Cl ₂
167.9	C ₂ H ₂ CL	186.6	C ₈ H ₇ O ₈ Cl	211.4	
168.6	C ₂ H ₂ OCl	187.0	C ₄ H ₄ O ₄ Cl ₂		C7H5OCl
108.0	Carracti	167.0	C4114O4C12	211.9	C ₈ H ₂ O ₂ Cl ₄
168.7	C ₁₀ H ₁₈ Cl	187.0	C ₅ H ₈ O ₂ Cl ₂	213.1	C ₁₀ H ₆ OCl ₂
169.0	C ₆ H ₆ O ₂ Cl ₂	187.1	C ₆ H ₁₂ O ₂ Cl ₂	213.5	· CaHaO2Cla
169.1	C7H14Cl2	187.4	C ₄ HO ₂ Cl ₂	214.3	CaHCla
170.6	C ₈ H ₇ O ₂ Cl	187.5	C ₆ H ₉ Cl ₂	215.0	C ₆ H ₈ O ₄ Cl ₂
170.6	C ₂ H ₁₁ OCl	188.7	C ₁₂ H ₉ Cl	215.0 215.1	C ₇ H ₁₂ O ₈ Cl ₂
110.0	Chritocr	10011	CHARLOT	210.1	∪71112∪8∪12
171.0	C4H4O2Cl2	189.0	C ₈ H ₆ OCl ₂	215.9	C ₆ H ₂ Cl ₄
171.0	C ₅ H ₈ O ₂ Cl ₂	190.6	C ₁₁ H ₇ OCl	216.3	CaHaCla
171.1	C ₆ H ₁₂ OCl ₂	190.7	C ₁₀ H ₁₉ OCl	216.7	CuH,OCl
172.6	C7H4O4Cl	190.8	C ₁₁ H ₂₂ Cl	216.7	C ₁₄ H ₁₈ Cl
172.7	C ₁₀ H ₁₇ Cl	191.0	C7H4O2Cl2	217.0	C ₈ H ₂ O ₈ Cl ₂
~	-Marel Co		-,,,	~21.0	

M.W.	Formula	M.W.	Formula .	M.W.	Formula
218.8	C ₁₂ H ₂₂ OCl	244.4	C ₈ H ₇ Cl ₈	285.6	C14H11Cla
218.8	C18H27Cl	244.6	C ₆ H ₆ O ₆ Cl	285.9	C ₈ O ₂ Cl ₄
219.5	CaHaO2Cla	244.7	C14H9O2Cl	288.9	C ₁₇ H ₂₂ OCl
219.9	C ₆ H ₆ Cl ₄	245.9	CaO2Cl4	288.9	C ₁₈ H _{a7} Cl
220.8	C ₁₂ H ₂₅ OCl	246.3	C ₂ HO ₂ Cl ₅	290.8	CeHeCle
220.0	Claristoci	2/20.0	CSTICSCIP	200.0	Cerrecie
221.0	$C_8H_6O_8Cl_2$	246.7	$C_{14}H_{11}O_{2}Cl$	290.8	$C_{20}H_{15}Cl$
221.5	$C_bH_7O_aCl_a$	246.8	C14H27OCl	294.4	C7HO2Cls
221.5	CaH11O2Cla	246.9	CisHs1Cl	296.8	CzOzCla
221.9	C ₄ O ₂ Cl ₄	247.1	C14H8Cl2	298.8	C7H2Cl6
223.1	C ₁₂ H ₈ Cl ₂	247.9	C ₆ H ₂ O ₂ Cl ₄	299.3	C ₄ H _a Cl ₇
	Olimbor.		-1-1-1-1		04-40-,
223.5	$C_8H_5OCl_8$	248.8	C ₈ Cl ₆	300.8	C ₆ OCl ₆
223.9	$C_4H_2O_2Cl_4$	248.8	C ₁₄ H ₂₉ OCl	300.9	C ₁₈ H ₂₈ OCl
224.0	C ₆ H ₁₀ Cl ₄	249.1	$C_{14}H_{10}Cl_2$	302.9	C ₁₈ H ₈₅ OCl
225.1	CoH14O2Cla	250.4	CaHCla	303.9	C ₈ H ₂ O ₄ Cl ₄
225.4	C ₇ H ₈ O ₂ Cl ₈	250.8	CaH ₂ Cl ₄	304.9	C ₁₈ H ₈₇ OCl
	0,200				-10
225.5	C ₈ H ₇ OCl ₈	251.1	$C_{12}H_8OCl_2$	308.8	C ₄ O ₃ Cl ₆
225.9	$C_4H_4O_2Cl_4$	251.2	$C_{14}H_{12}Cl_2$	312.8	C7OCl6
226.3	C ₄ HCl ₅	255.5	$C_8H_5O_8Cl_8$	316.8	$C_6O_2Cl_6$
226.7	CaH15O5Cl	258.4	C ₆ H ₉ Cl ₅	318.0	$C_{14}H_8Cl_4$
228.4	C ₄ H ₈ Cl ₅	259.9	$C_7H_2O_2Cl_4$	319.7	C ₂ Cl ₃
229.5	$C_6H_3O_5Cl_3$	260.8	C ₄ Cl ₆	319.7	$C_{12}H_{21}O_{3}Cl_{3}$
230.0	C7H4Cl4	260.8	$C_{15}H_{29}OCl$	320.1	$C_{14}H_{10}Cl_4$
230.3	CaHOCla	260.9	$C_{16}H_{33}Cl$	322.8	CaH2OaCla
230.4	C ₄ H ₅ Cl ₅	262.8	C ₄ H ₂ Cl ₆	333.3	C ₇ HCl ₇
230.7	C ₁₄ H ₁₁ OCl	264.4	C7H4Cl4	333.8	C ₄ H ₂ Cl ₈
231.5	$C_{10}H_5Cl_8$	264.8	$C_4H_4Cl_6$	343.7	C_5Cl_8
231.9	$C_6H_2OCl_4$	265.1	$C_{14}H_{10}OCl_2$	349.8	C ₄ H ₂ OCl ₈
232.8	C12H26OCl	266.4	C_6HOCl_5	354.5	C14H0Cls
232.8	C14H29Cl	270.0	C10H8CL	388.9	C14H8Cls
233.5	C7H11O2Cl3	274.9	C ₁₆ H ₃₁ OCl	403.8	C10Cla
200.0	0,1,-1,-0			418.6	C ₄ OCl ₁₀
234.7	C11H10O2Cl	274.9	C17HaaCl		
235.0	CaH4O4Cla	276.8	C ₄ OCl ₆		
235.5	C ₆ H ₉ O ₂ Cl ₂	276.9	C ₁₆ H ₃₅ OCl		
236.8	C ₂ Cl ₆	278.4	C ₇ HOCl ₆		
237.1	C ₁₃ H ₁₀ Cl ₂	278.8	C ₁₉ H ₁₅ Cl		
401.1	○1311 10○13	210.0	Clarifor		
236.1	C10H16O2Cl2	280.8	$C_8O_2Cl_6$		
239.9	C ₄ H ₂ O ₂ Cl ₄	281.1	C14H10O2Cl2		
242.7	C ₁₄ H ₇ O ₂ Cl	283.6	C ₁₄ H ₉ Cl ₂		
243.1	C ₈ H ₁₂ O ₄ Cl ₂	284.8	CoClo		
243.1	C ₇ H ₂ OCl ₄	285.2	CaHCl7		
240.V	O7112004	200.2	Observe!		

IV. INDEX OF COMPOUNDS ACCORDING TO CHEMICAL TYPES

The numerous individual compounds of Order III whose preparation, properties, and reactions comprise the main text of this book are there listed in progressively increasing order of melting points (Division A, Solids), boiling points (Division B, Liquids), or empirical formulas (Division C, liquids for which data at ordinary pressure are not available). Unlike the treatment of Order I in an earlier volume, the compounds of the present Order III are not subdivided into genera. For this reason a highly useful feature of this volume is the following Chemical Type Index in which each compound is listed in one (or more) of the following eight arbitrary units.

- UNIT 1. Chloro substitution products of saturated acyclic hydrocarbons.
- Unit 2. Chloro substitution products of unsaturated acyclic hydrocarbons.
- Unit 3. Chloro substitution products of cyclic hydrocarbons.
- Unit 4. Chloro substitution products of hydroxy compounds.
- Unit 5. Chlorosubstitution products (and their relatives) of carbonyl compounds.
- Unit 6. Chloro substitution products of carboxylic acids and anhydrides.
- UNIT 7. Acyl chlorides.
- UNIT 8. Chlorine substitution products of ethers and of esters.

In order to facilitate recognition of the extent of subdivision of the above eight *units*, a brief summary of the subclassification is placed at the head of each one. Note that the names employed in this index are those best suited to recognition of the chemical relationships involved, and are not necessarily the same as those selected as principal names in the individual descriptions in the text.

Attention is also called to the fact that, in addition to this chemical type index, this volume is provided with conventional alphabetical name index and with empirical formula index.

UNIT 1. CHLORO SUBSTITUTION PRODUCTS OF ACYCLIC SATURATED HYDROCARBONS

(Summary of Classification of Unit 1)

- A. Monochloro Derivatives.
 - 1. With primary halogen.
 - 2. With secondary halogen.
 - 3. With tertiary halogen.

B. DICHLORO DERIVATIVES.

- 1. With both chlorine atoms primary.
 - a. Both chlorine atoms on same carbon.
 - b. The two chlorine atoms on different carbons.
- 2. With both chlorine atoms secondary.
 - a. Both chlorine atoms on same carbon.
 - b. Both chlorine atoms on different carbons.
- 3. With both chlorine atoms tertiary.
- 4. With one chlorine primary and one secondary.
- 5. With one chlorine primary and one tertiary.
- 6. With one chlorine secondary and one tertiary.

C. TRICHLORO DERIVATIVES.

- 1. With all three chlorine atoms primary.
- 2. With two chlorine atoms primary and one secondary.
- 3. With two chlorine atoms primary and one tertiary.
- 4. With one chlorine atom primary and two secondary.
- 5. With one chlorine each primary, secondary, and tertiary.
- 6. With all three chlorine atoms secondary.
- 7. With two chlorine atoms secondary and one tertiary.

D. TETRACHLORO DERIVATIVES.

- 1. With all four chlorine atoms primary.
- 2. With three chlorine atoms primary and one secondary.
- 3. With two chlorine atoms primary and two secondary.
- 4. With one chlorine atom primary and three secondary.
- 5. With three chlorine atoms primary and one tertiary.
- 6. With two chlorine atoms primary, one secondary, and one tertiary.

E. PENTACHLORO DERIVATIVES.

- 1. With all five chlorine atoms primary.
- 2. With four chlorine atoms primary and one secondary.
- 3. With three chlorine atoms primary and two secondary.
- 4. With two chlorine atoms primary and three secondary.
- 5. With four chlorine atoms primary and one tertiary.

F. HEXACHLORO DERIVATIVES.

- 1. With all six chlorine atoms primary.
- 2. With five chlorine atoms primary and one secondary.
- 3. With four chlorine atoms primary and two secondary.
- G. HEPTACHLORO DERIVATIVES.
- H. OCTACHLORO DERIVATIVES.

UNIT 1. CHLORO SUBSTITUTION PRODUCTS OF SATURATED ACYCLIC HYDROCARBONS

	oro Derivatives primary halogen		C ₅ H ₉ Cl Contd.	Isoamyl chloride Neopentyl chloride	3:7365 3:7200
CH ₈ Cl	Methyl chloride	3:7005	$C_6H_{13}Cl$	1-Chlorohexane	3:7955
C_2H_5Cl	Ethyl chloride	3:7015		1-Chloro-2-methyl-	
C ₈ H ₇ Cl	n-Propyl chloride	3:7040		pentane 5-Chloro-2-methyl-	3:7563
C ₄ H ₉ Cl	n-Butyl chloride Isobutyl chloride			pentane 1-Chloro-3-methyl-	3:7695
C ₆ H ₉ Cl	n-Amyl chloride	3:7460		pentane	3:9348
	secButylcarbinyl chloride	3:7345		1-Chloro-2-ethyl- butane	3:7720

C ₆ H ₁₈ Cl Contd.	1-Chloro-2,2-di- methylbutane 4-Chloro-2,2-di-	3:7590	C ₆ H ₁₃ Cl Contd.	3-Chloro-2-methyl- pentane 4-Chloro-2-methyl-	3:7565
	methylbutane	3:7555		pentane	3:7495
C7H15Cl	1-Chloroheptane	3:8250		2-Chloro-3-methyl pentane	3:9359
	1-Chloro-3-methyl- hexane	3:8155		3-Chloro-2,2-di- methylbutane	3:7475
	5-Chloro-2,3-di- methylpentane	3:8153	C7H15Cl	2-Chloroheptane	3:9432
C ₈ H ₁₇ Cl	1-Chloro-octane	3:8585		3-Chloroheptane	3:8080 3:8095
	1-Chloro-2-ethyl- hexane 1-Chloro-3-ethyl-	3:8370		5-Chloro-2-methyl- hexane	8:7985
	hexane	3:9552		2-Chloro-3-methyl- hexane	3:9434
	1-Chloro-2-ethyl-3- methylpentane	3:9560		4-Chloro-3-methyl- hexane	3:9436
	1-Chloro-2,2,3,3-tetra- methylbutane	3:0945		2-Chloro-3-ethyl- pentane	3:9438
$C_9H_{19}Cl$	1-Chlorononane	3:8719		4-Chloro-2,2-di-	3:9440
$C_{10}H_{31}Cl$	1-Chlorodecane	3:8785	C H C	methylpentane	
	1-Chloro-3,7-di- methyloctane	3:9740	C ₈ H ₁₇ Cl	2-Chloro-octane	3:8378 3:9538
C ₁₁ H ₂₈ Cl	1-Chloroundecane	3:8803		6-Chloro-2-methyl- heptane	3:9540
$C_{12}H_{25}Cl$	1-Chlorododecane	3:8810		3-Chloro-4-methyl-	3:9548
C18H27Cl	$1\text{-}Chlorotridecane\dots$	3:9859		heptane	9:3020
$\mathrm{C}_{14}\mathrm{H}_{29}\mathrm{Cl}$	1-Chlorotetradecane	3:9874		2-Chloro-3,4-di- methylhexane	3:9558
$C_{15}H_{31}Cl$	1-Chloropentadecane .	3:9890	$C_9H_{19}Cl$	2-Chlorononane	3:8635
$\mathbf{C}_{16}\mathbf{H}_{88}\mathbf{Cl}$	1-Chlorohexadecane	3:0015		3-Chlorononane 5-Chlorononane	3:9638 3:9640
$C_{17}H_{85}Cl$	1-Chloroheptadecane .	3:0100	3. With	tertiary halogen	
C ₁₈ H ₈₇ Cl	1-Chloro-octadecane	3:9095	C ₄ H ₉ Cl	ter-Butyl chloride	3:7045
9. With	secondary halogen		$C_8H_{11}Cl$	ter-Amyl chloride	3:7220
C ₂ H ₇ Cl	2-Chloropropane	3:7025	$C_6H_{18}Cl$	2-Chloro-2-methyl- pentane	3:7 490
C ₄ H ₉ Cl	2-Chlorobutane	3:7125		3-Chloro-3-methyl-	V.120V
C ₅ H ₁₁ Cl	2-Chloropentane	3:7325		pentane	3:7585
	3-Chloropentane	3:7330		2-Chloro-2,3-di- methylbutane	3:7600
	8-Chloro-2-methyl- butane	8:7275	C7H18Cl	2-Chloro-2-methyl-	
C ₆ H ₁₃ Cl	2-Chlorohexane	3:7715 3:7676		hexane	3:7945 3:7950
					_

C7H18Cl Contd.	3-Chloro-3-ethyl- pentane	3:8055	C ₁₀ H ₂₁ Cl Contd.	4-Chloro-4-ethyl- octane	3:9736
	2-Chloro-2,3-di- methylpentane 3-Chloro-2,3-di-	.3:9442		3-Chloro-2,3-di- methyloctane	3:9738
	methylpentane 2-Chloro-2,4-di- methylpentane	3:7970 3:7750		4-Chloro-4-n-propyl- heptane	3:9742
	3-Chloro-2,2,3-tri- methylbutane	3:4020	B. Dichlore	4-Chloro-2,4,6-tri- methylheptane	3:9744
$C_8H_{17}Cl$	2-Chloro-2-methyl-	9.0100		both chlorine atoms prim	erv
	heptane	3:8100		th chlorine atoms on sam	-
	heptane4-Chloro-4-methyl-	3:95 44	CH_2Cl_2	Methylene dichloride .	3:5020
	heptane	3:9550	$C_2H_4Cl_2$	1,1-Dichloroethane	3:5035
	3-Chloro-3-ethyl- hexane	3:8 ^{nna}	$\mathrm{C_{8}H_{6}Cl_{2}}$	1,1-Dichloropropane	3:7230
		•••	$C_4H_8Cl_2$	1,1-Dichlorobutane	3:7550
	3-Chloro-2,3-di- methylhexane 2-Chloro-2,5-di	3:9554		1,1-Dichloro-2-methyl-	0.7407
	methylhexane	3:9556		propane	3:7425
	3-Chloro-3-ethyl-2-		$C_6H_{10}Cl_2$	1,1-Dichloropentane	3:8015
	methylpentane	3:8210		4,4-Dichloro-2-methyl- butane	3:7885
	4-Chloro-2,2,4-tri- methylpentane	3:8113	$C_7H_{14}Cl_2$	1,1-Dichloroheptane	3:8650
$C_9H_{19}Cl$	3-Chloro-3-methyl- octane	3:9642	b. The	two chlorine atoms on	different
	4-Chloro-4-methyl- octane	3:9644	$C_2H_4Cl_2$	1,2-Dichloroethane	3:5130
	3-Chloro-3-ethyl-	010011	$C_8H_6Cl_2$	1,3-Dichloropropane	3:5 450
	heptane 4-Chloro-4-ethyl-	3:9646	$C_4H_8Cl_2$	1,4-Dichlorobutane	3:5835
	heptane	3:9648		1,3-Dichloro-2-methyl- propane	3:7960
	3-Chloro-2,3-di- methylheptane 5-Chloro-2,5-di-	3:9650	C ₅ H ₁₀ Cl ₂	1,5-Dichloropentane	3:8575
	methylheptane	3:9652		1,4-Dichloro-2-methyl- butane	3:8360
	3-Chloro-2,2,3-tri- methylhexane	3:9654	C ₆ H ₁₂ Cl ₂	1,6-Dichlorohexane	3:8720
	3-Chloro-2,2-di- methyl-3-ethyl-		$C_7H_{14}Cl_2$	1,7-Dichloroheptane	3:9422
0 H 0	pentane	3:9656		1,5-Dichloro-3,3- dimethylpentane	3:9430
C ₁₀ H ₄₁ Cl	4-Chloro-4-methyl- nonane	3:9730	O TT 61		
	5-Chloro-5-methyl- nonane	3:9732	C ₈ H ₁₆ Cl ₂	1,8-Dichloro-octane	3:8895
	3-Chloro-3-ethyl-	J. W. 1916	$C_9H_{18}Cl_2$	1,9-Dichlorononane	3:8880
	octane	3:9734	C10H20Cl2	1,10-Dichlorodecane	3:9720

2. Wit	h both chlorine atoms sec	ondary	$\mathrm{C_{10}H_{20}Cl_2}$	2,7-Dichloro-2,7-	
a. I	Both chlorine atoms on sam	e carbon		dimethyloctane 3,4-Dichloro-3,4-	3:0840
$C_3H_6Cl_2$	2,2-Dichloropropane	3:7140		dimethylhexane	3:9724
C ₄ H ₈ Cl ₂	2,2-Dichlorobutane	3:7415		h one chlorine primary ndary	and one
$C_bH_{10}Cl_2$	2,2-Dichloropentane 3,3-Dichloropentane	3:7755 3:7895	$\mathrm{C_3H_6Cl_2}$	1,2-Dichloropropane	3:5200
	3,3-Dichloro-2-		$\mathrm{C_4H_8Cl_2}$	1,2-Dichlorobutane 1,3-Dichlorobutane	3:7680 3:7925
C.T	methylbutane	3:9230	$\mathrm{C_{b}H_{10}Cl_{2}}$	1,2-Dichloropentane 1,3-Dichloropentane	3:8140 3:9220
C ₆ H ₁₂ Cl ₂	2,2-Dichlorohexane	3:9342		1,4-Dichloropentane	3:9224
	3,3-Dichloro-2,2- dimethylbutane 4,4-Dichloro-2,2-	3:4325		1,3-Dichloro-2-methyl- butane	3:9228
	dimethylbutane .	3:8132		3,4-Dichloro-2-methyl- butane	3:8075
C7H14Cl2	2,2-Dichloroheptane 4,4-Dichloroheptane	3:9424 3:9426	$\mathrm{C_6H_{12}Cl_2}$	1,2-Dichlorohexane	3:8380 3:9340
	3,3-Dichloro-2,4-di- methylpentane	3:7610	$C_7H_{14}Cl_2$	1,2-Dichloroheptane	3:9420
C ₈ H ₁₆ Cl ₂	2,2-Dichloro-octane	3:8670		1,2-Dichloro-4,4- dimethylpentane	3:8516
	3,3-Dichloro-2,2,4- trimethylpentane	3:9536	$\mathrm{C_8H_{16}Cl_2}$	1,6-Dichloro-octane 1,7-Dichloro-octane	3:9530 3:9532
b. Bo	th chlorine atoms on $diffe$	rent car-		4-Chloro-3-(chloro- methyl)heptane	3:9534
C ₄ H ₈ Cl ₂	d,l-2,3-Dichloro- butane	3:7615	$C_9H_{18}Cl_2$	1,2-Dichlorononane	3:9632
	meso-2,3-Dichloro- butane	3:7580		one chlorine primary	and one
C ₅ H ₁₀ Cl ₂	2,3-Dichloropentane 2,4-Dichloropentane.	3:8010 3:8120	tertis C ₄ H ₈ Cl ₂	1,2-Dichloro-2- methylpropane	3:7430
C ₆ H ₁₂ Cl ₂	2,3-Dichlorohexane	3:8300 3:8525	$\mathrm{C_{5}H_{10}Cl_{2}}$	1,2-Dichloro-2- methylbutane 2,4-Dichloro-2-	3:7920
	3,4-Dichlorohexane.	3:9344		methylbutane	3:8105
	h both chlorine atoms tert	iary	$\mathbf{C_6H_{12}Cl_2}$	2,5-Dichloro-2- methylpentane	3:8540
C ₆ H ₁₂ Cl ₂	2,3-Dichloro-2,3- dimethylbutane	3:4520	6. With tertia	one chlorine secondary	and one
C7H14Cl2	2,4-Dichloro-2,4- dimethylpentane	3:9428	$\mathrm{C_{5}H_{10}Cl_{2}}$	2,3-Dichloro-2- methylbutane	3:7975
C ₈ H ₁₆ Cl ₂	2,5-Dichloro-2,5- dimethylhexane	3:1550	$\mathrm{C_6H_{12}Cl_2}$	2,3-Dichloro-2- methylpentane	3:9346
	3,4-Dichloro-3,4-	3:8315			u . 4020
	dimethylhexane	0.0010		o Derivatives	_
$C_9H_{18}Cl_2$	2,6-Dichloro-2,6-	0.0622		all three chlorine atoms	
	dimethylheptane	3:0455	CHCla	Chloroform	2 · KAKA

$C_2H_3Cl_3$	1,1,1-Trichlorethane 1,1,2-Trichloroethane.	3:5085 3:5330		th three chlorine atoms prints	nary and
$C_8H_5Cl_8$	1,1,1-Trichloropropane 1,1,3-Trichloropropane	3:527 0 3:5660	C ₂ H ₄ Cl ₄	1,1,1,2-Tetrachloro- propane 1,1,2,3-Tetrachloro-	3:5785
C ₅ H ₉ Cl ₃	4,4,4-Trichloro-2- methylbutane	3:9216	C ₄ H ₆ Cl ₄	propane	3:60 35
	two chlorine atoms prin	nary and		butane	3:5622
$\mathrm{C_8H_5Cl_3}$	1,1,2-Trichloropropane 1,2,3-Trichloropropane	3:5630 3:5840		h two chlorine atoms prim secondary	ary and
C ₄ H ₇ Cl ₃	1,1,3-Trichlorobutane.	3:9086	C ₈ H ₄ Cl ₄	1,1,2,2-Tetrachloro- propane 1,2,2,3-Tetrachloro-	3:5825
C ₅ H ₉ Cl ₈	1,3-Dichloro-2-(chloro- methyl)butane	3:9218	CHC	propane	3:5895
	two chlorine atoms primertiary 1,1,2-Trichloro-2-	ary and	C ₄ H ₆ Cl ₄	1,2,3,4-Tetrachloro- butane (solid isomer) (liquid isomer)	3:1760 3:9082
Ogra / Old	methylpropane 1,2,3-Trichloro-2- methylpropane	3:5710 3:5885	$C_6H_{10}Cl_4$	1,1,2,2-Tetrachloro- hexane	3:9332
	one chlorine atom prim	ary and		h one chlorine atom primi e secondary	ry and
$\mathrm{C_3H_5Cl_3}$	1,2,2-Trichloropropane	3:5475	$C_4H_6Cl_4$	1,2,2,3-Tetrachloro- butane	3:90 78
$C_4H_7Cl_3$	1,2,3-Trichlorobutane.	3:5935		1,2,3,3-Tetrachloro- butane	3:9080
secor	one chlorine each	primary,		h three chlorine atoms prime tertiary	ary and
$\mathrm{C_{5}H_{9}Cl_{3}}$	1,2,3-Trichloro-2- methylbutane	3:6100	C ₄ H ₆ Cl ₄	1,1,1,2-Tetrachloro-2- methylpropane	3:4725
C ₄ H ₇ Cl ₃	all three chlorine atoms so 2,2,3-Trichlorobutane. two chlorine atoms so	3:5680		1,1,2,3-Tetrachloro-2-	3:6165
	one tertiary 2.3.3-Trichloro-2-				3:6335
	methylbutane	3:4755		h two chlorine atoms prima ndary, and one tertiary	ry, one
	loro Derivatives all four chlorine atoms	neimaev	$C_5H_8Cl_4$	1,2,3-Trichloro-2-	
CC4	Carbon tetrachloride .	3:5100		(chloromethyl)- butane	3:52 30
C ₂ H ₂ Cl ₄	1,1,1,2-Tetrachloro- ethane.	3:5555		nloro Derivatives	_
	1,1,2,2-Tetrachloro- ethane	3:5750		h all five chlorine atoms 1	
C4H6Cl4	1,1,3-Trichloro-2-	3.3.00	C₂HCl₅ 2. Witi	Pentachloroethane	3:5880 cv and
	(chloromethyl)- propane	3:9084		secondary 1,1,1,2,3-Pentachloro-	
C ₅ H ₈ Cl ₄	1,3-Dichloro-2,2-bis- (chloromethyl)- propane	3:2657	√3113 €15	propane 1,1,2,3,3-Pentachloro-	3 : 4740 3 : 6280
	-				

3. With three chlorine atoms printed two secondary	mary and		h four chlorine atoms primary and secondary
C ₄ H ₅ Cl ₅ 1,1,2,3,4-Pentachloro- butane (solid isomer)	3:0750	$C_8H_2Cl_6$	1,1,2,2,3,3-Hexachloro- propane 3:6525
(liquid isomer) CaHrCla 3.3.4.4.4-Pentachloro-	3:996 8	$C_4H_4Cl_6$	1,1,2,3,4,4-Hexachloro- butane 3:3155
2-methylbutane	3:6725	G Wante	chloro Derivatives
C ₆ H ₉ Cl ₅ 1,1,1,2,2-Pentachloro-			
hexane			h six chlorine atoms primary and secondary
4. With two chlorine atoms print three secondary	mary and	C ₈ HCl ₇	1,1,1,2,3,3,3-Hepta- chloropropane 3:6860
C ₄ H ₅ Cl ₅ 1,2,2,3,4-Pentachloro-			cmoropropane •.•o••
butane	3:9070	2. Wit	h five chlorine atoms primary and
5. With four chlorine atoms prin	marv and		secondary
one tertiary		CaHCl7	1,1,1,2,2,3,3-Hepta-
C ₄ H ₅ Cl ₅ 1,1,1,2,3-Pentachloro- 2-methylpropane	3:1265	Oglicia	chloropropane 3:0200
1,1,2,3-Tetrachloro-2- (chloromethyl)- propane,	3:9072		h four chlorine atoms primary and e secondary
F. Hexachloro Derivatives		C ₄ H ₃ Cl ₇	1,1,2,2,3,4,4-Hepta- chlorobutane 3:9056
1. With all six chlorine atoms p	rimary		
C ₂ Cl ₅ Hexachloroethane	3:4835	H. Octach	loro Derivatives
2. With five chlorine atoms print two secondary	nary and	C_8Cl_8	Octachloropropane 3:4450
C ₈ H ₂ Cl ₆ 1,1,1,2,3,3-Hexachlo- ropropane	3:6460	C ₄ H ₂ Cl ₈	1,1,2,2,3,3,4,4-Octa- chlorobutane 3:200

UNIT 2. CHLORO SUBSTITUTION PRODUCTS OF UNSATURATED ACYCLIC HYDROCARBONS

(Summary of Classification of Unit 2)

A. OF MONO-OLEFINS.

- 1. With one chlorine on C attached to unsaturation.
 - a. This chlorine atom is primary.
 - aı Monochloro.
 - a₂ Dichloro.
 - as Polychloro.
 - b. This chlorine atom is secondary.
 - b₁ Monochloro.
 - b₂ Dichloro.
 - ba Polychloro.
- 2. With two chlorine atoms on C attached to unsaturation.
 - a. Both these chlorines are on same C atom.
 - b. These two chlorines are on different carbons.
- 3. With none of the chlorine atoms on C attached to unsaturation.
 - a. Monochloro.
 - b. Dichloro.
 - c. Polychloro.

- B. OF DIOLEFINS.

 - With "cumulative" unsaturation.
 With "conjugated" unsaturation.
 - a. C4 series.
 - b. C₅ series. c. C6 series.
 - d. Cs series.
 - 3. With "isolated" unsaturation.
- C. OF TRIOLEFINS.
- D. OF TETRAOLEFINS.
- E. OF ALKYNES.
 - 1. With chlorine attached to C also bearing triple bond.
 - a. Monochloro.
 - b. Dichloro.
 - 2. With chlorine (s) attached to some C other than that bearing triple bond.
 - a. Monochloro.
 - a₁ Chlorine is primary.
 - a₂ Chlorine is tertiary.
 - b. Dichloro.
- F. OF ALKADI-YNES.
- G. OF ALKENYNES.

UNIT 2. CHLORO SUBSTITUTION PRODUCTS OF UNSATURATED ACYCLIC HYDROCARBONS

A. Of M	ono-olefins		$C_4H_6Cl_2$	1,3-Dichlorobutene-1.	3:7650
 1. With one chlorine on C attached to unsaturation a. This chlorine atom is primary 				1,3-Dichloro-2-methyl- propene-1	3:5590
	81 MONOCHLORO			as POLYCHLORO	
C ₂ H ₃ Cl	Vinyl chloride	3:7010	$C_4H_5Cl_8$	1,3-Dichloro-2-(chloro-	
C_8H_5Cl	1-Chloropropene-1	3:7030		methyl)propene-1	3:9066
C ₄ H ₇ Cl	1-Chlorobutene-1	3:7110	C ₄ H ₄ Cl ₄	1,3,4,4-Tetrachloro- butene-1	3:9058
	1-Chloro-2-methyl- propene-1	3:71 20	C ₆ H ₇ Cl ₈	2-(Chloromethyl)1,3- dichlorobutene-1	3:9201
C_5H_9Cl	1-Chloropentene-1	3:7420	ь. Т	This chlorine atom is secon	dary
	1-Chloro-2-methyl-			b ₁ monochloro	
	butene-1	3:7303	C_8H_5Cl	2-Chloropropene-1	3:7020
	1-Chloro-3-methyl- butene-1	3:7215	C ₄ H ₇ Cl	2-Chlorobutene-1 2-Chlorobutene-2	3:7075 3:7105
$C_0H_{11}Cl$	1-Chlorohexene-1	3:7630	C ₆ H ₉ Cl	2-Chloropentene-1	3:7280
C7H18Cl	1-Chloroheptene-1	3:8219		2-Chloropentene-2 3-Chloropentene-2	3:7285 3:7240
C ₂ H ₄ Cl ₂	a ₂ DICHLORO 1,3-Dichloropropene-1	3:5280		3-Chloro-2-methyl- butene-2	8:7335

C ₆ H ₁₁ Cl	2-Chlorohexene-1 3-Chlorohexene-3		C ₈ H ₈ Cl ₈	1,1,2-Trichloro- propene-1	3:5395
	2-Chloro-3,3-dimethyl- butene-1		$C_4H_5Cl_3$	1,1,3-Trichloro-2- methylpropene-1	3:5025
C7H18Cl	2-Chloroheptene-1 4-Chloroheptene-3		$C_6H_9Cl_8$	1,1,2-Trichloro- hexene-1	3:9326
	3-Chloro-2,4-dimethyl- pentene-2		C_2Cl_4	Tetrachloroethylene	3:5460
C ₈ H ₁₅ Cl	2-Chloro-octene-1 2-Chloro-octene-2	3:8345	C ₈ HCl ₅	1,1,2,3,3-Pentachloro- propene-1	3:6075
	4-Chloro-octene-4 2-Chloro-3-ethyl-3-	3:8230	C ₃ Cl ₆	Hexachloropropene	3:6370
C ₁₀ H ₁₉ Cl	methylpentene-1 5-Chlorodecene-5	3:8115 3:9712		These two chlorines are o ent carbons (—C—C—)	n differ-
Chilipoi	b ₂ dichloro	0.0118		Cl Cl	
C ₃ H ₄ Cl ₂	2,3-Dichloropropene-1	3:5190	$\mathrm{C_2H_2Cl_2}$	cis-1,2-Dichloro- ethylene	3:5042
C ₄ H ₆ Cl ₂	2,3-Dichlorobutene-1 . 1,2-Dichlorobutene-2	3:9074		trans-1,2-Dichloro- ethylene	3:5028
	(hb.)	3:5615 3:5360	$C_8H_4Cl_2$	1,2-Dichloropropene-1 (hb. isomer) 1,2-Dichloropropene-1	3:5150
~ ~	1,3-Dichlorobutene-2.	3:5550		(lb. isomer)	3:5110
C ₅ H ₈ Cl ₂	2,5-Dichloropentene-2 3,4-Dichloropentene-2	3:9202 3:8045		cis-2,3-Dichloro- butene-2	3:5500
	1,3-Dichloro-2-methyl- butene-2	3:8170	O. TT. GI	butene-2	3:7395
	b ₈ POLYCHLORO		$\mathrm{C_{6}H_{10}Cl_{2}}$	1,2-Dichlorohexene-1.	3:9330
C ₄ H ₅ Cl ₈	1,2,4-Trichloro- butene-2 2,3,4-Trichloro-	3:9062	C ₂ HCl ₃	1,1,2-Trichloro- ethylene	3:5170
C4H4Cl4	butene-2	3:9064	$C_8H_3Cl_8$	1,1,2-Trichloropro- pene-1	3:5395
	butene-1	3:9060		1,2,3-Trichloropro- pene-1	3:5650
to u	h two chlorine atoms on Consaturation oth these chlorines are		$C_3H_2Cl_4$	1,2,3,3-Tetrachloro- propene-1	3:5920
_	atom	on same	G (0)		
$C_2H_2Cl_2$	1,1-Dichloroethylene	3:5005	C ₄ Cl ₄	Tetrachloroethylene	3:5460
C ₈ H ₄ Cl ₂	1,1-Dichloropropene-1	3:5120	$C_4H_2Cl_6$	1,1,2,3,4,4-Hexa- chlorobutene-2	
C ₄ H ₆ Cl ₂	1,1-Dichloro-2-methyl- propene-1	3:5300		(liquid isomer) (solid isomer)	3:9046 3:1945
C ₂ HCl ₃	1,1,2-Trichloro- ethylene	3:5170	$C_0H_0Cl_0$	1,2,3,4,5,6-Hexa- chlorohexene-3	3:1220

3. With none of the chlorine atoms on C attached to unsaturation			C ₇ H ₁₈ Cl 4-Chloro-2,4-dimethy Contd. pentene-1		8:7725
a. M	lonochloro			4-Chloro-2,4-dimethyl-	0.0440
C_8H_5Cl	3-Chloropropene-1	3:7035	$C_8H_{15}Cl$	pentene-2 3-Chloro-octene-1 4-Chloro-octene-2	3:9418 3:9518 3:8185
C ₄ H ₇ Cl	3-Chlorobutene-1 4-Chlorobutene-1	3:7 090 3:7151		4-Chloro-6-methyl-	
	1-Chlorobutene-2	3:7205		heptene-1	3:8205
	3-Chloro-2-methyl- propene-1	3:7145		6-Chloro-2-methyl- heptene-2 4-Chloro-3-methyl-	3:9520
C ₅ H ₉ Cl	3-Chloropentene-1	3:7260		heptene-24-Chloro-6-methyl-	3:9524
	4-Chloropentene-1 5-Chloropentene-1	3:7350 3:7410		heptene-2 5-Chloro-4-methyl-	3:9525
	1-Chloropentene-2 4-Chloropentene-2	3:7470 3:7400		heptene-3	3:9526
	5-Chloropentene-2	3:7455		4-Chloro-2,5-dimethyl- hexene-2 4-Chloro-3,5-dimethyl-	3:9529
	2-(Chloromethyl)- butene-1	3:9214		hexene-2 2-Chloro-2,5-dimethyl-	3:9528
•	3-Chloro-2-methyl-			hexene-3	3:9527
	butene-1	3:7300		1-Chloro-4-ethyl- hexene-3	3:8510
	1-Chloro-2-methyl- butene-2 4-Chloro-2-methyl-	3:7485	C ₉ H ₁₇ Cl	4-Chloro-7-methyl-	
	butene-2	3:7465		octene-2 5-Chloro-4-methyl- octene-3	3:9628 3:9624
$C_6H_{11}Cl$	3-Chlorohexene-1 4-Chlorohexene-1	3:9334 3:7655		4-Chloro-3,6-dimethyl-	J. 50#2
	5-Chlorohexene-1	3:7665		heptene-2	3:9630
	1-Chlorohexene-2 4-Chlorohexene-2	3:7620 3:7675	$\mathrm{C}_{10}\mathrm{H}_{19}\mathrm{Cl}$	4-Chloro-3,7-dimethyl- octene-2	3:9714
	1-Chlorohexene-3	3:9336		4-Chloro-3,4-diethyl- hexene-2	3:9716
	3-Chloro-2-methyl- pentene-1	3:7660	b. D:	ichloro	
	4-Chloro-4-methyl- pentene-1	3:7500	C ₈ H ₄ Cl ₂	3,3-Dichloropropene-1	3:5140
	5-Chloro-2-methyl- pentene-2	3:7915	$C_4H_6Cl_2$	3,4-Dichlorobutene-1.	3:5350
	4-Chloro-3-methyl- pentene-2	3:9338		1,1-Dichlorobutene-2. 1,4-Dichlorobutene-2.	3:7685 3:5725
	1-Chloro-2,3-di- methylbutene-2	3:7520		3-Chloro-2-(chloro- methyl) propene-1 3,3-Dichloro-2-methyl-	3:5633 3:7480
C ₇ H ₁₈ Cl	3-Chloroheptene-1 4-Chloroheptene-2	3:9412 3:8050	C ₅ H ₈ Cl ₂	3-Chloro-2-(chloro-methyl)-butene-1	3:9206
	4-Chloro-5-methyl- hexene-14-Chloro-3-methyl-	3:7730		3,3-Dichloro-2-methyl-	J. FAUU
	hexene-24-Chloro-5-methyl-	3:9414		butene-1	3:7690
	hexene-2	3:7890		butene-2	3:9204

c. I C ₂ H ₃ Cl ₃	Polychloro 3,3,3-Trichloro-	0.1047	$C_{\delta}H_{\delta}Cl_{2}$	1-Chloro-2-(chloro- methyl)-butadiene- 1,3	3:9195
	propene-1	3:53 <u>45</u>			0.0100
C ₄ H ₄ Cl ₃	3,3,3-Trichloro-2-		c. C	6 series	
	methylpropene-1	3:5605	C_0H_0Cl	3-Chlorohexadiene-1,3	3:9312
C ₄ H ₃ Cl ₅	1,1,1,4,4-Pentachloro- butene-2	3:9054		1-Chloro-3-methyl- pentadiene-1,3 2-Chloro-3-methyl-	3:9316
C ₄ H ₂ Cl ₆	Hexachlorobutene-X Hexachlorobutene-Y	3:9048 3:9050		pentadiene-1,3	3:9318
B. Of Diol	efins		$C_6H_8Cl_2$	1,3-Dichlorohexa- diene-2,4	3:9310
4 72744	h '' cumulative " unsature				
		-	$C_6H_6Cl_4$	1,3,4,6-Tetrachloro-	• ••••
C ₄ H ₅ Cl	4-Chlorobutadiene-1,2	3:7225		hexadiene-2,4	3:9306
C _b H ₇ Cl	1-Chloro-3-methyl-		d. C	s series	
	butadiene-1,2	3:73 90	$C_8H_{13}Cl$	3-Chloro-octadiene-1,3	3:9506
C_0H_0Cl	1-Chloro-3-methyl-		3. Witi	h " isolated" unsaturation	2
	pentadiene-1,2	3:9314	CaH ₇ Cla	3,3,6-Trichlorohexa-	
C ₇ H ₁₁ Cl	1-Chloro-3-ethyl-			diene-1,4	3:9308
C/11IIO.	pentadiene-1,2	3:9406			•
			$\mathbf{C}_{7}\mathbf{H}_{11}\mathbf{C}\mathbf{l}$	4-Chlorohepta-	
	h '' conjugated'' unsatura	tio n		diene-1,6	3:8085
	4 series		C ₂ H ₁₅ Cl	2-Chloro-6-methyl-5-	
C ₄ H ₅ Cl	1-Chlorobutadiene-1,3 2-Chlorobutadiene-1,3	3:7210 3:7080		methyleneheptene-2	3:9614
		000	C. Of Trio	lefins '	
$C_4H_4Cl_2$	1,2-Dichlorobuta-		C ₆ H ₆ Cl ₂	3,6-Dichlorohexa-	
	diene-1,3	3:9057		triene-1,3,4	3:9304
	diene-1,3	3:5220	$C_6H_5Cl_8$	3,4,6-Trichlorohexa- triene-1,2,4	3:9302
$C_4H_8Cl_8$	1,2,3-Trichlorobuta-			0110110-1,2,1	U . 93UR
	diene-1,3	3:99 52	D. Of Tetr	aolefins	
C ₄ H ₂ Cl ₄	1,2,3,4-Tetrachloro- butadiene-1,3		C ₆ H ₅ Cl	3-Chlorohexa- tetraene-1,3,4,5	3:7735
	(solid isomer)	3:0870	C ₆ H ₄ Cl ₂	3,4-Dichlorohexa-	
	(liquid isomer)	3:6150	Cerriois	tetraene-1,2,4,5	3:9300
C4HCl4	1,1,2,3,4-Pentachloro-		E. Of Alky	nes	
	butadiene-1,3	3:9 011	•		
C ₄ Cl ₆	Hexachlorobuta-	9.0492		t chlorine attached to C al riple bond	so bear-
	diene-1,3	3:6425	a. M	onochloro	
8. C	series		C ₂ HCl	Chloroacetylene	3:7000
C ₄ H ₇ Cl	3-Chloropenta-		C _s H _s Cl	•	
	diene-1,3	8:7860		1-Chlorohexyne-1	3:9320
	1-Chloro-2-methyl- butadiene-1,3	3:9200	C ₇ H ₁₁ Cl	1-Chloroheptyne-1 1-Chloro-3-ethyl- pentyne-1	3:8033
	3-Chloro-2-methyl-			F	8:9410
	butadiene-1,3 4-Chloro-2-methyl-	3:7 290	C ₈ H _u Cl	1-Chloro-octyne-1	3:9510
	butadiene-1,3	3:7855	C _b H ₁₅ Cl	1-Chlorononyne-1	3:9618

ъ.	Dichloro		$C_8H_{18}Cl$	3-Chloro-3-methyl-	
C_2Cl_2	Dichloroacetylene	3:5010		heptyne-4	3:9516
	ith chlorine(s) attached to ter than that bearing triple		C ₉ H ₁₅ Cl	2-Chloro-2-methyl- octyne-3	3:9622
a.	Monochloro a1 CHLORINE IS PRIMARY		C ₁₀ H ₁₇ Cl	3-Chloro-3-methyl- nonyne-4	3:9710
C ₂ H ₂ Cl	3-Chloropropyne-1	3:7100	b.	Dichloro	
C4H5Cl	1-Chlorobutyne-2		$C_8H_{12}Cl_2$	2,5-Dichloro-2,5- dimethylhexene-3	3:9504
CaH12Cl	1-Chloro-octyne-2	3:9514	F. Of Alka	di-ynes	
C _k H ₇ Cl	82 CHLORINE IS TERTIARY 3-Chloro-3-methyl-	0,002	C ₄ Cl ₂	1,4-Dichlorobuta- di-yne-1,3	3:9040
0,11,01	butyne-1	3:7155	G. Of Alke	nynes	
C ₆ H ₉ Cl	3-Chloro-3-methyl- pentyne-1	3:9322	C ₄ H ₃ Cl	1-Chlorobuten-3- yne-1	3:7070
	4-Chloro-4-methyl- pentyne-2		C ₇ H ₉ Cl	5-Chloro-5-methyl- hexen-1-yne-3	3:9402

UNIT 3. CHLORO SUBSTITUTION PRODUCTS OF HYDROCARBONS CONTAINING CYCLIC NUCLEI

(Summary of Classification of Unit 3)

- A. OF CYCLOALKANES.
- B. OF MONONUCLEAR AROMATIC HYDROCARBONS.
 - 1. With all chlorine in nucleus.
 - 2. With all chlorine in side chain(s).
 - a. Saturated side chain(s).
 - b. Unsaturated side chain(s).
 - 3. With chlorine both in ring and in side chain(s).
- C. OF POLYNUCLEAR AROMATIC HYDROCARBONS.
 - 1. With all chlorine in nucleus.
 - a. Systems with uncondensed rings.
 - b. Systems with condensed rings.
 - 2. With all chlorine in side chain(s).
 - a. Systems with two uncondensed rings.
 - b. Systems with two condensed rings.
 - c. Systems with three uncondensed rings.
 - 3. With chlorine both in nucleus and side chain.

UNIT 3. CHLORO SUBSTITUTION PRODUCTS OF HYDROCARBONS CONTAINING CYCLIC NUCLEI

A. Of Cycloalkanes			B. Of Mononuclear Aromatic		
C ₅ H ₉ Cl	Chlorocyclopentane	3:7545	Hydro	carbons	
CaHuCl Chlorocyclohexane	3:8040	1. With all chlorine in nucleus			
Canno	C ₆ H ₁₁ Cl Chlorocyclohexane	O.OUZU	C_6H_5Cl	Chlorobenzene	3:7903
C ₆ H ₆ Cl ₆	cis-1,2,3,4,5,6-Hexa- chlorocyclohexane trans-1,2,3,4,5,6-Hexa-	8:4410	C ₆ H ₄ Cl ₂	o-Dichlorobensene m-Dichlorobensene	3:6055 3:5960
	chlorocyclohexane	3: 4990		p-Dichlorobenzene	3:0960

C ₆ H ₈ Cl ₈	1,2,3-Trichlorobenzene 1,2,4-Trichlorobenzene 1,3,5-Trichlorobenzene	3:6420	C9H11Cl Contd.	2-Chloro-1,3,5-tri- methylbenzene	3:8725
C ₆ H ₂ Cl ₄	1,2,3,4-Tetrachloro-		$\mathrm{C}_{10}\mathrm{H}_{13}\mathrm{Cl}$	2-Chloro-p-cymene 3-Chloro-p-cymene	3:8775 3:8770
	benzene	3:0655 3:0915	2. Wi	th all chlorine in side chai	n(s)
	1,2,4,5-Tetrachloro-	0.0000	a.	Saturated side chain(s)	
	benzene	3:4115	C7H7Cl	Benzyl chloride	3:8535
C ₆ HCl ₅	Pentachlorobenzene	3:2290	$C_7H_6Cl_2$	Benzal (di)chloride	3:6327
C ₆ Cl ₆	Hexachlorobenzene	3:4939	$C_7H_5Cl_8$	Benzotrichloride	3:6540
C7H7Cl	o-Chlorotoluene m-Chlorotoluene p-Chlorotoluene	3:8245 3:8275 3:8287	C ₈ H ₉ Cl	α -Chloroethylbenzene β -Chloroethylbenzene.	3:8667 3:8712
C7H6Cl2	2,3-Dichlorotoluene	3:6345	$\mathrm{C_8H_8Cl_2}$	α,β -Dichloroethylbenzene	3:6685
	2,4-Dichlorotoluene 2,5-Dichlorotoluene 2,6-Dichlorotoluene 3,4-Dichlorotoluene	3 : 6290 3 : 6245 3 : 6270 3 : 6355	C_8H_9Cl	o-Xylyl chloride m-Xylyl chloride p-Xylyl chloride	3:8710 3:8700 3:8660
C7H5Cl3	3,5-Dichlorotoluene 2,3,4-Trichlorotoluene	3:6310 3:0425	$\mathrm{C_8H_8Cl_2}$	o-Xylylene (di)-	
5,0,-	2,3,5-Trichlorotoluene 2,3,6-Trichlorotoluene	3:0610 3:0625		chloride	3:1040 3:0310
	2,4,5-Trichlorotoluene 2,4,6-Trichlorotoluene 3,4,5-Trichlorotoluene	3:2100 3:0380 3:0580		p-Xylylene (di)- chloride	3:2825
C7H4Cl4	2,3,4,5-Tetrachloro-		C ₉ H ₁₁ Cl	γ -Chloro- n -propyl- benzene	3:8777
	toluene 2,3,4,6-Tetrachloro-	3:2710		α-Chloroisopropyl- benzene	3:9610
	toluene	3:2480	$C_{10}H_{13}Cl$	2,3,6-Trimethylbenzyl	
G II GI	toluene	3:2575		chloride	3:9701
C7H2Cl5	2,3,4,5,6-Pentachloro- toluene	3:4937		chloride2,4,6-Trimethylbenzyl	3:9702
C ₈ H ₉ Cl	o-Chloro-ethylbenzene p-Chloro-ethylbenzene	3:8550 3:8570		chloride	3:0372
	3-Chloro-1,2-dimethyl-	0.0010		4-Isopropylbenzyl chloride	3:8795
	benzene4-Chloro-1,2-dimethyl-	3:8645		β-Chloro-ter-butyl- benzene	3:8780
	benzene	3:8675	b. T	Insaturated side chain(s)	
	2-Chloro-1,3-dimethyl- benzene	3:8590	C ₈ H ₆ Cl	ω-Chlorophenyl-	0.0404
	4-Chloro-1,3-dimethyl- benzene	3:8665		acetylene	3:9494 3:9497
	5-Chloro-1,3-dimethyl- benzene	3:8640		acetylene	3:9497 3:9500
	2-Chloro-1,4-dimethyl- benzene	3:8600		p-Chlorophenyl- acetylene	3:0590
		J.0000			
C ₀ H ₁₁ Cl	4-Chloro-isopropyl- benzene	3:8705	C ₈ H ₇ Cl	α -Chlorovinylbenzene β -Chlorovinylbenzene.	3:8715 3:8717

C_9H_9Cl	1-Chloro-1-phenylpro-	9.0004	C7H3Cl5	2,4,5-Trichlorobenzal	3:6910
	pene-1	3:9604	Contd.	(di)chloride	0 : 09 TA
	pene-1	3:9606		(di)chloride	3:0142
	3-Chloro-1-phenylpro- pene-1	3:0010	C7H2Cl6	2,3,4,5-Tetrachloro-	
	pene-1	3. WI	-,20	benzal (di)chloride .	3:9397
	1-Chloro-2-phenylpro-			2,3,4,6-Tetrachloro-	9.0000
	pene-1	3:8742		benzal (di)chloride . 2,3,5,6-Tetrachloro-	3:6980
	1-Chloro-3-phenylpro-			benzal (di)chloride .	3:6980
	pene-1	3:8737	C7HCl5	Pentachlorobenzal	
	2-Chloro-3-phenylpro-		Cilicis	(dı)chloride	3:3590
	penc-1	3:9 60 8			
9 With	chlorine both in ring and	l in side	_	nuclear Aromatic Hydrocar	bons
chain				all chlorine in nucleus	•
C7H6Cl2	o-Chlorobenzyl			ystems with uncondensed	_
0/116012	chloride	3:6400	C ₁₂ H ₉ Cl	2-Chlorobiphenyl 3-Chlorobiphenyl	3:0300 3:8940
	m-Chlorobenzyl			4-Chlorobiphenyl	3:1912
	chloride	3: 644 5	C ₁₂ H ₈ Cl ₂	2,2'-Dichlorobiphenyl.	3:1325
	chloride	3:0220	C12118C12	2,3-Dichlorobiphenyl.	3:9850
				2,4'-Dichlorobiphenyl.	3:0670
$C_7H_5Cl_3$	2,6-Dichlorobenzyl	0.0440		2,5-Dichlorobiphenyl.	3:9854
	chloride 3,4-Dichlorobenzyl	3:0410		3,3'-Dichlorobipehnyl. 3,4-Dichlorobiphenyl.	3:0180 3:0685
	chloride	3:6795		3,5-Dichlorobiphenyl .	3:0360
	3,5-Dichlorobenzyl			4,4'-Dichlorobiphenyl.	3:4300
	chloride	3:0350	C18H10Cl2	4,4'-Dichlorodiphenyl-	
	o-Chlorobenzal		C181110C12	methane	3:1057
	(di)chloride	3:6625	C14H10Cl2	1,1-Di-(p-chloro-	
	m-Chlorobenzal	9.0716	C141110C12	phenyl)ethylene	3:2475
	(di)chloride p-Chlorobenzal	3:6710	$\mathbf{C_{14}H_{12}Cl_2}$	1,1-Di-(p-chloro-	
	(di)chloride	3:6700		phenyl)ethane	3:0995
~ ** ~*	0.4.70.11. 1. 1.		ъ. 1	Systems with condensed ri	ngs
C7H4Cl4	2,4-Dichlorobenzal (di)chloride	3:9399	C ₁₀ H ₇ Cl	1-Chloronaphthalene .	3:6878
	2,5-Dichlorobenzal	0.000		2-Chloronaphthalene.	3:1285
	(di)chloride	3:0490	$C_{10}H_6Cl_2$	1,2-Dichloronaphtha-	
	2,6-Dichlorobenzal (di)chloride	3:9398	-100	lene	3:0320
	(ui)emoride	o. 900G		1,3-Dichloronaphtha-	9. 1910
	3,4-Dichlorobenzal			lene 1,4-Dichloronaphtha-	3:1310
	(di)chloride	3:6867		lene	3:1655
	3,5-Dichlorobenzal (di)chloride	3:0370		1,5-Dichloronaphtha-	0.0000
	(41)01114011111111	510010		lene	3:3200
	o-Chlorobenzotri-			lene	3:0810
	chloride	3:6880		1,7-Dichloronaphtha-	0.400=
	chloride	3:6845		lene 1,8-Dichloronaphtha-	3:1385
	p-Chlorobenzotri-			lene	3:2435
	chloride	3:6825		2,3-Dichloronaphtha-	0.000-
C7H2Cl5	2,3,4-Trichlorobenzal			lene	3:3665
~1116018	(di)chloride	3:2212		lene	3: 4040
	2,3,6-Trichlorobenzal	0.0420		2,7-Dichloronaphtha-	
	(di)chloride	3:2178		lene	3:3445

C ₁₀ H ₆ Cl ₈	1,2,3-Trichloro- naphthalene 1,2,4-Trichloro-	3:2125	C ₁₄ H ₁₁ Cl ₂	1,1,1-Trichloro-2,2- diphenylethane	3:1420
	naphthalene 1,2,5-Trichloro-	3:2490	C14H16Cl4	1,1,2,2-Tetrachloro-1, 2-diphenylethane	3:4496
	naphthalene 1,2,6-Trichloro- naphthalene	3:193 9 3:2515	C14H10Cl2	cis-1,2-Dichloro-1,2- diphenylethylene	3:1380
	1,2,7-Trichloro- naphthalene	3:2825		trans-1,2-Dichloro- 1,2-diphenylethyl-	0,2000
	1,2,8-Trichloro- naphthalene	3:2220		ene	3:4210
	1,3,5-Trichloro- naphthalene	3:3015		1,1-Dichloro-2,2-di- phenylethylene	3:1938
	1,3,6-Trichloro- naphthalene	3:1975	ь sı	stems with two condense	
	1,3,7-Trichloro- naphthalene	3:3400	C ₁₁ H ₉ Cl	1-(Chloromethyl)-	va 1 men
	1,3,8-Trichloro- naphthalene	3:2420	On-Lioi	naphthalene 2-(Chloromethyl)-	3:0250
	1,4,5-Trichloro- naphthalene	3:4005		naphthalene	3:0747
	1,4,6-Trichloro- naphthalene	3:1625		vstems with three unco	ndensed
	2,3,5-Trichloro- naphthalene	3:3300	C ₁₉ H ₁₅ Cl	α-Chlorotriphenyl-	
	2,3,6-Trichloro- naphthalene	3:2455		methane	3:3410
C10Cl8	Octachloronaptha-	3:4893	C ₂₀ H ₁₈ Cl	1-Chloro-1,2,2- triphenylethylene	3:3560
C10HaCl4	1,2,3,4-Tetrachloro-	0,200		ı chlorine both in nucleu chain	s and in
	1,2,3,4-tetrahydro-	0.4876	C ₁₄ H ₁₀ Cl ₄	1,1-Dichloro-2,2-	
	naphthalene 5,6,7,8-Tetrachloro-	3:4750	CHILIOCH	bis-(p-chloro- phenyl)ethane	3:3320
	1,2,3,4-tetrahydro- naphthalene	3:4703		1,1-Dichloro-2-(o-	0.00.00
C14H8Cl2	9,10-Dichloro- anthracene	3:4916		chlorophenyl)-2-(p - chlorophenyl)-	
0 12744	h all chlorine in side chai	n(e)		ethane	3:1890
	Systems with two unce		$C_{14}H_9Cl_5$	1,1,1-Trichloro-2,2-	
:	rings			bis-(o-chlorophenyl)- ethane	3:9865
C ₁₈ H ₁₁ Cl	α -Chloro- diphenylmethane	3:0060		1,1,1-Trichloro-2,2- bis-(p-chloro-	
C18H10Cl2	α,α-Dichloro- diphenylmethane	3:6960		phenyl)ethane	3:3298
C14H12Cl	1,1-Diphenylethyl			1,1,1-Trichloro-2-(o- chlorophenyl)-2-	
0,,2,	chloride	3:9870		(p-chlorophenyl)- ethane	3:1820
	chloride	3:9871		1,1,1-Trichloro-2-(m-chlorophenyl)-2-	3.22.00
C14H12Cl2	6,l-1,2-Dichloro-1,2- diphenylethane	3:2570		(p-chlorophenyl)- ethane	3:9867
	meso-1,2-Dichloro-1,2- diphenylethane	3:4854	a Fran		3.5001
			$C_{13}H_8Cl_6$	1,1,1,2-Tetrachloro- 2 ,	
	1,1-Dichloro-2,2-	3:1940		2-bis-(p-chloro- phenyl)ethane	3:2477

C ₁₄ H ₉ Cl ₂	1-Chloro-2,2-bis-(p-chlorophenyl)- ethylene	3:1430	C14H8Cl4 Contd.	1,1-Dichloro-2-(o- chlorophenyl)-2- (p-chlorophenyl)- ethylene	3:1925
$C_{14}H_8Cl_4$	1,1-Dichloro-2,2-bis-			ethylene	9:19/0
	(p-chlorophenyl)- ethylene	3:2438		1,1-Dichloro-2-(m- chlorophenyl)-2- (p-chlorophenyl)- ethylene	2:9863

UNIT 4. CHLORO SUBSTITUTION PRODUCTS OF HYDROXY COMPOUNDS

(Summary of Classification of Unit 4)

A. OF ALCOHOLS.

- 1. Of acyclic alcohols.
 - a. Saturated monohydric.
 - a₁ Primary.
 - a₂ Secondary.
 - as Tertiary.
 - b. Saturated dihydric.
 - c. Unsaturated (olefinic) monohydric.
 - c1 Primary.
 - c2 Secondary.
- 2. Of cyclanols (alicyclic alcohols).
- 3. Of aromatic alcohols.
- 4. Of alcohols containing also other functional groups.

 - a. Ether/alcohols. b. Ester/alcohols.
 - c. Ether/ester/alcohols.
 - d. Acid/alcohols (hydroxy acids).

B. OF PHENOLS.

- 1. Of mononuclear phenols.
 - a. Monohydric.
 - a₁ Derivatives of phenol.
 - a₂ Derivatives of methylphenols.
 - as Derivatives of xylenols.
 - a4 Derivatives of miscellaneous alkylphenols.
 - as Derivatives of phenolic aldehydes.
 - as Derivatives of phenolic acids.
 - a7 Derivatives of phenolic acid chlorides.
 - b. Dihydric.
 - b₁ Derivatives of pyrocatechol.
 - b₂ Derivatives of resorcinol.
 - ba Derivatives of hydroquinone.
 - c. Trihydric.
- 2. Of binuclear phenols.
 - a. Monohydric.
 - a₁ With uncondensed rings.
 - as With condensed rings.

UNIT 4. CHLORO SUBSTITUTION PRODUCTS OF HYDROXY COMPOUNDS

•	cyclic alcohols		C ₈ H ₅ OCl ₈	1,1,1-Trichloro- propanol-2	3:0846
	turated monohydric		C ₈ H ₄ OCl ₄	1,1,1,3-Tetrachloro-	
C ₂ H ₅ OCl	2-Chloroethanol-1	3:5552		propanol-2	3:9036
$C_2H_4OCl_2$	2,2-Dichloroethanol-1.	3:5745		propanol-2	3:9037
C ₂ H ₈ OCl ₃	2,2,2-Trichloro- ethanol-1	3:5775	C ₄ H ₉ OCl	1-Chlorobutanol-2 3-Chlorobutanol-2 erythro-3-Chloro-	3:8025 3:8000
C ₈ H ₇ OCl	2-Chloropropanol-1 3-Chloropropanol-1	3:7917 3:8285		butanol-2 threo-3-Chloro- butanol-2	3:8004 3:8002
C ₈ H ₆ CCl ₂	2,3-Dichloro- propanol-1	3:6060	C4H8OCl2	4-Chlorobutanol-2 1,3-Dichlorobutanol-2	3:9175 3:9145
G ₄ H ₉ OCl	2-Chlorobutanol-1 3-Chlorobutanol-1 4-Chlorobutanol-1	3:9160 3:9165 3:9170		1,1-Dichloro-2-methyl- propanol-2	3:5772
C4H7OCl8	2,2,3-Trichloro- butanol-1	3:1336	C ₄ H ₇ OCl ₃	1,1,1-Trichloro- butanol-2	3:5955
C ₄ H ₉ OCl	2-Chloro-2-methyl- propanol-1	3:7905	C ₆ H ₁₁ OCl	1-Chloropentanol-2 1-Chloropentanol-3	3:8225 3:8500
	3-Chloro-2-methyl- propanol-1	3:9180		2-Chloro-2-methyl- butanol-3	3:9290
$C_bH_{11}OCl$	5-Chloropentanol-1	3:9295	8.3	TERTIARY	
C ₆ H ₁₈ OCl	6-Chlorohexanol-1	3:9395	C ₄ H ₉ OCl	1-Chloro-2-methyl- propanol-2	3:7752
$C_7H_{15}OCl$	7-Chloroheptanol-1	3:0013	C ₄ H ₈ OCl ₂	1,3-Dichloro-2-methyl-	
C ₈ H ₁₇ OCl	8-Chloro-octanol-1	3:9590		propanol-2	3:5977
$C_9H_{19}OCl$	9-Chlorononanol-1	3:0170	C ₄ H ₇ OCl ₈	1,1,1-Trichloro-2- methylpropanol-2	3:2662
$C_{10}H_{21}OCl$	$10\text{-}Chlorodecanol-1\dots$	3:0014	C _b H ₁₁ OCl	1-Chloro-2-methyl-	
$\mathrm{C}_{12}\mathrm{H}_{25}\mathrm{OCl}$	12-Chloro- dodecanol-1	3:0172		butanol-2 3-Chloro-2-methyl- butanol-2	3:8175 3:8030
C ₁₄ H ₂₉ OCl	14-Chloro- tetradecanol-1	3:0375		4-Chloro-2-methyl- butanol-2	3:8335
C ₁₆ H ₈₈ OCl	16-Chloro- hexadecanol-1	3:0525	b. Sa C₃H7O₃Cl	turated dihydric 3-Chloropropanediol- 1,2	3:9038
C ₁₈ H ₈₇ OCl	18-Chloro- octadecanol-1	3:0985		2-Chloropropanediol- 1,3	8:9039
-	SECONDARY		C ₄ H ₉ O ₂ Cl	3-Chloro-2-methyl- propanediol-1,2	3:9190
C ₈ H ₇ OCl	1-Chloropropanol-2	3:7747	. **		
C ₂ H ₆ OCl ₂	1,1-Dichloro- propanol-2 1,3-Dichloro- propanol-2	3:5755 3:5985		nsaturated (olefinic) mon PRIMARY 2-Chloropropen-2-ol-1. 3-Chloropropen-2-ol-1.	3:5635 3:5820

C ₄ H ₇ OCl	2-Chlorobuten-2-ol-1 . 3-Chlorobuten-2-ol-1 . 4-Chlorobuten-2-ol-1 . 2-Chlorobuten-3-ol-1	3:8240 3:8270 3:9114 3:9113	a. M	nois onuclear phenois onobydric derivatives of phenoi	L
	3-Chloro-2-methyl- propen-2-ol-1	3:8340	C_6H_5OCl	o-Chlorophenol m-Chlorophenol p-Chlorophenol	3:5980 3:0255 3:0475
_	SECONDARY			•	
C ₄ H ₇ OCl	1-Chlorobuten-3-ol-2 3-Chlorobuten-3-ol-2.	3:8110 3:9115	C ₆ H ₄ OCl ₂	2,3-Dichlorophenol 2,4-Dichlorophenol 2,5-Dichlorophenol	3:1175 3:0560 3:1190
2. Of cy	clanols (alicyclic alcohol:	s)		2,6-Dichlorophenol	3:1595
C ₆ H ₁₁ OCl	cis-2-Chlorocyclo- hexanol-1 trans-2-Chlorocyclo-	3:9374		3,4-Dichlorophenol 3,5-Dichlorophenol	3:1 460 3:167 0
	hexanol-1	3:0175	C ₆ H ₈ OCl ₈	2,3,4-Trichlorophenol.	3:2185
	4-Chlorocyclo- hexanol-1	3:9376		2,3,5-Trichlorophenol. 2,3,6-Trichlorophenol. 2,4,5-Trichlorophenol.	3:1340 3:1160 3:1620
3. Of an	omatic alcohols			2,4,6-Trichlorophenol.	3:1673
C ₈ H ₉ OCl	Styrene chlorohydrin.	3:9570		3,4,5-Trichlorophenol.	3:2885
	nicohols containing als ional groups	o other	C ₆ H ₂ OCl ₄	2,3,4,5-Tetrachloro- phenol.	3:3523
a. Et	her/alcohols			2,3,4,6-Tetrachloro- phenol	3:1687
$C_4H_9O_2Cl$	2-(β-Chloroethoxy)-			2,3,5,6-Tetrachloro-	0.1001
	ethanol-1	3:9185		phenol	3:3460
b. Es	ter/alcohols		C ₆ HOCl ₅	Pentachlorophenol	3:4850
C ₄ H ₇ O ₈ Cl	β -Hydroxyethyl chloroacetate	3:6780	-	DERIVATIVES OF THE	
C ₄ H ₆ O ₃ Cl ₂	β-Hydroxyethyl di-			PHENOLS (CRESOLS)	
C4118O3C12	chloroacetate	3:9107	C7H7OCl	3-Chloro-2-methyl- phenol.	3:2280
C ₄ H ₅ O ₈ Cl ₈	β-Hydroxyethyl tri- chloroacetate	3:9099		4-Chloro-2-methyl- phenol 5-Chloro-2-methyl-	3:0780
C ₅ H ₉ O ₅ Cl	β-Chloro-γ-hydroxy-			phenol	3:1815
	n-propyl acetate	3:6648		6-Chloro-2-methyl-	
	γ-Chloro-β-hydroxy-			phenol	3:8615
	n-propyl acetate	3:6775	C7H4OCl2	4,5-Dichloro-2-	
	β -Chloro- β' -hydroxy-isopropyl acetate	3:6517	CALIGOUS	methylphenol 4,6-Dichloro-2-	3:2910
_ TA	her/ester alcohols			methylphenol	3:1020
	•		C ₇ H ₇ OCl	2-Chloro-3-methyl-	
C ₆ H ₁₁ O ₄ Cl	Diethylene glycol mono(chloroacetate)	3:9390	Canada	phenol4-Chloro-3-methyl-	3:1055
C ₈ H ₁₅ O ₅ Cl	Triethylene glycol mono(chloroacetate)	3:9588		phenol6-Chloro-3-methyl-	3:1535
d. A	eid/alcohols			phenol	3:0700
C ₄ H ₆ O ₃ Cl ₂	β,β-Dichloro-α-		C7H6OCl2	2,4-Dichloro-3-	
~4440V8V12	hydroxyisobutyric		-,04	methylphenol	3:1205
	acid	3:2145		2,6-Dichloro-3-	
	β , β' -Dichloro- α -			methylphenol	3:0150
	hydroxyisobutyric acid	3:2565		4,6-Dichloro-3- methylphenol	8:1745

C7H6OCl8	2,4,6-Trichloro-3- methylphenol	3:0618	8.5	DERIVATIVES OF PHENOI HYDES	IC ALDE-
~ ** ~ ~ .			C7H5O2Cl	3-Chloro-2-hydroxy-	
C7H7OCl	2-Chloro-4-methyl- phenol	3:6215		benzaldehyde	3:1010
	3-Chloro-4-methyl-	9: UAI9		4-Chloro-2-hydroxy- benzaldehyde	3:0960
	phenol	3:1025		5-Chloro-2-hydroxy-	0 : UV UU
				benzaldehyde	3:2800
C7H6OCl2	2,6-Dichloro-4-	3:0400			
	methylphenol	3:0100	$C_7H_4O_2Cl_2$	3,5-Dichloro-2-hy-	9.0007
۵.	DERIVATIVES OF THE X	TARNOTA		droxybenzaldehyde.	3:2637
-			C7H5O2Cl	2-Chloro-3-hydroxy-	
C ₈ H ₉ OCl	5-Chloro-o-3-xylenol 6-Chloro-o-3-xylenol	3:2115 3:2218		benzaldehyde	3:4085
	o-chioro-o-ayrenor	0. NN 10		4-Chloro-3-hydroxy-	0 - 0800
	3-Chloro-o-4-xylenol .	3:0158		benzaldehyde 6-Chloro-3-hydroxy-	3:3780
	5-Chloro-o-4-xylenol	3:1754		benzaldehyde	3:3350
	6-Chloro-o-4-xylenol	3:2705			
	5-Chloro-m-4-xylenol .	3:8784	$C_7H_4O_2Cl_2$	2,4-Dichloro-3-hy-	
	6-Chloro-m-4-xylenol .	3:2460		droyxbenzaldehyde. 2.6-Dichloro-3-hy-	3:4140
			•	droxybenzaldehyde.	3:4160
	2-Chloro-m-5-xylenol .	3:3505 3:2180		4,6-Dichloro-3-hy-	
	5-Chloro-m-5-xylenol. 6-Chloro-m-5-xylenol.	3:0844		droxybenzaldehyde.	3:3952
	5-Chloro-p-2-xylenol	3:1822	C II O OI	0.40 Thiskland 2 hrs	
			C ₇ H ₈ O ₂ Cl ₈	2,4,6-Trichloro-3-hy- droxybenzaldehyde.	3:3520
C ₈ H ₈ OCl ₂	4,5-Dichloro-o-3-	9.9449		arony bondanaony ao-	0.00.00
	xylenol	3:2 44 2	$C_7H_5O_2Cl$	2-Chloro-4-hydroxy-	
	3,5-Dichloro-o-4-			benzaldehyde	3:4280
	xylenol	3:0935		3-Chloro-4-hydroxy- benzaldehyde	3:4065
	3,6-Dichloro-o-4-	0.0010		3,5-Dichloro-4-hy-	0.200
	xylenol	3:2216		droxybenzaldehyde	3:4400
	xylenol	3:3005			
			-	DERIVATIVES OF PHENOL	IC ACIDS
	2,4-Dichloro-m-5-	0.0100	C7H5O8Cl	3-Chloro-2-hydroxy- benzoic acid	3:4745
	xylenol 2,6-Dichloro-m-5-	3:2182		4-Chloro-2-hydroxy-	0.2120
	xylenol	3:2638	•	benzoic acid	3:4908
				5-Chloro-2-hydroxy-	
C ₈ H ₇ OCl ₈	Trichloro-o-3-xylenol .	3:4742		benzoic acid 6-Chloro-2-hydroxy-	3:4705
	Trichloro-o-4-xylenol .	3:4747		benzoic acid	3:4610
	Tremoro-o-1-Aylenor.	9.2727		DOMESTIC MOTOR TOTAL TOT	0.1010
	Trichloro-m-4-xylenol.	3:4707	$C_7H_4O_3Cl_2$	3,5-Dichloro-2-hy-	
	m-t-11 r11	0.4710		droxybenzoic acid	3: 493 5
	Trichloro-m-5-xylenol.	3:4713	C7H5O3Cl	2-Chloro-3-hydroxy-	
	Trichloro-p-xylenol	3:47 09		benzoic acid	3:4395
•				4-Chloro-3-hydroxy-	
	DERIVATIVES OF MISCEL	LANEOUS		bensoic acid 6-Chloro-3-hydroxy-	3:4 9 33
	ALKYLPHENOLS			benzoic acid	3:4720
$C_{10}H_{18}OCl$	2-Chloro-4-n-butyl-				
	phenol	3:8830	C7H5O8Cl	2-Chloro-4-hydroxy-	
	2-Chloro-4-ter-butyl- phenol	3:9760		benzoic acid 3-Chloro-4-hydroxy-	3:4430
	p.1011011111111111111111111111111111111	J. 9100		benzoic acid	3:4675
	p-Chlorocarvacrol	3:0480		3,5-Dichloro-4-hy-	
	p-Chlorothymol	3:1293		droxybensoic acid	3: 4950

8.7	PHENOLIC ACID CHLORID	E8			
C7H5O2Cl	2-Hydroxybenzoyl chloride	3:0085	C ₆ H ₈ O ₅ Cl ₈ Contd.	3,5,6-Trichloro-2-hy- droxyhydroquinone.	8: 4444
	3-Hydroxybenzoyl chloride	3: 944 6		2,4,6-Trichlorophloro-	3:4030
	4-Hydroxybenzoyl chloride	3: 944 7		glucinol	5 : 1 030
				lear phenois	
b. Di	hydrie			onohydric	
$\mathbf{b_i}$	DERIVATIVES OF PYROCA	TECHOL		WITH UNCONDENSED RIN	GS
$C_6H_5O_2Cl$	3-Chlorocatechol	3:0745 3:2470	C ₁₂ H ₉ OCl	3-Chloro-2-hydroxy- biphenyl 5-Chloro-2-hydroxy-	3:1757
$\mathrm{C_6H_4O_2Cl_2}$	3,5-Dichlorocatechol 4,5-Dichlorocatechol	3:2192 3:3525		biphenyl3-Chloro-4-hydroxy-	3:8980
C ₆ H ₃ O ₂ Cl ₃	3,4,5-Trichloro-			biphenyl4'-Chloro-4-hydroxy-	3:1900
0611802018	catechol	3:3448		biphenyl	3:4262
C ₆ H ₂ O ₂ Cl ₄	Tetrachlorocatechol	3:4875		WITH CONDENSED RINGS	
b .	DANIEL BLANCE OF DESCRIPTION		C ₁₀ H ₇ OCl	2-Chloronaphthol-1 3-Chloronaphthol-1	3:1490 3:4170
_	DERIVATIVES OF RESORCE			4-Chloronaphthol-1	8:3720
C ₆ H ₅ O ₂ Cl	2-Chlororesorcinol	3:2690		5-Chloronaphthol-1 6-Chloronaphthol-1	3:3960 3:2615
	4-Chlororesorcinol 5-Chlororesorcinol	3:3100 3:3530		7-Chloronaphthol-1 8-Chloronaphthol-1	3:381 0 3:1610
$\mathrm{C_6H_4O_2Cl_2}$	4,6-Dichlororesorcinol	3:3380	$\mathrm{C}_{10}\mathrm{H}_6\mathrm{OCl}_2$.2,3-Dichloro- naphthol-1	3:2935
C ₆ H ₈ O ₂ Cl ₈	2,4,6-Trichloro- resorcinol	3:2174		2,4-Dichloro- naphthol-1 5,7-Dichloro-	3:3250
$\mathrm{C_6H_2O_2Cl_4}$	Tetrachlororesorcinol.	3:4135		naphthol-1 5,8-Dichloro-	3:3985
b ₃	DERIVATIVES OF HYDROQ	UINONE		naphthol-1 6.7-Dichloro-	3:3420
C ₆ H ₅ O ₂ Cl	2-Chlorohydro- quinone	3:3130		naphthol-1	3:4315
0.77.0.01	0.0.701.111. 1.			naphthol-1	3:2635
C ₆ H ₄ O ₂ Cl ₂	2,3-Dichlorohydro- quinone 2,5-Dichlorohydro-	3:4220	C ₁₀ H ₇ OCl	1-Chloronaphthol-2 3-Chloronaphthol-2	3:1700 3:2545
	quinone	3:4690		4-Chloronaphthol-2 5-Chloronaphthol-2	3:3045 3:3945
	2,6-Dichlorohydro- quinone	3:4600		6-Chloronaphthol-2 7-Chloronaphthol-2	3:3500 3:3925
$C_6H_8O_2Cl_8$	2,3,5-Trichlorohydro- quinone	3:4052	G 77 001	8-Chloronaphthol-2	3:2965
			C ₁₀ H ₆ OCl ₂	1,3-Dichloro- naphthol-2	3:1990
C ₆ H ₂ O ₂ Cl ₄	Tetrachlorohydro- quinone	3:4941		1,4-Dichloro- naphthol-2	3:3840
$C_6H_2O_4Cl_2$	2,5-Diehloro-3,6-dihy- droxybenzoquinone-			1,6-Dichloro- naphthol-2	3:3600
	1,4	3:4970		3,4-Dichloro- naphthol-2	3:3295
e Tv	ihydric			4,8-Dichloro- naphthol-2	3:4420
C ₆ H ₂ O ₂ Cl ₂	4,5,6-Trichloro-			5,8-Dichloro-	
	pyrogallol	3:4782		naphthol-2	3:4155

UNIT 5. CHLORO SUBSTITUTION PRODUCTS OF CARBONYL COMPOUNDS (AND THEIR RELATIVES)

(Summary of Classification of Unit 5)

A. OF ALDEHYDES.

- 1. Acyclic aldehydes.
 - a. Saturated.
 - b. Unsaturated.
 - c. Relatives of the above.
 - c1 Hydrates.
 - c₂ Hemiacetals.
 - cs Diethylacetals.
 - c4 Acetals with chlorine only in alcohol radicals;
 - c. Polymers.
- 2. Aromatic aldehydes.
 - a. Simple aldehydes.
 - b. Phenolic aldehydes.
- B. OF KETONES.
 - 1. Dialkyl ketones.
 - 2. Alicyclic ketones.
 - 3. Alkyl aryl ketones.
 - a. With chlorine only in alkyl.
 - b. With chlorine both in alkyl and aryl.
 - c. With chlorine only in aryl.
 - 4. Diaryl ketones.
 - 5. Ketones containing also other functional groups.
 - a. Keto-acid chlorides.
 - b. Keto-acid esters.

C. OF QUINONES.

- 1. Mononuclear quinones.
- 2. Dinuclear quinones.
- 3. Trinuclear quinones.

UNIT 5. CHLORO SUBSTITUTION PRODUCTS OF CARBONYL COMPOUNDS (AND THEIR RELATIVES)

•	ohydes <i>dic Aldehydes</i> aturated		C ₄ H ₇ OCl	α-Chloro-n- butyraldehyde β-Chloro-n-	
C_2H_3OCl	$Chloroacetal dehyde \dots$	3:7212		butyraldehyde γ -Chloro- n -	3:9110
$C_2H_2OCl_2$	Dichloroacetaldehyde.	3:5180		butyraldehyde	3:9111
C ₂ HOCl ₃	Trichloroacetaldehyde	3:5210	$C_4H_6OCl_2$	α,β -Dichloro- n -	
C ₂ H ₅ OCl	α-Chloropropionalde- hyde	3:5160 3:5576	$\mathrm{C_4H_5OCl_3}$	butyraldehyde α,α,β-Trichloro-n- butyraldehyde α,α,γ-Trichloro-n-	3:9102 3:5910
C ₃ H ₄ OCl ₂	α,α-Dichloropropion- aldehyde	: 9033-A		butyraldehyde	3:9094
	aldehyde	3:9034	C ₄ H ₇ OCl	α-Chloro-iso- butyraldehyde	3:7235
C ₂ H ₄ OCl ₃	α, α, β -Trichloropropionaldehyde	3:9033		β-Chloro-iso- butyraldehyde	3:9112

b. Ui	nsaturated		C7H4OCl2	2,3-Dichlorobenzal-	0.1400
C ₈ H ₈ OCl	α-Chloroacrolein	3:9031		dehyde	3:1480
C ₄ H ₅ OCl	α-Chlorocrotonalde- hyde	3:8117		dehyde	3:1800
c. Re	latives of the above			hyde 2,6-Dichlorobenzal-	3:1145
c ₁	HYDRATES			dehyde	3:1690
C ₂ H ₄ O ₂ Cl ₂	Dichloroacetaldehyde hydrate	3:1085		hyde	3:0550
$C_2H_3O_2Cl_2$	Chloral hydrate	3:1270		hyde	3:1475
C ₄ H ₇ O ₂ Cl ₈	Butyrchloral hydrate.	3:1905	C7H8OCl3	2,3,4-Trichlorobenzal- dehyde	3:2445
C ₂	HEMIACETALS			2,3,5-Trichlorobenzal- dehyde	3:1060
$\mathrm{C_4H_8O_2Cl_2}$	Dichloroacetaldehyde ethyl alcoholate	3:5310		2,3,6-Trichlorobenzal- dehyde	3:2287
$C_4H_7O_2Cl_8$	Chloral ethyl alcohol-			2,4,5-Trichlorobenzal- dehyde	3:3375
	ate	3:0860		2,4,6-Trichlorobenzal- dehyde	3:1200
$C_6H_{11}O_2Cl_3$	Chloral n-butyl- alcoholate	3:0843		3,4,5-Trichlorobenzal-	
		0.0020		dehyde	3:2440
	Chloroacetaldchyde diethylacetal	3:8228	C7H2OCl4	2,3,4,5-Tetrachloro- benzaldehyde 2,3,4,6-Tetrachloro-	3:3140
$C_6H_{12}O_2Cl_2$	Dichloroacetaldehyde diethylacetal	3:6110		benzaldehyde 2,3,5,6-Tetrachloro- benzaldehyde	3:2700 3:2700
C6H11O2Cl3	Chloral diethylacetal .	3:6317	C TTOCI	•	00.000
$\mathrm{C_7H_{15}O_2Cl}$	β-Chloropropionalde- hyde diethylacetal	3: 9490	C7HOCl5	Pentachlorobenzal- dehyde	3:4892
C ₈ H ₁₇ O ₂ Cl	β-Chloro-n-butyralde-			enolic aldehydes	
0,1,0201	hyde diethylacetal .	3:95 94	C7H5O2Cl	3-Chloro-2-hydroxy- benzaldehyde	3:1010
	ACETALS WITH CHLORIN	E ONLY		4-Chloro-2-hydroxy- benzaldehyde	3:0960
	IN ALCOHOL RADICALS Formaldehyde β,β'-di-			5-Chloro-2-hydroxy-	
06111202012	chlorosopropyl-			benzaldehyde	3:2800
	ethyl-acetal Acetaldehyde bis-(β-	3:9 394		2-Chloro-3-hydroxy-	
	chloroethyl)acetal	3:6210		benzaldehyde 4-Chloro-3-hydroxy-	3:4085
Cā	POLYMERS			benzaldehyde	3:3780
C ₆ H ₉ O ₈ Cl ₃	Parachloro-			6-Chloro-3-hydroxy- benzaldehyde	3:3350
	acetaldehyde	3:2300		9 Chloro 4 hardnown	
C12H21O8Cl3	Para-β-chloro-n- butyraldehyde	3:2650		2-Chloro-4-hydroxy- benzaldehyde 3-Chloro-4-hydroxy-	3:4280
	Para-α-chloroiso- butyraldehyde	3:3220		benzaldehyde	3:4065
Q Arom	atic aldehudes	•	C7H4O2Cl2	3,5-Dichloro-2-	
	nple aldehydes			hydroxybenzal-	3:2637
C7H6OCl	o-Chlorobenzaldehyde	3:6410		dehyde	J. 2001
	<i>m</i> -Chlorobenzaldehyde <i>p</i> -Chlorobenzaldehyde	3:6475 3:0765		2,4-Dichloro-3-hy- droxybenzaldehyde.	3:41 40

C ₇ H ₄ O ₂ Cl ₂ Contd.	2,6-Dichloro-3-hy- droxybenzaldehyde. 4,6-Dichloro-3-hy- droxybenzaldehyde.	3:4160 3:3952	C ₆ OCl ₆	Hexachlorocyclo- hexadien-2,5-one-1 (" Hexachloro- phenol ")	3:3180
C7H4O2Cl3	3,5-Dichloro-4-hy- droxybensaldehyde. 2,4,6-Trichloro-3- hydroxybensal- dehyde	3:4400 3:8520	C ₆ O ₂ Cl ₆	1,2,3,4,6,6-Hexachloro- cyclohexen-1-dione- 3,5 ("Hexachloro- resorcinol") 2,3,5,5,6,6-Hexachloro- cyclohexen-2- dione-1,4	3:3470 3:2360
B. Of Ketor	168			,	0.2000
	yl ketones		•	l aryl ketones	
C _a H _a OCl	Chloroacetone	3:5425	a. w C ₈ H ₇ OCl	ith chlorine only in alkyl ω-Chloroaceto-	
Carract	Chioroacetone	J. 0420	Cantoci	phenone	3:1212
C ₃ H ₄ OCl ₂	α,α -Dichloroacetone α,α' -Dichloroacetone .	3:5430 3:0563	$C_8H_6OCl_2$	ω,ω-Dichloroaceto- phenone	3:6835
C ₈ H ₈ OCl ₈	α,α,α -Trichloro- acetone	3:5620	$\mathrm{C_8H_5OCl_3}$	ω,ω,ω-Trichloroaceto-	
	α,α,α' -Trichloro- acetone	3:5957		phenone	3:6847
C ₈ H ₂ OCl ₄	$\alpha,\alpha,\alpha,\alpha'$ -Tetrachloro-		C ₉ H ₉ OCl	α-Chloroethyl phenyl ketone	3:9664
	acetone $\alpha, \alpha, \alpha', \alpha'$ -Tetrachloro-acetone	3:6085 3:6050		β-Chloroethyl phenyl ketone	3:1115
C ₈ HOCl ₅	Pentachloroacetone	3:6205		ω-Chloro-o-methyl- acetophenone	3:9660
C ₈ OCl ₆	Hexachloroacetone	3:6312		ω-Chloro- p -methyl-acetophenone	3:1130
C ₄ H ₇ OCl	1-Chlorobutanone-2 3-Chlorobutanone-2 4-Chlorobutanone-2	3:8012 3:7598 3:7640	$\mathrm{C}_{10}\mathrm{H}_{11}\mathrm{OCl}$	ω-Chloro-2,4-di- methylacetophenone ω-Chloro-2,5-di-	3:1355
C ₄ H ₆ OCl ₂	1,3-Dichlorobutanone-	3:5900		methylacetophenone ω-Chloro-3,4-di- methylacetophenone	3:0245 3:1775
C ₅ H ₉ OCl	1-Chloropentanone-2. 3-Chloropentanone-2. 4-Chloropentanone-2. 5-Chloropentanone-2.	3:8217 3:7893 3:8243 3:9267	C ₁₄ H ₁₁ OCl	p-Phenylphenacyl chloride α-Chlorobenzyl phenyl ketone	3:3934 3:1618
	1-Chloropentanone-3 . 2-Chloropentanone-3 .	3:9268 3:7935	b. Wi	ith chlorine both in alkyl a p-Chlorophenacyl	_
	1-Chloro-2-methyl- butanone-3	3:9269	c Wi	chlorideth chlorine only in aryl	3:2990
	2-Chloro-2-methyl- butanone-3	3:7597	C ₈ H ₇ OCl	o-Chloroacetophenone m-Chloroacetophenone p-Chloroacetophenone	3:6615 3:6815 3:6735
2. Alicycl	lic ketones		C ₉ H ₉ OCl	p-Chlorophenyl ethyl	
C_6H_9OCl	2-Chlorocyclo-	9.6196		ketone	3:0340
	hexanone-1 3-Chlorocyclo-	3:0120	4. Diary	l ketones	
	hexanone-14-Chlorocyclo- hexanone-1	3:9360 3:9364	C ₁₈ H ₀ OCl	2-Chlorobenzophenone 3-Chlorobenzophenone 4-Chlorobenzophenone	3:0715 3:2160 3:1914
	TIONORIOTIA-T			OTTO LONGUE OF THE LIGHT	A. 1414

C ₁₈ H ₈ OCl ₈ 2,2'-Dichlorobenso- phenone	3:0717 3:9859-A 3:0825	C ₆ H ₂ O ₂ Cl ₂	2,3-Dichlorobenso- quinone-1,4	3:2855 3:4476 3:3750
phenone	3:1565 3:2340	C ₆ H ₂ O ₄ Cl ₂	2,5-Dichloro-3,6- dihydroxybenzo- quinone-1,4	3:4976
phenone	3:2285 3:3860	$\mathrm{C_6HO_2Cl_3}$	2,3,5-Trichlorobenzo- quinone-1,4	8:4672
phenone	3:3070 3:3415	C ₆ O ₂ Cl ₄	Tetrachlorobenzo- quinone-1,2 Tetrachlorobenzo- quinone-1,4	3:3965 3:4978
phenone 4,4 '-Dichlorobenzo- phenone	3:1505 3:4270		clear quinones	
5. Ketones containing also oth tional groups	er func-	$\mathrm{C}_{10}\mathrm{H}_{5}\mathrm{O}_{2}\mathrm{Cl}$	3-Chloronaphtho- quinone-1,2 4-Chloronaphtho-	3:4704
a. Keto-acid chlorides			quinone-1,2	3:4000
$C_4H_4O_2Cl_2$ Acetoacetyl chloride $C_4H_4O_2Cl_2$ γ -Chloroacetoacetyl	3:9098		2-Chloronaphtho- quinone-1,4	3:3580
chloride	3:9088		5-Chloronaphtho- quinone-1,4	3:4492
$\begin{array}{ccc} C_{14}H_9O_2Cl & \text{o-Benzoylbenzoyl} \\ & \text{c-hloride} \end{array}$	3:9880		6-Chloronaphtho- quinone-1,4	3:3145
b. Keto-acid esters		$\mathrm{C}_{10}\mathrm{H}_4\mathrm{O}_2\mathrm{Cl}_2$	3,4-Dichloronaphtho-	
C ₆ H ₉ O ₃ Cl Ethyl α-chloroaceto- acetate	3:6207		quinone-1,2 2,3-Dichloronaphtho- quinone-1,4	3:4775 3:4857
Ethyl γ -chloroaceto-acetate	3:6375	3. Trinı	uclear quinones	012301
C. Of Quinones		C14H7O4Cl	1-Chloroanthra-	
1. Mononuclear quinones		01911/0301	quinone	3:4480
C ₆ H ₃ O ₂ Cl 2-Chlorobenzo- quinone-1,4	3:1100		2-Chloroanthra- quinone	3:4922

UNIT 6. CHLORO SUBSTITUTION PRODUCTS OF CARBOXYLIC ACIDS AND ANHYDRIDES

(Summary of Classification of Unit 6)

A. OF ACYCLIC ACIDS.

- 1. With no other functional group.
 - a. Saturated monobasic.
 - b. Saturated dibasic.
 - c. Unsaturated (olefinic) monobasic.d. Unsaturated (olefinic) dibasic.

 - e. Unsaturated (acetylenic) monobasic.
- 2. With some other functional group.
 - a. Hydroxy monobasic.

- B. OF ISOCYCLIC ACIDS.
 - 1. With no other functional group.
 - a. Monobasic.

 - b. Dibasic.c. Tribasic.
 - 2. With some other functional group.
 - a. Phenolic acids.
 - b. Ether acids.
- C. ANHYDRIDES OF ACYCLIC ACIDS.
 - 1. Saturated.
 - 2. Unsaturated.
- D. ANHYDRIDES OF ISOCYCLIC ACIDS.

UNIT 6. CHLORO SUBSTITUTION PRODUCTS OF CARBOXYLIC ACIDS AND ANHYDRIDES

(For acyl chlorides see Unit 7)

A. Of Acyc			C4H5O2Cl3	α, α, γ -Trichloro- n -	0.4004
	no other functional grou	Þ	Contd.	butyric acid α, β, β -Trichloro- n -	3:1831
a. Sa C ₂ H ₃ O ₂ Cl	turated monobasic Chloroacetic acid	3:1370		butryic acid γ, γ, γ -Trichloro- n -	3:0925
$\mathrm{C_2H_2O_2Cl_2}$	Dichloroacetic acid	3:6208		butryic acid	3:1000
$\mathrm{C_2HO_2Cl_3}$	Trichloroacetic acid	3:115 0	C ₄ H ₇ O ₂ Cl	α-Chloroisobutyric acid	3:0235
$C_3H_5O_2Cl$	α -Chloropropionic acid β -Chloropropionic acid	3:6125 3:0460		β-Chloroisobutyric acid	3:9132
C ₈ H ₄ O ₂ Cl ₂	α, α -Dichloropropionic acid α, β -Dichloropropionic acid	3:6162 3:0855	C ₆ H ₉ O ₂ Cl	α -Chloro- n -valeric acid β -Chloro- n -valeric acid γ -Chloro- n -valeric acid δ -Chloro- n -valeric acid	3:8783 3:0270 3:9270 3:0075
	β,β -Dichloropropionic acid	3:1058		α-Chloro-α-methyl-n- butyric acid α-Chloro-β-methyl-n-	3:8718
C ₈ H ₈ O ₂ Cl ₃	α,α,β -Trichloropropionic acid	3:1275		butyric acid β -Chloro- α , α -dimethyl-	3:0050
C ₃ H ₂ O ₂ Cl ₄	$\alpha, \alpha, \beta, \beta$ -Tetrachloro- propionic acid	3:1850	1 0	propionic acid	3:0440
C ₈ HO ₂ Cl ₅	Pentachloropropionic acid	3:4895	C ₄ H ₄ O ₄ Cl ₂	turated dibasic d,l - α,α' -Dichloro-	0.4844
C ₄ H ₇ O ₂ Cl	α-Chloro-n-butyric acid	3:9130		succinic acid $meso-\alpha,\alpha'$ -Dichlorosuccinic acid	3:4711 3:4930
	β-Chloro-n-butyric acid	3:0035	c. Ur	saturated (olefinic) mon	obasic
	γ -Chloro- n -butyric acid	3:0020	C ₈ H ₃ O ₂ Cl	α -Chloroacrylic acid β -Chloroacrylic acid	3:1445 3:2240
C ₄ H ₆ O ₂ Cl ₂	α,β-Dichloro-n-butyric acid Higher-melting isomer Lower-melting isomer.	3:1903 3:1375	C ₂ H ₂ O ₂ Cl ₂	α,β -Dichloroacrylic acid β,β -Dichloroacrylic acid	3:2265 3:1875
$C_4H_5O_2Cl_3$	α,α,β-Trichloro-n- butyric acid	3:1280	C ₈ HO ₂ Cl ₈	α,β,β -Trichloroacrylic acid	3:18 40

C₄H₄O₂Cl	α-Chlorocrotonic acid. α-Chloroisocrotonic acid β-Chlorocrotonic acid. β-Chloroisocrotonic	3:2760 3:1615 3:2625	$\mathrm{C_8H_7O_2Cl}$	3-Chloro-2-methylbenzoic acid 4-Chloro-2-methylbenzoic acid 5-Chloro-2-methyl-	3:4435 3:4700
	acid γ -Chlorocrotonic acid.	3:1300 3:2170		benzoic acid 6-Chloro-2-methyl- benzoic acid	3:4670 3:3275
d. U	nsaturated (olefinic) dibas	sic			
C ₄ H ₃ O ₄ Cl	Chlorofumaric acid Chloromaleic acid	3:4853 3:3432		4-Chloro-3-methyl- benzoic acid 5-Chloro-3-methyl-	3: 49 15
$C_4H_2O_4Cl_2$	Dichloromaleic acid	3:3634		benzoic acid 6-Chloro-3-methyl-	3:4715
e. Ur	nsaturated (acetylenic) m	onobasic		benzoic acid	3:4615
C_3HO_2Cl	Chloropropiolic acid	3:1685		2-Chloro-4-methyl-	
	some other functional gr ydroxy monobasic	оир		benzoic acid 3-Chloro-4-methyl-	3:4355
	β , β -Dichloro- α -hydroxy-	_		benzoic acid	3:4900
0411603012	isobutyric acid β,β' -Dichloro- α -hydroxy isobutyric acid.	3:2145		2-Chlorophenylacetic acid	3:2640
	•	3.7000		3-Chlorophenylacetic acid	3:1910
B. Of Isocy				4-Chlorophenylacetic	9.9195
	no other functional grou <u>f</u> Ionabasia	,		acid	3:3135
C7H5O2Cl	Ionobasic o-Chlorobenzoic acid m-Chlorobenzoic acid.	3:4150 3:4392	C ₁₄ H ₁₁ O ₂ Cl	Diphenyl-chloroacetic acid	3:3585
	p-Chlorobenzoic acid .	3:4940	$C_{14}H_{10}O_{2}Cl_{2}$	Di-(p-chlorophenyl)-	
$C_7H_4O_2Cl_2$	2,3-Dichlorobenzoic	0.4050		acetic acid	3:4612
	acid	3:4650	C ₂ H ₅ O ₂ Cl	o-Chlorophenylpro-	
	acid	3:4560		piolie acid	3:3956
	2,5-Dichlorobenzoic acid	3:43 40		m-Chlorophenylpro- piolic acid	3:4102
	2,6-Dichlorobenzoic	0.4000	•	p-Chlorophenylpro-	9.4907
	acid 3,4-Dichlorobenzoic .	3:4200		piolie acid	3:4265
	acid	3:4925	$C_{11}H_7O_2Cl$	2-Chloronaphthoic	
	3,5-Dichlorobenzoic acid	3:4840		acid-14-Chloronaphthoic acid-1	3:4330 3:4936
$C_7H_8O_2Cl_8$	2,3,4-Trichlorobenzoic	3:4810		5-Chloronaphthoic	
	acid			acid-1 6-Chloronaphthoic	3:4944
	acid	3:4485		acid-1	3:4845
	2,3,6-Trichlorobenzoic acid	3:4500		7-Chloronaphthoic acid-1	3:4942
	2,4,5-Trichlorobenzoic acid	3:4630		8-Chloronaphthoic acid-1	3:4680
	2,4,6-Trichlorobenzoic	3:4545			~ · #400
	acid			1-Chloronaphthoic acid-2	3:4885
	acid	3:4920		3-Chloronaphthoic	
C7H2O2Cl4	2,3,4,5-Tetrachloro- benzoic acid	3:4790		acid-2 5-Chloronaphthoic acid-2	3:4982 3:4952
C7HO2Cl5	Pentachlorobenzoic acid	3: 4910		8-Chloronaphthoic acid-2	3:4948

b. Di			C7H5O8Cl Contd.	2-Chloro-4-hydroxy- bensoic acid	3:4430
C ₈ H ₅ O ₄ Cl	3-Chlorophthalic acid. 4-Chlorophthalic acid.	3:4820 3:4390	Control.	3-Chloro-4-hydroxy- benzoic acid	3:4675
C ₈ H ₄ O ₄ Cl ₂	3,4-Dichlorophthalic acid	.3:4880	$C_7H_4O_8Cl_2$	3,5-Dichloro-4-hydroxy- benzoic acid	3:4950
	acid	3:4580	b. Et	her acids	
	3,6-Dichlorophthalic acid	3:4870	C ₈ H ₇ O ₈ Cl	o-Chlorophenoxyacetic	3:4260
	acid	3:4890		m-Chlorophenoxyacetic	
C ₈ H ₂ O ₄ Cl ₄	Tetrachlorophthalic acid	3:4946		acidp-Chlorophenoxyacetic acid	3:3325 3:4375
C ₈ H ₅ O ₄ Cl	4-Chloroisophthalic acid	3:4980	$C_8H_6O_8Cl_2$	2,4-Dichlorophenoxy- acetic acid	3:409 5
	acid	3:4960	$\mathrm{C_8H_5O_3Cl_3}$	2,4,5-Trichlorophenoxy- acetic acid	3:4335
C ₈ H ₄ O ₄ Cl ₂	4,6-Dichloroisophthalic acid	3:4965	C. Anhydri	des of Acyclic Acids	
C ₈ H ₅ O ₄ Cl	Chloroterephthalic acid	3:4 99 5	C ₄ H ₄ O ₈ Cl ₂	Chloroacetic acid anhydride	3:0730
$C_8H_4O_4Cl_2$	2,5-Dichloroterephthalic acid	3:4985	$C_4H_2O_3CL_4$	Dichloroacetic acid anhydride	3:6430
c. Tr			$\mathbf{C_4O_3Cl_6}$	Trichloroacetic acid anhydride	8:6575
C ₉ H ₆ O ₆ Cl	5-Chlorobenzenetri- carboxylic acid-1,2,4	3:4855	2. Unsa	•	0.00.0
	2-Chlorobenzenetri- carboxylic acid-1,3,5	3:4975	C4HO3Cl	Chloromaleic an- hydride	3:0280
2. With	some other functional gre	oup	C ₄ O ₃ Cl ₂	Dichloromaleic	
a. Ph	enolic acids		0403012	anhydride	3:3635
C7H6O3Cl	3-Chloro-2-hydroxy- benzoic acid	3:4745		des of Isocyclic Acids	
	4-Chloro-2-hydroxy- benzoic acid 5-Chloro-2-hydroxy-	3:4908	C ₈ H ₃ O ₃ Cl	3-Chlorophthalic anhydride 4-Chlorophthalic	3:3900
	benzoic acid	3:4705		anhydride	3:2725
	6-Chloro-2-hydroxy- benzoic acid	3:4610	$\mathrm{C_8H_2O_8Cl_2}$	3,4-Dichlorophthalic	3:3695
$\mathrm{C}_7\mathrm{H}_4\mathrm{O}_8\mathrm{Cl}_2$	3,5-Dichloro-2-hydroxy- benzoic acid	3:4935		3,5-Dichlorophthalic anhydride	3:2375
0 11 0 01				3,6-Dichlorophthalic	
C7H5O8Cl	2-Chloro-3-hydroxy- benzoic acid	3:4395		anhydride	3:4860
	4-Chloro-3-hydroxy- benzoic acid	3:4933		anhydride	3:4830
	6-Chloro-3-hydroxy- benzoic acid	8:4720	C ₈ O ₃ Cl ₄	Tetrachlorophthalic anhydride	3:4947
		·			

UNIT 7. ACYL CHLORIDES

(Summary of Classification of Unit 7)

A. OF ACYCLIC ACIDS (R.CO.Cl).

- 1. The radical (R) contains no chlorine.
 - a. Corresponding acid is saturated and monobasic.
 - b. Corresponding acid is saturated and dibasic.
 - c. Corresponding acid is unsaturated and monobasic.
 - d. Corresponding acid is unsaturated and dibasic.
 - e. Corresponding acid contains also other functional groups.
 - e₁ Ether/acyl chloride.
 - e₂ Ester/acyl chloride.
 - es Keto/acyl chloride.
- 2. The radical (R) does contain chlorine.
 - a. Corresponding acid is saturated and monobasic.
 - b. Corresponding acid is saturated and dibasic.
 - c. Corresponding acid is unsaturated and monobasic.
 - d. Corresponding acid is unsaturated and dibasic.
 - e. Corresponding acid contains other functional groups.

B. OF ISOCYCLIC ACIDS.

- 1. The radical (R) contains no chlorine.
 - a. Corresponding acid is monobasic.
 - at With -COOH group attached to ring.
 - a2 With -COOH group attached to saturated side chain.
 - as With -- COOH group attached to unsaturated side chain.
 - as With —COOH group attached to ring containing another functional group.
 - b. Corresponding acid is dibasic.
- 2. The radical (R) does contain chlorine.
 - Corresponding acid is monobasic.

C. OF HETEROCYCLIC ACIDS.

- 1. The radical (R) contains no chlorine.
 - a. Corresponding acid is monobasic.

UNIT 7. ACYL CHLORIDES

A. Of Acyc	lic Acids (R.CO.OH)		C ₆ H ₁₁ OCl	n-Caproyl chloride	3:8168
1. The	radical (R) contains no	chlorine			
	orresponding acid is satura conobasic	ited and		α-Methyl-n-valeryl chloride	3:8020
C ₂ H ₃ OCl	Acetyl chloride	3:7065		β-Methyl-n-valeryl chloride	3:8035
C ₈ H ₅ OCl	Propionyl chloride	3:7170		γ -Methyl- n -valeryl chloride	3:8090
C ₄ H ₇ OCl	n-Butyryl chloride Isobutyryl chloride			α-Ethyl-n-butyryl chloride	3:7 990
C_bH_0OCl	n-Valeryl chloride	3:77 49		a,a-Dimethyl-n-	
	α-Methyl-n-butyryl chloride	3:7603		butyryl chloride a, \beta-Dimethyl-n- butyryl chloride	
	β-Methyl-n-butyryl chloride	3:7560		β , β -Dimethyl- n -butyrylchloride	3:7880
	α,α -Dimethylpropionyl chloride	3:7450	C7H18OCl	n-Heptanoyl chloride .	8:8520

C7H18OCl Contd.	α-Methyl-n-caproyl chloride	3:9452	$C_7H_{10}O_2Cl_2$	Pimelyl (di)chloride 3:945
COLICA.	β -Methyl- n -caproyl		$\mathrm{C_8H_{12}O_2Cl_2}$	Suberyl (di)chloride 3:9576
	chloride γ-Methyl- <i>n</i> -caproyl	3:8305	$C_9H_{14}O_2Cl_2$	Azelayl (di)chloride 3:9686
	chloride δ-Methyl-n-caproyl chloride	3:8355 3:8365	C ₁₀ H ₁₆ O ₂ Cl ₂	Sebacyl (di)chloride 3:978
	α-Ethyl-n-valeryl	4.000		orresp. acid is unsaturated and
	chloride	3:8235	C ₃ H ₃ OCl	Acrylyl chloride 3:715
	α, α -Dimethyl- n -valeryl		C_4H_5OCl	α-Crotonoyl chloride 3:769
	chloride α,β -Dimethyl- n -valeryl	3:9456	C_bH_7OCl	cis-\alpha-Methylcrotonoyl
	chloride γ, γ -Dimethyl- n -valeryl		G TT 0.01	chloride 3:924
	chloride	3:9460	C ₁₈ H ₈₈ OCl	Elaidyl chloride 3:9950 Oleyl chloride 3:9940
	α-Ethyl-β-methyl-n- butyryl chloride α,α,β-Trimethyl-n-	3:9462		orresp. acid is unsaturated and
	butyryl chloride	3:8145	$\mathrm{C_4H_2O_2Cl_2}$	Fumaryl (di)chloride . 3:5878
C ₈ H ₁₅ OCl	n-Octanoyl chloride	3:8680		orresp. acid contains also other
C ₉ H ₁₇ OCl	Pelargonyl chloride	3:8765	e₁ C₃H₅O₂Cl	ETHER/ACYL CHLORIDE Methoxyacetyl
C ₁₀ H ₁₉ OCl	n-Decanoyl chloride	3:8800	081180201	chloride 3:5226
C ₁₁ H ₂₁ OCl	n-Undecanoyl chloride	3:9800	$C_4H_7O_2Cl$	Ethoxyacetyl chloride 3:7745
C ₁₂ H ₂₈ OCl	n-Lauroyl chloride	3:9858	C ₄ H ₄ O ₃ Cl ₂	Diglycoloyl (di)- chloride 3:909%
C ₁₈ H ₁₈ OCl	<i>n</i> -Tridecanoyl chloride	3:9860	_	ESTER/ACYL CHLORIDE
C ₁₄ H ₂₇ OCl	Myristoyl chloride	3:9885	(For esters C ₄ H ₅ O ₃ Cl	of chloroformic acid see Unit 8) Ethoxalyl chloride 3:5625
C ₁₅ H ₂₉ OCl	n-Pentadecanoyl chloride	3:9900		Carbomethoxyacetyl chloride 3:9098-A
C ₁₆ H ₈₁ OCl	Palmitoyl chloride	3:9912	$C_5H_7O_8Cl$	β-(Carbomethoxy)pro- pionyl chloride 3:9247
C ₁₇ H ₈₈ OCl	Margaroyl chloride	3:9925		Carbethoxyacetyl chloride 3:9246
C ₁₈ H ₈₆ OCl	Stearoyl chloride	3:9960	$C_6H_9O_8C1$	γ-(Carbomethoxy)-n-
b. Co	orresp. acid is saturated	and di-	C ₁₁ H ₁₉ O ₈ Cl	butyryl chloride 3:9373 (Carbomethoxy)-
COCl	Carbonyl (di)chloride			pelargonyl chloride. 3:9792
	(phosgene)	3:5000	e ₃ C ₄ H ₅ O ₂ Cl	KETO/ACYL CHLORIDE Acetoacetyl chloride. 3:9098
$C_2O_2Cl_2$	Oxalyl (di)chloride	3:5060		•
C ₈ H ₂ O ₂ Cl ₂	Malonyl (di)chloride	3:9030		adical (R) does contain chlorine rresp. acid is saturated and mono-
C ₄ H ₄ O ₂ Cl ₂	Succinyl (di)chloride	3:6200	bas C ₂ H ₂ OCl ₂	sic Chloroacetyl chloride . 3:5235
C ₅ H ₆ O ₂ Cl ₂	Glutaryl (di)chloride .	3:6500	C ₂ H ₂ OCl ₂	
C ₆ H ₈ O ₂ Cl ₂	Adipyl (di)chloride	3:9352	O3110/C18	Dichloroacetyl chloride 3:5290

C2OCL	Trichloroacetyl chloride	3:5420	C ₄ HO ₂ Cl ₃ Contd.	Chloromaleyl (di)- chloride 3:6158
C ₂ H ₄ OCl ₂	α-Chloropropionyl chloride	3:5320	C ₄ O ₂ Cl ₄	Dichloromaleyl (di)- chloride 3:6197
	chloride	3:5690		orresp. acid contains other func-
C ₈ H ₈ OCl ₈	α,α-Dichloropropionylchlorideα,β-Dichloropropionyl	3:5372	C ₄ H ₄ O ₂ Cl ₂	γ-Chloroacetoacetyl chloride 3:9888
	chloride	3:9032	B. Of Isocy	yclic Acids
	β,β -Dichloropropionyl chloride 3	: 9032-A	1. The	radical (R) contains no chlorine
			aC	orresp. acid is monobasic
C ₃ OCl ₆	Pentachloropropionyl chloride	3:0470	a _i	WITH —COOH ATTACHED TO RING
$C_4H_6O_2Cl_2$	α-Chloro-n-butyryl chloride	3:5570	C7H11OCl	Hexahydrobenzoyl chloride 3:8589
	β-Chloro-n-butyryl chloride	3:9100	C_7H_6OCl	Benzoyl chloride 3:6240
	γ-Chloro-n-butyryl chloride	3:5970	C ₈ H ₇ OCl	o-Toluyl chloride 3:8740 m-Toluyl chloride 3:6535 p-Toluyl chloride 3:6600
	α-Chloro-isobutyryl chloride	3:5385		p = 0.000
	β-Chloro-isobutyryl chloride	3:9101	C ₁₀ H ₁₁ OCl	2,4,6-Trimethyl- benzoyl chloride 3:9750
$C_6H_8OCl_2$	α-Chloro-n-valeryl chloride	3:5860	C ₁₁ H ₇ OCl	α -Naphthoyl chloride. 3:6930 β -Naphthoyl chloride. 3:0900
	γ-Chloro-n-valeryl chloride	3:9260	82	WITH —COOH GROUP ATTACHED TO SATURATED SIDE CHAIN
	δ-Chloro-n-valeryl chloride	3:9264	$C_8H_7O_2Cl$	Phenylacetyl chloride. 3:9567
	α-Chloro-α-methyl-n- butyryl chloride α-Chloro-β-methyl-n-	3:5670	C ₉ H ₉ OCl	β-Phenylpropionyl chloride 3:8787
	butyryl chloride	3:8144	C ₁₂ H ₉ OCl	α -Naphthylacetyl chloride 3:9856
	β -Chloro- α , α -di-			000
	methylpropionyl chloride	3:9266	8.8	WITH —COOH GROUP ATTACHED TO UNSATURATED SIDE CHAIN
	rresp. acid is saturated	and di-	C ₉ H ₇ OCl	Cinnamoyl chloride 3:0339
	asic		C ₉ H ₅ OCl	Phenylpropiolyl
C ₄ H ₂ O ₂ Cl ₄	d,l-α,α'-Dichloro- succinyl (di)chloride	3:0395		chloride 3:9658
	meso-α,α'-Dichloro- succinyl (di)chloride	3:9087	84	WITH —COOH ATTACHED TO RING CONTAINING ANOTHER FUNC- TIONAL GROUP
	rresp. acid is unsaturat onobasic	ed and	$C_7H_6O_2Cl$	2-Hydroxybenzoyl chloride 3:9085
C ₈ OCl ₄	Trichloroacryloyl chloride	3:5845		3-Hydroxybenzoyl chloride 3:9446
	orresp. acid is unsaturated	and di-		4-Hydroxybenzoyl chloride 3:9447
ba C ₄ HO ₂ Cl ₃	Chlorofumaryl (di)- chloride	3:6105	C ₈ H ₇ O ₂ Cl	2-Methoxybenzoyl chloride 3:6879

Contd. 3-Methoxybensoyl chloride		3:6797		the radical (R) does contain chlorine. Corresp. acid is monobasic	
	chloride	3:6899	C7H4OCl2	o-Chlorobenzoyl chloride m-Chlorobenzoyl	3:6640
	chloride	3:8790		chloride p-Chlorobenzoyl	3:6590
$C_8H_4O_8Cl$	Piperonyloyl chloride.	3:1960		chloride	3:6550
C ₁₄ H ₉ O ₂ Cl	o-Benzoylbenzoyl chloride	3:9880	C7OCl6	Pentachlorobenzoyl chloride	3:2295
b. Co	orresp. acid is dibasic		CHOCh	α-Chloro-diphenyl-	
C ₈ H ₄ O ₂ Cl ₂	chloride	9.0000	01411100012	acetyl chloride	3:0885
unsymo-Phthalyl (di)chloride	3:2395		rocyclic Acids		
	Isophthalyl (di)- chloride	3:0520	a. Co	re R contains no chlorine orresp. acid is monobasic	
	Terephthalyl (di)-	3:2205	C ₅ H ₂ O ₂ Cl	Furoyl chloride	3:8515

UNIT 8. CHLORO SUBSTITUTION PRODUCTS OF ETHERS AND OF ESTERS

(Summary of Classification of Unit 8)

A. ETHERS.

- 1. Completely acyclic saturated ethers.
 - a. Monoethers.
 - a₁ Derived from symmetrical ethers.
 - a2 Derived from unsymmetrical ethers.
 - b. Diethers.
 - c. Ethers containing also other functions.
 - c1 Ether/alcohols.
 - c₂ Ether/esters.
 - ca Ether/ester/alcohols.
 - c4 Ether/ester/acyl halides.
- 2. Completely acyclic unsaturated ethers.
- 3. Cyclic ethers.
 - a. Non-aromatic.
 - a₁ Monoethers.
 - a₂ Diethers.
 - b. Aromatic ethers (phenol ethers).
 - c. Heterocyclic ethers.

B. ESTERS.

- 1. Esters of aliphatic acids.
 - a. Acids containing no chlorine.
 - a₁ From acetic acid.
 - as From oxalic acid.
 - as From carbonic acid.
 - b. Saturated monobasic acids containing chlorine.
 - b₁ From chloroacetic acid.
 - ba From dichloroscetic scid.
 - be From trichloroacetic acid.

- b4 From chloropropionic acid.
- bs From chlorobutyric acids.
- be From chlorovaleric acids.
- c. Saturated dibasic acids containing chlorine.
 d. Unsaturated monobasic acids containing chlorine.
- e. Unsaturated dibasic acids containing chlorine.
- f. Esters of chloroformic acid.
- g. Esters of keto acids.
- 2. Esters of aromatic acids.
 - a. Acids containing no chlorine.
 - b. Acids containing chlorine.
- 3. Esters of inorganic acids.
- 4. Esters containing also other functional groups.
 - a. Ester/alcohols.
 - a₁ From acids containing no chlorine.
 - a₂ From acids containing chlorine.
 - b. Ester/acyl chlorides.
 - c. Ester/ethers.
 - d. Ester/ether/alcohols.
 - e. Ester/ether/acyl chlorides.

UNIT 8. CHLORINE SUBSTITUTION PRODUCTS OF ETHERS AND ESTERS

A. Ethers 1. Com	pletely acyclic saturated (ethers	C ₆ H ₁₂ OCl ₂ Contd.	β , β' -Dichloro-di- isopropyl ether	3:8605
	Ionoethers			82 DERIVED FROM UNSYMB	IETRICAL
a ₁	DERIVED FROM SYMMETR ETHERS	ICAL	C₃H₁OCl	ETHERS Ethyl chloromethyl	
C ₂ H ₅ OCl	Chloromethyl methyl ether	3:7085		ether	3:7195 3:7150
C ₂ H ₄ OCl ₂	symDichlorodimethyl ether	3:5245		β-Chloroethyl methyl ether	3:7265
C ₄ H ₉ OCl	α-Chloroethyl ethyl	3:7305	C ₆ H ₁₁ OCl	α-Chloroethyl n- propyl ether	3:7525
	ether β-Chloroethyl ethyl ether	3:7463	C ₆ H ₁₈ OCl	α-Chloroethyl n- butyl ether	3:9396
C ₄ H ₈ OCl ₃	α, α' -Dichlorodiethyl ether	3:7595	C7H15OCl	α -Chloroethyl n - amyl ether	3:9480
	α,β -Dichlorodiethyl ether	3:5640	b. Di	ethers	
	α, β' -Dichlorodiethyl ether	3:9150	C ₆ H ₁₂ O ₂ Cl ₂	Ethylene glycol bis- (β-chloroethyl) ether	2 · 88KK
	ether	3:6025			
C ₄ H ₂ OCl ₈	Octachlorodiethyl ether	3:0738	tio		er iune-
C4OCl10	Decachlorodiethyl ether	3:1676	$C_4H_9O_2Cl$	β-Chloro-β'-hydroxy- diethyl ether	3:9185
C ₆ H ₁₂ OCl ₂	β, β' -Dichloro-di- n - propyl ether	3:8610	_	ETHER/ESTERS	
	γ, γ' -Dichloro-di- n propyl ether	3:8745	C ₅ H ₉ O ₅ Cl	β-Methoxyethyl chloroacetate	3.: 9265

C ₅ H ₇ O ₈ Cl ₈	β-Methoxyethyl tri- chloroacetate	3:9250	c. H C₅H ₉ OCl	eterocyclic ethers Tetrahydro-α- furfuryl chloride	3:8152
Cs	ETHER/ESTER/ALCOHOLS	l.		1411419	
C ₆ H ₁₁ O ₄ Cl	Diethylene glycol mono(chloroacetate)	3:9390		ed according to acid rad on according to alkyl or a	
$C_8H_{16}O_5Cl$	Triethylene glycol mono(chloroacetate)	3:9588	cals see Alı	phabetical Index.	aryi radi-
٠.	ETHER/ESTER/ACYL HALI	rnwa		cids containing no chloris	10
	· · · · · · · · · · · · · · · · · · ·	DES	u. A	cids containing no emorn	10
C ₄ H ₇ O ₃ Cl	β-Methoxyethyl chloroformate	3:9140	a ₁ C ₈ H ₅ O ₂ Cl	FROM ACETIC ACID Chloromethyl acetate.	3:5356
C ₅ H ₉ O ₃ Cl	β-Ethoxyethy! chloroformate	3:9280	C ₄ H ₇ O ₂ Cl	α-Chloroethyl acetate. β-Chloroethyl acetate.	3:7625 3:5735
2. Com	pletely acyclic unsaturate	d ethers			
C ₄ H ₇ OCl	β-Chloroethyl vinyl	3:7464	$C_6H_9O_2C1$	β-Chloro- n -propyl acetate $γ$ -Chloro- n -propyl	3:8180
	ether	0.7101		acetate	3:8310
C ₄ H ₆ OCl ₈	α,β -Dichlorovinyl ethyl ether	3:5540	$\mathrm{C_{5}H_{8}O_{2}Cl_{2}}$	β, γ -Dichloro- n - propyl acetate	3:6220
C4OCl6	Di-(trichlorovinyl) ether	3:6373	$\mathrm{C_{5}H_{9}O_{2}Cl}$	β-Chloroisopropyl acetate	3:8150
3. Cycli	c ethers				
-	on-aromatic		$\mathrm{C_{5}H_{8}O_{2}Cl_{2}}$	β, β' -Dichloroisopropyl	
	MONOETHERS			acetate	3:6318
C ₈ H ₆ OCl	3-Chloro-1,2- epoxypropane	3:5358	$\mathrm{C_6H_9O_2Cl_3}$	β,β,β -Trichloro-terbutyl acetate	3:6180
C ₈ H ₃ OCl ₈	3,3,3-Trichloro-1,2- epoxypropane	3:5760	$C_7H_{11}O_4Cl_8$	3-Chloropropane- diol-1,2 diacetate	3:6840
C ₄ H ₇ OCl	3-Chloro-2-methyl-1, 2-epoxypropane	3:7657	$\mathrm{C_6H_8O_4Cl_2}^{\mathrm{fl_2}}$	FROM OXALIC ACID bis-(β-Chloroethyl) oxalate	3:0572
82	DIETHERS				0.0000
$C_4H_6O_2Cl_2$	2,3-Dichlorodioxane- 1,4	3:9105	C _{\$} O _{\$} Cl ₆	bis-(Trichloromethyl) carbonate	3:1915
b. Ar	omatic ethers (phenol eth	hers)			
C7H7OCl	o-Chloroanisole m-Chloroanisole	3:6255 3:6195	$\mathbf{C_5H_8O_3Cl_2}$	Di- $(\beta$ -chloroethyl) carbonate	3:6790
	p-Chloroanisole ω-Chloroanisole	3:6300 3:9448	$\mathrm{C_7H_{12}O_3Cl_2}$	Di- $(\gamma$ -chloro- n -propyl) carbonate	3:6895
C ₈ H ₉ OCl	o-Chlorophenetole m-Chlorophenetole p-Chlorophenetole	3:8735 3:6323 3:0090		turated monobasic acids on chlorine	contain-
	ω-Chlorophenetole	3:0165	$\mathbf{b_1}$	FROM CHLOROACETIC ACI	9
			$C_3H_5O_2Cl$	Methyl chloroacetate.	3:5585
C ₁ H ₁₁ OCl	γ-Chloro-n-propyl phenyl ether	3:8820	C ₄ H ₇ O ₂ Cl	Ethyl chloroacetate	3:5700
C ₁₀ H ₁₈ O ₂ Cl	β -Chloroethyl β' - phenoxyethyl ether.	3:9770	$C_4H_6O_2Cl_2$	β -Chloroethyl chloro- acetate	3:6230

C ₄ H ₇ O ₈ Cl	β -Hydroxyethyl chloro- acetate	3:6780	C ₅ H ₇ O ₈ Cl ₃	β -Methoxyethyl tri- chloroacetate	3:9250
$C_bH_9O_8Cl$	β-Methoxyethyl chloro- acetate	3:9285	$C_6H_7O_2Cl_8$	n-Propyl trichloro- acetate	3:6135
C ₅ H ₉ O ₂ Cl	n-Propyl chloroacetate	3:8295		Isopropyl trichloro- acetate	3:5975
	Isopropyl chloro- acetate	3:8160	C ₆ H ₉ O ₂ Cl ₃	n-Butyl trichloro-	0.000
C.H. O.Cl			0611403013	acetate	3: 63 15
$C_6H_{11}O_2Cl$	n-Butyl chloroacetate Isobutyl chloro-	3:8530		Isobutyl trichloro- acetate	3:61 40
	acetatesecButyl chloro-	3:8375		secButyl trichloro- acetate	3:9372
	*acetate ter-Butyl chloro-	3:8350		ter-Butyl trichloro- acetate	3:0138
	acetate	3:8220	C ₇ H ₁₁ O ₂ Cl ₃		
C ₄ H ₇ O ₃ Cl	Ethylene glycol mono- (chloroacetate)	3:6780	O/MIO2OI3	acetate Isoamyl trichloro-	3:6560
$\mathrm{C_6H_8O_4Cl_2}$	Ethylene glycol bis- (chloroacetate)	3:0720		acetate ter-Amyl trichloro- acetate	3:6490 3:6185
C ₈ H ₂₁ O ₄ Cl	Diethylene glycol		h .	FROM CHLOROPROPIONIC	0.0100
Ogrinotor	mono(chloroacetate)	3:9390		ACIDS	
$\mathrm{C_8H_{1\delta}O_{\delta}Cl}$	Triethylene glycol mono(chloroacetate)	3:9588	C ₄ H ₇ O ₂ Cl	Methyl α -chloropropionate	3:7908
C ₈ H ₇ O ₂ Cl	Phenyl chloroacetate .	3:0565	$C_5H_9O_2Cl$	Ethyl α-chloropro- pionate	3:8125
b_2	FROM DICHLOROACETIC AC	CID	$C_6H_{11}O_2Cl$	n-Propyl α-chloro-	
$\mathrm{C_8H_4O_2Cl_2}$	Methyl dichloro- acetate	3:5655		propionate Isopropyl α-chloro- propionate	3:9384 3:8165
$C_4H_6O_2Cl_2$	Ethyl dichloroacetate.	3:5850	C7H18O2Cl	n-Butyl α-chloropro-	010200
C ₄ H ₆ O ₃ Cl ₂	β -Hydroxyethyl		C/11/80201	pionate	3:8595
	dichloroacetate	3:9107		Isobutyl α -chloropropionate	3:9470
$\mathrm{C_{5}H_{8}O_{2}Cl_{2}}$	n-Propyl dichloro- acetate	3:6000	$\mathrm{C_8H_{15}O_2Cl}$	Isoamyl α -chloropropionate	3:9580
	acetate	3:5890	C ₄ H ₇ O ₂ Cl	Methyl β-chloropro- pionate	3:5765
b ₈	FROM TRICHLOROACETIC	CID	C T O CI	_	
$\mathrm{C_3H_3O_2Cl_3}$	Methyl trichloro- acetate	3:5800	C ₈ H ₉ O ₂ Cl	Ethyl β -chloropropionate	3:8290
$\mathrm{C_{8}O_{2}Cl_{6}}$	Trichloromethyl trichloroacetate	3:0290	C ₆ H ₁₁ O ₂ Cl	n -Propyl β -chloropropionate Isopropyl β -chloropro-	3:8545
C ₄ H ₅ O ₂ Cl ₃	Ethyl trichloro-	- -		pionate	3:9388
O4119O3O13	acetate	3:5950	$C_7H_{18}O_2Cl$	n-Butyl β-chloropro- pionate	3:9474
C ₄ H ₄ O ₂ Cl ₄	β-Chloroethyl tri- chloroacetate	3:6510		Isobutyl β -chloropropionate	3:8655
C ₄ H ₅ O ₅ Cl ₅	β -Hydroxyethyl tri- chloroacetate	3:9099	C ₈ H ₁₅ O ₂ Cl	Isoamyl β-chloropro- pionate	3:8730

C ₄ H ₆ O ₂ Cl ₂	Methyl α,β -dichloropropionate	3:9103	$C_8H_{12}O_4Cl_2$	Diethyl d,l - α,α -di- chlorosuccinate	3:9578
C ₅ H ₅ O ₂ Cl ₂	Ethyl α,β-dichloro- propionate	3:6090	$C_6H_8O_4Cl_2$	Dimethyl meso-a,a-di- chlorosuccinate	3:0240
b	FROM CHLOROBUTYRIC		$C_8H_{12}O_4Cl_2$	Diethyl meso-a,a-di- chlorosuccinate	3:1364
C ₈ H ₉ O ₂ Cl	Methyl α-chloro-n- butyrate	3:8103		om unsaturated monoba ntaining chlorine	sic acids
C ₆ H ₁₁ O ₂ Cl	Ethyl α -chloro- n -butyrate	3:8307	C ₄ H ₅ O ₂ Cl	Methyl α-chloro- acrylate	3:9096
C ₅ H ₉ O ₅ Cl	Methyl β -chloro- n -butyrate	3:8224	C ₅ H ₇ O ₂ Cl	Ethyl α -chloro- * acrylate	,3:9242
C ₆ H ₁₁ O ₂ Cl	Ethyl β-chloro-n- butyrate	3:8373	C ₆ H ₇ O ₂ Cl	Methyl α -chloro- crotonate	3:5870
C ₅ H ₉ O ₂ Cl	Methyl γ-chloro-n- butyrate	3:8517	C ₆ H ₉ O ₂ Cl	Ethyl α-chloro- crotonate	3:8523
C ₆ H ₁₁ O ₂ Cl	Ethyl γ-chloro-n- butyrate	3:8597	$C_6H_7O_2Cl$	Methyl β-chloro- crotonate	3:9244
C ₈ H ₉ O ₂ Cl	Methyl α-chloroiso- butyrate	3:7918	$C_6H_9O_2Cl$	Ethyl β -chloro-crotonate	3:8538
C ₆ H ₁₁ O ₂ Cl	Ethyl α-chloroiso- butyrate	3:8147	$C_6H_9O_2Cl$	Ethyl γ-chloro- crotonate	3:8657
C ₆ H ₉ O ₂ Cl ₃	Ethyl α,α,β -trichloro- n-butyrate	3:6380	$C_6H_9O_2Cl$	Ethyl α -chloroiso-crotonate	3:9368
b ₆	FROM CHLOROVALERIC		$C_6H_7O_2Cl$	Methyl β -chloroiso-crotonate	3:8028
C ₆ H ₁₁ O ₂ Cl	Methyl α-chloro-n- valerate	3:8264	$C_6H_9O_2Cl$	Ethyl β -chloroiso-crotonate	3:8325
C7H18O2Cl	Ethyl α -chloro- n -valerate	3:8596		om unsaturated dibasic ac ning chlorine	cids con-
C7H18O2Cl	Ethyl β -chloro- n -valerate	3:8629	C ₆ H ₇ O ₄ Cl	Dimethyl chloro- fumarate	3:6582
C7H18O2Cl	Ethyl γ-chloro-n-valerate	3:87 03	C ₈ H ₁₁ O ₄ Cl	Diethyl chloro- fumarate	3:6864
C7H18O2Cl	Ethyl &-chloro-n-valerate	3:8727	C ₆ H ₇ O ₄ Cl	Dimethyl chloro- maleate	3:9351
C7H18O3Cl	Ethyl α-chloro-α- methyl-n-butyrate .	3:8518	C ₈ H ₁₁ O ₄ Cl	Diethyl chloro- maleate	3:6697
	Ethyl α-chloro-β- methyl-n-butyrate	3:8528	f. Fro C ₂ H ₂ O ₂ Cl	om chloroformic acid Methyl chloroformate	3:5075
	om saturated dibasic ac ning chlorine	ids con-	$C_2H_2O_2Cl_2$	Chloromethyl chloro- formate	3:5275
C ₅ H ₅ O ₂ Cl ₂	Dimethyl d,l-α,α- dichlorosuccinate	3:0485	C ₂ HO ₂ Cl ₃	Dichloromethyl chloro- formate	3:5315

C ₂ O ₂ Cl ₄	Trichloromethyl chloroformate	8:5515	C ₈ H ₇ O ₂ Cl	Methyl p-chloro- benzoate	3:0535
$\mathrm{C_8H_5O_2Cl}$	Ethyl chloroformate	8:7295	$C_9H_9O_2Cl$	Ethyl p-chloro- benzoate	3:67 <i>5</i> 0
C ₂ H ₄ O ₂ Cl ₂	β-Chloroethyl chloro- formate	3:5780		s of inorganic acids	
C ₄ H ₇ O ₃ Cl	β-Methoxyethyl chloro- formate	3:9140	C ₂ H ₄ OCl	Ethyl hypochlorite ter-Butyl hypochlorite	3:7 02 2 3:71 6 5
C ₆ H ₉ O ₈ Cl	β -Ethoxyethyl chloroformate	3:9280	C ₈ H ₁₁ OCl	ter-Amyl hypochlorite.	3:9287
C ₄ H ₇ O ₂ Cl	n-Propyl chloro- formate	3:7540	grou		ınctional
$C_4H_6O_2Cl_2$	γ-Chloro-n-propyl chloroformate	3:6010		ster/alcohols FROM ACIDS WITH NO C β-Chloro-α-hydroxy-	HLORINE
C ₄ H ₇ O ₂ Cl	Isopropyl chloro- formate	3:7405		n-propyl acetate α-Chloro-β-hydroxy- n-propyl acetate	3:6775 3:6648
C ₆ H ₉ O ₂ Cl	n-Butyl chloro- formate Isobutyl chloro-	3:7980		β-Chloro-β'-hydroxy- isopropyl acetate	3:6517
C ₆ H ₁₁ O ₂ Cl	formate n-Amyl chloroformate	3:7760 3:9380	82	FROM ACIDS CONTAINING	īG
	Isoamyl chloroformate	3:8215	C ₄ H ₇ O ₈ Cl	β -Hydroxyethyl chloro- acetate	3:6780
C ₄ H ₅ O ₂ Cl	Allyl chloroformate Isopropenyl chloro- formate	3:7487 3:7358	$\mathrm{C_4H_6O_3Cl_2}$	β -Hydroxyethyl di- chloroacetate	3:9107
C7H11O2Cl	Cyclohexyl chloro- formate	3:5770	C ₄ H ₅ O ₈ Cl ₈	β -Hydroxyethyl tri- chloroacetate	3:9099
$C_8H_7O_2Cl$	Benzyl chloroformate.	3:9565	b. Es	ter/acyl halides Ethoxalyl chloride	9.7097
a. Ke	to acids		Carrect	Carbomethoxyacetyl	3:5625
C ₆ H ₉ O ₃ Cl	Ethyl α -chloroaceto-	3:6207			:9098-A
	acetate Ethyl γ -chloroaceto-acetate	3:6375	C ₈ H ₇ O ₈ Cl	β-(Carbomethoxy)pro- pionyl chloride Carbethoxyacetyl	3:9247
	s of aromatic acids			chloride	3:9246
a. Fr C ₉ H ₉ O ₂ Cl	om acids containing no c β-Chloroethyl benzoate	3:8860	$C_6H_9O_3Cl$	γ-(Carbomethoxy)-n- butyryl chloride	3:9373
b. Fro	om acids containing chlor Methyl o-chloro- benzoate	ine 3:6695	C11H19O3Cl	ω -(Carbomethoxy)- pelargonyl chloride .	3:9792
G TT O G	This all a shipper		c. Es	ter/ethers	
C ₉ H ₉ O ₉ Cl	Ethyl o-chloro- benzoate	3:6800	C ₅ H ₉ O ₈ Cl	β-Methoxyethyl chloroacetate	3:9285
C ₈ H ₇ O ₂ Cl	Methyl m-chloro- benzoate	3:6670	C ₆ H ₇ O ₂ Cl ₃	β-Methoxyethyl tri- chloroacetate	3:9250
C ₉ H ₉ O ₂ Cl	Ethyl m-chloro- benzoate	3:6770	C ₅ H ₂ O ₅ Cl ₅	Chloralide	3:3510

đ. Es	ter/ether/alcohols		e. Es	ster/ether/acyl halides	
C ₆ H ₁₁ O ₄ Cl	Diethylene glycol mono(chloroacetate)	3:9390	C ₄ H ₇ O ₃ Cl	β -Methoxyethyl chloroformate	3:9140
$C_8H_{15}O_5Cl$	Triethylene glycol mono(chloroacetate)	3:9588	$C_8H_9O_8Cl$	β -Ethoxyethyl chloroformate	3:9280

V. ALPHABETICAL NAME INDEX TO COMPOUNDS OF ORDER 3

- 1. Note that this index refers only to numbered compounds of Order 3; for practical reasons it cannot include the large number of related products which are incidentally mentioned within the text of these numbered individuals.
- 2. In this alphabetical name index all literal prefixes (such as those below) are ignored in establishing the alphabetical sequence. Note, however, that "iso" is not recognized as a prefix but is construed as an integral part of the name and therefore indexed under the letter I.
- 3. Within any given group of related prefixes the following sequences are employed:

- 4. Note that except when needed to distinguish from other stereoisomers the prefix d,l is omitted from the alphabetical index names even when included in text of the individual compound.
- 5. Whenever in a particular name the syllable (di) is inserted in parentheses to avoid possible ambiguity, such syllable is ignored in establishing the alphabetical sequence.
- 6. For a given family of derivatives of the same halogen-free parent, the sequence of listing is based upon the parent, e.g., all the dichloro substitution products of naphthol-1 precede all those derived from naphthol-2.

	A	3:8150	2-Acetoxy-1-chloropropane
3:6210	Acetaldehyde bis-(\beta-chlorethyl)-	3:8180	1-Acetoxy-2-chloropropane
	acetal	3:8310	1-Acetoxy-3-chloropropane
3:9098	Acetoacetyl chloride	3:7065	Acetyl chloride
3:6517	β -Aceto- α -chlorohdryin	3:5042	cis-Acetylene dichloride
3:6775	γ -Aceto- α -chlorohydrin	3:5028	trans-Acetylene dichloride
3:6648	α-Aceto-β-chlorohydrin	3:5030	Acetylene dichloride (ordinary
3:6220	γ -Aceto- α , β -dichlorohydrin		mixt.)
3:6318	β -Aceto- α , γ -dichlorohydrin	3:5750	Acetylene tetrachloride
3:7140	"Acetone (di)chloride"	3:5555	Acetylidene tetrachloride
3:2662	Acetone chloroform	3:9034	Acrolein dichloride
3:6180	"Acetone chloroform" acetate	3:51 40	" Acrolein dichloride "
3:5425	Acetonyl chloride	3:5576	Acrolein hydrochloride

0.2420			
3:7153 3:9352	Acryloyl chloride	3:7345	secButylcarbinyl chloride
3:6060	Adipyl (di)chloride	3:7200	ter-Butylcarbinyl chloride
3:7 63 5	Allyl alcohol dichloride Allyl chloride	3:5910	"Butylchloral" n-Butyl chloride
3:7487	Allyl chlorocarbonate	3:7160 3:7125	secButyl chloride
3:7487	Allyl chloroformate	3:7045	ter-Butyl chloride
3:7500	Allyl-dimethyl-carbinyl chloride	3:8530	n-Butyl chloroacetate
3:7 6 55	Allyl-ethyl-carbinyl chloride	3:8350	sccButyl chloroacetate
8:5140	Allylidene (di)chloride	3:8220	ter-Butyl chloroacetate
3:8205	Allyl-isobutyl-carbinyl chloride	3:7980	n-Butyl chlorocarbonate
3:7730	Allyl-isopropyl-carbinyl chloride	3:9396	n-Butyl α-chloroethyl ether
3:8305	secAmyl-(2)-acetyl chloride	3:7980	n-Butyl chloroformate
3:7590	ter-Amyl-carbinyl chloride	3:8595	n-Butyl α-chloropropionate
3:7 460	n-Amyl chloride	3:9474	n -Butyl β -chloropropionate
3:7325	sec(2)-Amyl chloride	3:8185	α-(n-Butyl)crotyl chloride
3:7330	sec(3)-Amyl chloride	3:9646	n-Butyl-diethyl-carbinyl chloride
3:7220	ter-Amyl chloride	3:9656	ter-Butyl-diethyl-carbinyl
3:9390	n-Amyl chlorocarbonate		chloride
3:9 48 0	n -Amyl α -chloroethyl ether	3:7 94 5	n-Butyl-dimethyl-carbinyl
3:9380	n-Amyl chloroformate		chloride
3:9734	n-Amyl-diethyl-carbinyl chloride	3:9442	secButyl-dimethyl-carbinyl
3:8100	n-Amyl-dimethyl-carbinyl		chloride
	chloride	3:4020	ter-Butyl-dimethyl-carbinyl
3:7975	ter-Amylene dichloride		chloride
3:9 64 2	n-Amyl-ethyl-methyl-carbinyl	3:8025	α-Butylene chlorohydrin
3:9287	chloride	3:8000	β-Butylene chlorohydrin
3:9738	ter-Amyl hypochlorite n-Amyl-isopropyl-methyl-car-	3:8000 3:7680	pseudo-Butylene chlorohydrin
0.9100	binyl chloride	3:7615	α -Butylene dichloride β -Butylene dichloride
3:9432	n-Amyl-methyl-carbinyl chloride	3:7580	meso-β-Butylene dichloride
3:9730	n-Amyl-methyl-n-propyl-	3:9436	secButyl-ethyl-carbinyl chloride
0.0.00	carbinyl chloride	3:9544	n-Butyl-ethyl-methyl-carbinyl
3:6560	n-Amyl trichloroacetate	0.0011	chloride
3:6185	ter-Amyl trichloroacetate	3:9736	n-Butyl-ethyl-n-propyl-carbinyl
3:6870	o-Anisoyl chloride	0.0.00	chloride
3:6797	m-Anisoyl chloride	3:7165	ter-Butyl hypochlorite
3:6890	p-Anisoyl chloride	3:7550	n-Butylidene (dı)chloride
3:9680	Azelayl (di)chloride	3:9650	n-Butyl-isopropyl-methyl-
	, n		carbinyl chloride
	В	3:94 52	n-Butyl-methyl-acetyl chloride
3:6327	Benzal (di)chloride	3:9458	secButyl-methyl-acetyl chloride
3:4410	α-Benzene hexachloride	3:7715	n-Butyl-methyl-carbinyl chloride
3:4990	β-Benzene hexachloride	3:9350	secButyl-methyl-carbinyl
3:0060	Benzohydryl chloride		chloride
3:6960	Benzophenone (di)chloride	8:7475	ter-Butyl-methyl-carbinyl chloride
3:6540 3:9880	Benzotrichloride	3:9 611	n-Butyl-methyl-n-propyl-
3:9880	o-Benzoylbenzoyl chloride o-Benzoylbenzoyl pseudo-	3:9654	carbinyl chloride
u. 900u	chloride	0.000I	ter-Butyl-methyl-n-propyl- carbinyl chloride
3:6240	Benzoyl chloride	3:9538	n-Butyl-n-propyl-carbinyl
3:8712	Benzylcarbinyl chloride	0.000	chloride
3:8535	Benzyl chloride	3:6315	n-Butyl trichloroacetate
3:9565	Benzyl chlorocarbonate	3:9372	secButyl trichloroacetate
3:9565	Benzyl chloroformate	3:0138	ter-Butyl trichloroacetate
3:6327	Benzylidene (di)chloride	3:9412	n-Butyl-vinyl-carbinyl chloride
3:7665	Biallyl hydrochloride	3:5910	"Butyrchloral"
3:17 60	Butadiene tetrachloride (solid	3:1905	"Butyrchloral hydrate"
	isomer)	8:7370	n-Butyryl chloride
3:9082	Butadiene tetrachloride (liquid		0
	isomer)	0.0000	C
3:8035	secButylacetyl chloride	3:8800	n-Caprinyl chloride
3:7880	ter-Butylacetyl chloride	3:8168 3:8680	n-Caproyl chloride
3:7 460	n-Butylcarbinyl chloride	9:000A	n-Capryloyl chloride

3:92 46	Carbethoxyacetyl chloride	3:6710	m-Chlorobenzal (di)chloride
3:9565	"Carbobenzoxy chloride"	3:6700	p-Chlorobenzal (di)chloride
3:9098-A	Carbomethoxyacetyl chloride	3:6410	o-Chlorobenzaldehyde
3:9378		3:6475	
0:0010	γ -(Carbomethoxy)- n -butyryl		m-Chlorobenzaldehyde
	chloride	3:0765	<i>p</i> -Chlorobenzaldehyde
3:9792	ω-(Carbomethoxy)pelargonyl	3 : 7 90 3	Chlorobenzene
	chloride	3:4980	4-Chlorobenzenedicarboxylic
3:9247	β-(Carbomethoxy) propionyl		acid-1,3
0.0721	chloride	3:4960	
		0.2500	5-Chlorobenzenedicarboxylic
3:5100	Carbon tetrachloride		acid-1,3
3:5000	Carbonyl chloride	3:499 5	2-Chlorobenzenedicarboxylic
3:9280	"Cellosolve" chloroformate		acid-1.4
3:0015	Cetyl chloride	3:4855	5-Chlorobenzenetricarboxylic
		0.2000	
3:5210	Chloral		acid-1,2,4
3:0860	Chloralalcoholate	3:4975	2-Chlorobenzenetricarboxylic
3:0843	Chloral n-butylalcoholate		acid-1,3,5
3:6317	Chloral diethylacetal	3:4150	o-Chlorobenzoic acid
3:0860	Chloral ethylalcoholate	3:4392	m-Chlorobenzoic acid
3:1270	Chloral hydrate	3:4940	p-Chlorobenzoic acid
3:3510	Chloralide	3: 0 715	2-Chlorobenzophenone
3:4978	Chloranil	3:2160	3-Chlorobenzophenone
3:4970	Chloranilic acid	3:1914	4-Chlorobenzophenone
	"Chlorbutol "	3:1100	
3:2662			2-Chlorobenzoquinone-1,4
3:7015	Chlorethane	3:6880	c-Chlorobenzotrichloride
3:2662	" Chloretone "	3:6845	m-Chlorobenzotrichloride
3:6180	"Chloretone" acetate	3:6825	p-Chlorobenzotrichloride
3:6025	"Chlorex "	3:6640	o-Chlorobenzoyl chloride
3:8228	Chloroacetal	3:6590	m-Chlorobenzoyl chloride
3:7212	Chloroacetaldehyde	3:6550	p-Chlorobenzoyl chloride
3:8228	Chloroacetaldehyde diethylacetal	3:6400	o-Chlorobenzyl chloride
3:2300	Chloroacetaldehyde trimer	3:6445	m-Chlorobenzyl chloride
3:1370		3:0220	p-Chlorobenzyl chloride
	Chloroacetic acid		
3:0730	Chloroacetic acid anhydride	3:6625	o-Chlorobenzylidene (di)chloride
3:90 88	γ-Chloroacetoacetyl chloride	3:6710	m-Chlorobenzylidene (di)chloride
3:5425	Chloroacetone	3:6700	p-Chlorobenzylidene (di)chloride
3:1212	α-Chloroacetophenone	3:1618	α-Chlorobenzyl phenyl ketone
3:1212	ω-Chloroacetophenone	3:0300	2-Chlorobiphenyl
3:6615	o-Chloroacetophenone	3:8940	3-Chlorobiphenyl
3:6815	m-Chloroacetophenone	3:1912	4-Chlorobiphenyl
3:6735	p-Chloroacetophenone	3:7225	4-Chlorobutadiene-1,2
3:3934	4-(Chloroacetyl)biphenyl	3:7210	1-Chlorobutadiene-1,3
3:5235		3:7080	2-Chlorobutadiene-1.3
	Chloroacetyl chloride		
3:7000	Chloroacetylene	3:9109	2-Chlorobutanal-1
3:9031	α-Chloroacrolein	3:9110	3-Chlorobutanal-1
3:1445	α-Chloroacrylic acid	3:9111	4-Chlorobutanal-1
3:2240	β-Chloroacrylic acid	3:7160	1-Chlorobutane
3:5635	β-Chloroallyl alcohol	3:7125	2-Chlorobutane
3:5820	γ-Chloroallyl alcohol	3:9160	2-Chlorobutanol-1
3:8737	γ -Chloroallylbenzene	3:9165	3-Chlorobutanol-1
3:8737	ω-Chloroallylbenzene	3:9170	4-Chlorobutanol-1
3:5190	β-Chloroallyl chloride	3:8025	1-Chlorobutanol-2
		3:8000	3-Chlorobutanol-2
: 5280	γ-Chloroallyl chloride		
: 9295	ω-Chloro-n-amyl alcohol	3:8004	d,l-erythro-3-Chlorobutanol-2
: 8030	3-Chloro-ter-amyl alcohol	3:8002	d,l-threo-3-Chlorobutanol-2
: 4970	Chloroanilic acid	3:9175	4-Chlorobutanol-2
:9448	α-Chloroanisole	3:9175	1-Chlorobutanol-3
		3:8012	1-Chlorobutanone-2
: 944 8	ω-Chloroanisole		
: 6255	o-Chloroanisole	3:759 8	3-Chlorobutanone-2
: 6195	m-Chloroanisole	3:76 40	4-Chlorobutanone-2
: 6300	p-Chloroanisole	3:7640	1-Chlorobutanone-3
: 4480	1-Chloroanthraquinone	8:7110	1-Chlorobutene-1
: 4922	2-Chloroanthraquinone	3:7075	2-Chlorobutene-1
: 6625	o-Chlorobensal (di)chloride	3:7 090	3-Chlorobutene-1

3:7151	4-Chlorobutene-1	3:1025	3-Chloro-p-cresol
3:7205	1-Chlorobutene-2	3:8117	α-Chlorocrotonaldehyde
3:7105	2-Chlorobutene-2	3:1615	allo-α-Chlorocrotonic acid
3:8117	2-Chlorobuten-2-al-1	3:2760	α -Chlorocrotonic acid
3:1615	cis-2-Chlorobuten-2-oic acid-1	3:2625	β -Chlorocrotonic acid
3:2760	trans-2-Chlorobuten-2-oic acid-1	3:2170	γ-Chlorocrotonic acid
3:1300	cis-3-Chlorobuten-2-oic acid-1	3:8240	β-Chlorocrotonyl alcohol
3:2625	trans-3-Chlorobuten-2-oic acid-1	3:8270	y-Chlorocrotonyl alcohol
3:2170	4-Chlorobuten-2-oic acid-1	3:8705	p-Chlorocumene
3:8240	2-Chlorobuten-2-ol-1	3:8040	Chlorocyclohexane
3:8270	3-Chlorobuten-2-ol-1	3:9374	cis-2-Chlorocyclobexanol-1
3:9114	4-Chlorobuten-2-ol-1	3:0175	trans-2-Chlorocyclohexanol-1
3:9113	2-Chlorobuten-3-ol-1	3:9376	4-Chlorocyclohexanol-1
3:8110	1-Chlorobuten-3-ol-2	3:0120	2-Chlorocyclohexanone-1
3:9115	3-Chlorobuten-3-ol-2	3:9360	3-Chlorocyclohexanone-1
3:9114	1-Chlorobuten-2-ol-4	3:936 4	4-Chlorocyclohexanone-1
3:8270	2-Chlorobuten-2-ol-4	3:7545	Chlorocylopentane
3:7070	1-Chlorobuten-3-yne-1	3:8775	2-Chloro-p-cymene
3:9160	β-Chloro-n-butyl alcohol	3:8770	3-Chloro-p-cymene
3:9165	γ -Chloro- n -butyl alcohol	3:8785	1-Chlorodecane
3:9170	δ -Chloro- n -butyl alcohol	3:0014	10-Chlorodecanol-1
3:7752	Chloro-ter-butyl alcohol	3:9712	5-Chlorodecene-5
3:8780	(β-Chloro-ter-butyl) benzene	3:0014	ω -Chloro- n -decyl alcohol
3:7090	γ -Chloro- α -butylene	3:1618	α -Chlorodesoxy benzoin
3:7205	α -Chloro- β -butylene	3:1618	ms-Chlorodesoxybenzoin
3:8830	2-Chloro-4-n-butylphenol	3:7305	α-Chlorodiethyl ether
3:9760	2-Chloro-4-ter-butylphenol	3:9716	4-Chloro-3,4-diethylhexene-2
3:7175	1-Chlorobutyne-2	3:793 5	α-Chlorodiethylketone
3:9594	β -Chlorobutyracetal	3:1355	ω-Chloro-2,4-dimethylacoto-
3:9109	α-Chloro-n-butyraldehyde		phenone
3:9110	β-Chloro-n-butyraldehyde	3:1775	ω-Chloro-3,4-dimethylaceto-
3:9111	γ-Chloro-n-butyraldehyde		phenone
3:95 94	β -Chloro- n -butyraldehyde	3:0245	ω-Chloro-2,5-dimethylaceto-
	diethylacetal		phenone
3:9130	α-Chloro-n-butyric acid	3:8645	3-Chloro-1,2-dimethylbenzene
3:0035	β -Chloro- n -butyric acid	3:8675	4-Chloro-1,2-dimethylbenzene
3:0020	γ-Chloro-n-butyric acid	3:8590	2-Chloro-1,3-dimethylbenzene
3:5570	a-Chloro-n-butyryl chloride	3:8665	4-Chloro-1,3-dimethylbenzene
3:9100	β-Chloro-n-butyryl chloride	3:8640	5-Chloro-1,3-dimethylbenzene
3:5970 3:0480	γ-Chloro-n-butyryl chloride	3:8600 3:7590	2-Chloro-1,4-dimethylbenzene
3:0250	p-(5)-Chlorocarvacrol 3-Chlorocatechol	3:7475	1-Chloro-2,2-dimethylbutane
3:07±3 3:2470	4-Chlorocatechol	3:7555	3-Chloro-2,2-dimethylbutane
3:9195	1-Chloro-2-(chloromethyl)-	3:7600	4-Chloro-2,2-dimethylbutane
0.0100	butadiene-1,3	3:7340	2-Chloro-2,3-dimethylbutane 2-Chloro-3,3-dimethylbutene-1
3:9206	3-Chloro-2-(chloromethyl)-	3:7520	1-Chloro-2,3-dimethylbutene-2
6.0×00	butene-1	3:7340	3-Chloro-2,2-dimethylbutene-3
3:9534	4-Chloro-3-(chloromethyl)-	3:7085	Chlorodimethyl ether
0.0001	heptane	3:8780	$(\beta$ -Chloro- α , α -dimethyl) ethyl-
3:5633	3-Chloro-2-(chloromethyl)-	0.0.00	benzene
0.000	propene-1	3:9656	3-Chloro-2,2-dimethyl-3-ethyl-
3:5633	1-Chloro-2-(chloromethyl)-		pentane
	propene-2	3:9650	3-Chloro-2,3-dimethylheptane
3:1430	1-Chloro-2,2-bis-(p-chlorophenyl)-	3:9652	5-Chloro-2,5-dimethylheptane
	ethylene	3:9630	4-Chloro-3,6-dimethylheptene-2
3:2280	3-Chloro-o-cresol	3:9554	3-Chloro-2,3-dimethylhexane
3:0780	4-Chloro-o-cresol	3:9556	2-Chloro-2,5-dimethylhexane
3:1815	5-Chloro-o-cresol	3:9558	2-Chloro-3,4-dimethylhexane
3:8615	6-Chloro-o-cresol	3:9529	4-Chloro-2,5-dimethylhexene-2
3:1055	2-Chloro-m-cresol	3:9528	4-Chloro-3,5-dimethylhexene-2
3:1535	4-Chloro-m-cresol	3:9527	2-Chloro-2,5-dimethylhexene-3
3:0700	6-Chloro-m-cresol	3:9528	3-Chloro-2,4-dimethylhexene-4
3:6215	2-Chloro-p-cresol	3:9738	3-Chloro-2,3-dimethyloctane
	-		

3:9740	8-Chloro-2,6-dimethyloctane	3:5780	β -Chloroethyl chloroformate
3:9714	4-Chloro-3,7-dimethyloctene-2	3:5900	α-Chloroethyl chloromethyl
3:9714	5-Chloro-2.6-dimethyloctene-6		ketone
3:9440	4-Chloro-2,2-dimethylpentane	3:8030	α-Chloroethyl-dimethyl-carbinol
3:9442	2-Chloro-2,3-dimethylpentane	3:8335	β -Chloroethyl-dimethyl-carbinol
3:7970	3-Chloro-2,3-dimethylpentane	3:7595	bis-(α-Chloroethyl) ether
3:8153	5-Chloro-2,3-dimethylpentane	3:6025	bis-(β-Chloroethyl) ether
3:7750	2-Chloro-2,4-dimethylpentane	3:8500	β-Chloroethyl-ethyl-carbinol
3:8153	1-Chloro-3,4-dimethylpentane	3:7305	α-Chloroethyl ethyl ether
3:7725	4-Chloro-2,4-dimethylpentene-1	3:7463	β -Chloroethyl ethyl ether
3:7605	3-Chloro-2,4-dimethylpentene-2	3:7935	α -Chloroethyl ethyl ketone
3:9418	4-Chloro-2,4-dimethylpentene-2	3:9268	β -Chloroethyl ethyl ketone
3:9418	2-Chloro-2,4-dimethylpentene-3	3:9646	3-Chloro-3-ethylheptane
3:2218	4-Chloro-2,3-dimethylphenol	3: 964 8	4-Chloro-4-ethylheptane
3:2115	5-Chloro-2,3-dimethylphenol	3:8370	1-Chloro-2-ethylhexane
3:2460	5-Chloro 2,4-dimethylphenol	3:9552	1-Chloro-3-ethylhexane
3:8784	6-Chloro-2,4-dimethylphenol	3:8223	3-Chloro-3-ethylhexane
3:1822	4-Chloro-2,5-dimethylphenol	3:8510	1-Chloro-4-ethylhexene-3
3:2180	4-Chloro-2,6-dimethylphenol	3:9185	α-Chloroethyl β-hydroxyethyl
3:0158	2-Chloro-3,4-dimethylphenol		ether
3:2705	5-Chloro-3,4-dimethylphenol	3:5330	Chloroethylidene (di)chloride
3:1754	6-Chloro-3,4-dimethylphenol	3:7150	α-Chloroethyl methyl ether
3:0844	2-Chloro-3,5-dimethylphenol	3:7265	β -Chloroethyl methyl ether
3:3505	4-Chloro-3,5-dimethylphenol	3:7598	α-Chloroethyl methyl ketone
3:7200	1-Chloro-2,2-dimethylpropane	3:7640	β-Chloroethyl methyl ketone
3: 044 0	β -Chloro- α , α -dimethylpropionic	3:8210	3-Chloro-3-ethyl-2-methyl-
	acid	0.0447	pentane
3:9266	β -Chloro- α , α -dimethylpropionyl	3:8115	2-Chloro-3-ethyl-3-methyl-
	chloride	0.0004	pentene-1
3:3585	α-Chloro-diphenylacetic acid	3:9734	3-Chloro-3-ethyloctane
3:0885	α-Chloro-diphenylacetyl chloride	3:9736 3:9406	4-Chloro-4-ethyloctane
3:0060	α-Chlorodiphenylmethane	3:9438	1-Chloro-3-ethylpentadiene-1,2 2-Chloro-3-ethylpentane
3:9870	Chloro-diphenyl-methyl- methane	3:8055	3-Chloro-3-ethylpentane
*n . 001A	1-Chlorododecane	3:9410	1-Chloro-3-ethylpentyne-1
3:8810 3:0172	12-Chlorododecanol-1	3:9770	β -Chloroethyl β' -phenoxyethyl
3:0172	ω-Chloro-n-dodecyl alcohol	0.0110	ether
3:9702	ω-Chlorodurene	3:0165	β-Chloroethyl phenyl ether
3:5358	3-Chloro-1,2-epoxypropane	3:9664	α-Chloroethyl phenyl ketone
3:7015	Chloroethane	3:1115	β-Chloroethyl phenyl ketone
3:5552	β-Chloroethanol	3:7525	α-Chloroethyl n-propyl ether
3:5552	2-Chloroethanol-1	3:6510	β-Chloroethyl trichloroacetate
3:7010	Chloroethene	3:7464	β-Chloroethyl vinyl ether
3:6210	$\alpha.\alpha$ -bis-(β -Chloroethoxy)ethane	3:7000	Chloroethyne
3:6655	$\alpha.\beta$ -bis-(β -Chloroethoxy)ethane	3:9494	Chloroethynylbenzene
3:9185	2-(β-Chloroethoxy)ethanol-1	3:5050	Chloroform
3:6655	β -(β -Chloroethoxy)ethyl β -	3:4853	Chlorofumaric acid
	chloroethyl ether	3:6105	Chlorofumaryl (di)chloride
3:7625	α-Chloroethyl acetate	3:8803	1-Chlorohendecane
3:5735	β-Chloroethyl acetate	3:0100	1-Chloroheptadecane
3:5552	β-Chloroethyl alcohol	3:8085	1-Chloroheptadiene-1,6
3:9480	α -Chloroethyl n -amyl ether	3:8250	1-Chloroheptane
3:8667	α -Chloroethylbenzene	3:9432	2-Chloroheptane
3:8712	β -Chloroethylbenzene	3:8080	3-Chloroheptane
3:8712	ω -Chloroethylbenzene	3:8095	4-Chloroheptane
3:8550	o-Chloroethylbenzene	3:0013	7-Chloroheptanol-1
3:8570	p-Chloroethylbenzene	3:8219	1-Chloroheptene-1
3:8860	β-Chloroethyl benzoate	3:7988	2-Chloroheptene-1
3:7720	1-Chloro-2-ethylbutane	3:9412	3-Chloroheptene-1
3:9396	α-Chloroethyl n-butyl ether	3:8050	4-Chloroheptene-2
3:6230	β-Chloroethyl chloroacetate	3:8023	4-Chloroheptene-3
3:5780	β-Chloroethyl chlorocarbonate	3:0013 3:8032	ω-Chloro-n-heptyl alcohol 1-Chloroheptyne-1
3:9150	α -Chloroethyl β -chloroethyl ether	a : 300%	1-CHOLOUGhFAUG-1

3: 00 15	1-Chlorohexadecane	3:4980	4-Chloroisophthalic acid
3:0525	16-Chlorohexadecanol-1	3: 4960	5-Chloroisophthalic acid
3:0525	ω-Chloro-n-hexadecyl alcohol	3:7290	"β-Chloroisoprene "
3:9312	3-Chlorohexadiene-1,3	3:8150	β-Chloro-isopropyl acetate
3:0945	Chlorohexamethylethane	3:7747	β-Chloro-isopropyl alcohol
3:7955	1-Chlorohexane	3:9610	α-Chloro-isopropylbenzene
3:7715	2-Chlorohexane	3:8705	4-Chloro-isopropylbenzene
3:7670	3-Chlorohexane	3:8605	bis-(β-Chloro-isopropyl) ether
3:9395	6-Chlorohexanol-1	3:8775	2-Chloro-4-isopropyl-1-methyl-
8:7785	3-Chlorohexatetraene-1,3,4,5		benzene
3:7630	1-Chlorohexene-1	3:8770	3-Chloro-4-isopropyl-1-methyl-
3:7530	2-Chlorohexene-1		benzene
3:9334	3-Chlorohexene-1	3:9290	α-Chloroisopropyl-methyl-
3:7 65 5	4-Chlorohexene-1		carbinol
3:7 66 5	5-Chlorohexene-1	3:1293	4-Chloro-2-isopropyl-5-methyl-
3:7620	1-Chlorohexene-2		phenol
3:7675	4-Chlorohexene-2	3:0480	4-Chloro-5-isopropyl-2-methyl-
3:9336	cis-1-Chlorohexene-3		phenol
3:7 53 5	3-Chlorohexene-3	3:3220	$2,4,6$ -tris-(α -Chloro-isopropyl)-
3:939 5	ω -Chloro- n -hexyl alcohol		trioxane-1,3,5
3:9320	1-Chlorohexyne-1	3:0050	α-Chloro-isovaleric acid
3:3130	2-Chlorohydroquinone	3:81 44	α-Chloro-isovaleryl chloride
3:1010	3-Chloro-2-hydroxybenzaldehyde	3:90 88	γ -Chloro- β -keto- n -butyryl
3:0960	4-Chloro-2-hydroxybenzaldehyde		chloride
3:2800	5-Chloro-2-hydroxybenzaldehyde	3:0172	ω-Chlorolauryl alcohol
3:4085	2-Chloro-3-hydroxybenzaldehyde	3:3432	Chloromaleic acid
3:3780	4-Chloro-3-hydroxybenzaldehyde	3:0280	Chloromaleic anhydride
3:3350	6-Chloro-3-hydroxybenzaldehyde	3:6158	Chloromaleyl (di)chloride
3:4280	2-Chloro-4-hydroxybenzaldehyde	3:8725	eso-Chloromesitylene
3:4065	3-Chloro-4-hydroxybenzaldehyde	3:7005	Chloromethane
3:3350	2-Chloro-5-hydroxybenzaldehyde	3:8210	3-Chloro-3-methoethylpentane
3:4745	3-Chloro-2-hydroxybenzoic acid	3:5356	Chloromethyl acetate
3:4908 3:4705	4-Chloro-2-hydroxybenzoic acid	3:9660 3:1130	ω-Chloro-o-methylacetophenone
3:4610	5-Chloro-2-hydroxybenzoic acid	3:8340	ω-Chloro-p-methylacetophenone
3:4395	6-Chloro-2-hydroxybenzoic acid 2-Chloro-3-hydroxybenzoic acid	3:4435	γ-Chloro-β-methylallyl alcohol
3:4933	4-Chloro-3-hydroxybenzoic acid	3:4700	3-Chloro-2-methylbenzoic acid
3:4720	6-Chloro-3-hydroxybenzoic acid	3:4670	4-Chloro-2-methylbenzoic acid 5-Chloro-2-methylbenzoic acid
3:4430	2-Chloro 4-hydroxybenzoic acid	3:3275	6-Chloro-2-methylbenzoic acid
3:4675	3-Chloro-4-hydroxybenzoic acid	3:4915	4-Chloro-3-methylbenzoic acid
3:1757	3-Chloro-2-hydroxybiphenyl	8:4715	5-Chloro-3-methylbenzoic acid
3:8980	5-Chloro-2-hydroxybiphenyl	3:4615	6-Chloro-3-methylbenzoic acid
3:1900	3-Chloro-4-hydroxybiphenyl	3:4355	2-Chloro-4 methylbenzoic acid
3:4262	4'-Chloro-4-hydroxybiphenyl	3:4900	3-Chloro-4-methylbenzoic acid
3:9185	β -Chloro- β' -hydroxydiethyl ether	3:9570	α-(Chloromethyl)benzyl alcohol
3:6517	β-Chloro-β'-hydroxy-isopropyl	3:7390	1-Chloro-3-methylbutadiene-1.2
	acetate	3:9200	1-Chloro-2-methylbutadiene-1,3
3:6648	β -Chloro- γ -hydroxy- n -propyl	3:7290	3-Chloro-2-methylbutadiene-1,3
	acetate	8:7355	4-Chloro-2-methylbutadiene-1,3
3:6775	γ -Chloro- β -hydroxy- n -propyl	3:7355	1-Chloro-3-methylbutadiene-1,3
	acetate	3:7290	2-Chloro-3-methylbutadiene-1,3
3:7 90 5	β -Chloroisobutyl alcohol	3:7396	4-Chloro-2-methylbutadiene-2,3
3:7120	α -Chloroisobutylene	3:734 5	1-Chloro-2-methylbutane
8:7145	γ-Chloroisobutylene	3:7220	2-Chloro-2-methylbutane
3:7235	a-Chloro-isobutyraldehyde	3:7275	3-Chloro-2-methylbutane
3:9112	β-Chloro-isobutyraldehyde	3:7365	4-Chloro-2-methylbutane
3:0235	α-Chloro-isobutyric acid	8:7365	1-Chloro-3-methylbutane
3:9132	β-Chloro-isobutyric acid	3:8175	1-Chloro-2-methylbutanol-2
3:5385	α-Chloro-isobutyryl chloride	3:8030	3-Chloro-2-methylbutanol-2
3:9101	β-Chloro-isobutyryl chloride	3:8335	4-Chloro-2-methylbutanol-2
3:1615	α-Chloroisocrotonic acid	3:9290	2-Chloro-2-methylbutanol-3
3:1300 3:0372	β-Chloroisocrotonic acid α²-Chloroisodurene	3:9269 3:7597	1-Chloro-2-methylbutanone-3
y: y 9///	α -∩motoraodmana	e : 1071	2-Chloro-2-methylbutanone-3

3: 9 214	2-(Chloromethyl)butene-1	3:961 <u>4</u>	2-Chloro-6-methyl-5-methylene-
8:7803	1-Chloro-2-methylbutene-1		heptene-2
3:7300	3-Chloro-2-methylbutene-1	3:7085	Chloromethyl methyl ether
3:7215	1-Chloro-3-methylbutene-1	3:9560	4-(Chloromethyl)-3-methyl-
3:7485	1-Chloro-2-methylbutene-2		hexane
3:7335	3-Chloro-2-methylbutene-2	3:0250	1-(Chloromethyl)naphthalene
3:7465	4-Chloro-2 methylbutene-2	3:0747	2-(Chloromethyl)naphthalene
3:7215	4-Chloro-2-methylbutene-3	3:9730	4-Chloro-4-methylnonane
3:7155	3-Chloro-3-methylbutyne-1	3:9732	5-Chloro-5-methylnonane
3:7155	2-Chloro-2-methylbutyne-3	3:9710	3-Chloro-3-methylnonyne-4
3:8718	α -Chloro- α -methyl- n -butyric	3:9642	3-Chloro-3-methyloctane
	acid	3:9644	4-Chloro-4-methyloctane
3:0050	α-Chloro-β-methyl-n-butyric	3:9628	4-Chloro-7-methyloctene-2
	acid	3:9624	5-Chloro-4-methyloctene-3
3:5670	α-Chloro-α-methyl-n-butyryl	3:9628	5-Chloro-2-methyloctene-6
	chloride	3:9622 3:9314	2-Chloro-2-methyloctyne-3
3:8144	α-Chloro-β-methyl-n-butyryl	3:9314	1-Chloro-3-methylpentadiene-1,2
	chloride	3:9318	1-Chloro-3-methylpentadiene-1,3
3:5275	Chloromethyl chlorocarbonate	3:7720	2-Chloro-3-methylpentadiene-1,3
3:5275	Chloromethyl chloroformate	3:7563	3-(Chloromethyl)pentane 1-Chloro-2-methylpentane
3:2990	Chloromethyl p-chlorophenyl	3:7490	2-Chloro-2-methylpentane
0.0001	ketone 2-(Chloromethyl)-1,3-dichloro-	3:7565	3-Chloro-2-methylpentane
3:9201	butene-1	3:7495	4-Chloro-2-methylpentane
3:7657	3-Chloro-2-methyl-1,2-epoxy-	3:7695	5-Chloro-2-methylpentane
9:1001	propane	3:9348	1-Chloro-3-methylpentane
3:5245	bis-(Chloromethyl) ether	3:9350	2-Chloro-3-methylpentane
3:5358	(Chloromethyl)ethylene oxide	3:7585	3-Chloro-3-methylpentane
3:7195	Chloromethyl ethyl ether	3:7660	3-Chloro-2-methylpentene-1
3:8012	Chloromethyl ethyl ketone	3:7500	4-Chloro-4-methylpentene-1
3:8175	Chloromethyl-ethyl-methyl-	3:7915	5-Chloro-2-methylpentene-2
U. 02.0	carbinol	3:9338	4-Chloro-3-methylpentene-2
3:8370	3-(Chloromethyl)heptane	3:7500	2-Chloro-2-methylpentene-4
3:8100	2-Chloro-2-methylheptane	3:9322	3-Chloro-3-methylpentyne-1
3:9540	6-Chloro-2-methylheptane	3:9324	4-Chloro-4-methylpentyne-2
3:9544	3-Chloro-3-methylheptane	3:2280	3-Chloro-2-methylphenol
3:9548	3-Chloro-4-methylheptane	3:0780	4-Chloro-2-methylphenol
3:9550	4-Chloro-4-methylheptane	3:1815	5-Chloro-2-methylphenol
3:8205	4-Chloro-6-methylheptene-1	3:8615	6-Chloro-2-methylphenol
3:9520	6-Chloro-2-methylheptene-2	3:1055	2-Chloro-3-methylphenol
3:9524	4-Chloro-3-methylheptene-2	3:1535	4-Chloro-3-methylphenol
3:9525	4-Chloro-6-methylheptene-2	3:0700	6-Chloro-3-methylphenol
3:9526	5-Chloro-4-methylheptene-3	3:6215	2-Chloro-4-methylphenol
3:9525	4-Chloro-2-methylheptene-5	3:1025	3-Chloro-4-methylphenol
3:8205	4-Chloro-2-methylheptene-6	3:0700	2-Chloro-5-methylphenol
3:9516	3-Chloro-3-methylheptyne-4	3:9570	Chloromethyl-phenyl-carbinol
3:7945	2-Chloro-2-methylhexane	3:9448	Chloromethyl phenyl ether
3:7985	5-Chloro-2-methylhexane	3:1212 3:7235	Chloromethyl phenyl ketone
3:8155	1-Chloro-3-methylhexane		2-Chloro-2-methylpropanal-1
8: 9434	2-Chloro-3-methylhexane	3:9112 3:7135	3-Chloro-2-methylpropanal-1
3:7950	3-Chloro-3-methylhexane	3:7 04 5	1-Chloro-2-methylpropane
3:9436	4-Chloro-3-methylhexane	3:7043 3:9190	2-Chloro-2-methylpropane 3-Chloro-2-methylpropanediol-1,2
3:7730	4-Chloro-5-methylhexene-1	3:7905	2-Chloro-2-methylpropanol-1
3:9414	4-Chloro-3-methylhexene-2 4-Chloro-5-methylhexene-2	3:9180	3-Chloro-2-methylpropanol-1
3:7890	3-Chloro-2-methylhexene-4	3:7752	1-Chloro-2-methylpropanol-2
3:78 90 3:7730	3-Chloro-2-methylnexene-5	3:7120	1-Chloro-2-methylpropene-1
3:7730 3:9402	5-Chloro-5-methylhexen-1-yne-3	3:7145	3-Chloro-2-methylpropene-1
3:9402 3:9402	2-Chloro-2-methylhexen-5-yne-3	3:8340	3-Chloro-2-methylpropen-2-ol-1
3:940% 3:8795	1-Chloromethyl-4-isopropyl-	3:8225	Chloromethyl-n-propyl-carbinol
0:0180	benzene	3:8217	Chloromethyl-n-propyl ketone
3:0563	bis-(Chloromethyl) ketone	3:8742	β-Chloro-α-methylstryene
3:7747	Chloromethyl-methyl-carbinol	3:9604	α-Chloro-β-methylstyrene
a	~		

	0.001		
3:9606	β-Chloro-β-methylstyrene	3:9514	1-Chloro-octyne-2
3:8152 3: 9660	2-(Chloromethyl) tetrahydrofuran	3:0525	ω-Chloropalmityl alcohol
3:1130	Chloromethyl o-tolyl ketone	3:9890	1-Chloropentadecane
3:2300	Chloromethyl p-tolyl ketone	3:7360	3-Chloropentadiene-1,3
9 . KOUU	2,4,6-tris-(Chloromethyl)tri- oxane-1,3,5	3:7460 3:7325	1-Chloropentane 2-Chloropentane
3:8110	Chloromethyl-vinyl-carbinol	3:7330	3-Chloropentane
3:3934	Chloromethyl p-xenyl ketone	3:9295	5-Chloropentanol-1
3:0375	ω-Chloromyristyl alcohol	3:8225	1-Chloropentanol-2
3:6878	1-Chloronaphthalene	3:8500	1-Chloropentanol-3
3:1285	2-Chloronaphthalene	3:8217	1-Chloropentanone-2
3:4330	2-Chloronaphthoic acid-1	3:7893	3-Chloropentanone-2
3:4936	4-Chloronaphthoic acid-1	3:8243	4-Chloropentanone-2
3:4944	5-Chloronaphthoic acid-1	3:9267	5-Chloropentanone-2
3:4845	6-Chloronaphthoic acid-1	3:9268	1-Chloropentanone-3
3:4 94 2	7-Chloronaphthoic acid-1	3:7935	2-Chloropentanone-3
3:4680	8-Chloronaphthoic acid-1	3:7420	1-Chloropentene-1
3:4885	1-Chloronaphthoic acid-2	3:7280	2-Chloropentene-1
3:492 8	3-Chloronaphthoic acid-2	3:7260	3-Chloropentenc-1
3:4952	5-Chloronaphthoic acid-2	3:7350	4-Chloropentene-1
3: 494 8	8-Chloronaphthoic acid-2	3:7410	5-Chloropentene-1
3:1490	2-Chloronaphthol-1	3:7470	1-Chloropentene-2
3:1470	3-Chloronaphthol-1	3:7285	2-Chloropentene-2
3:3720	4-Chloronaphthol-1	3:7240	3-Chloropentene-2
3:3960	5-Chloronaphthol-1	3:7400	4-Chloropentene-2
3:2615	6-Chloronaphthol-1	3:7455	5-Chloropentene-2
3:3810	7-Chloronaphthol-1	3:7455 3:7400	1-Chloropentene-3
3:1610 3:1700	8-Chloronaphthol-1	3:7400 3:2990	2-Chloropentene-3 p-Chlorophenacyl chloride
3:2545	1-Chloronaphthol-2 3-Chloronaphthol-2	3:8735	o-Chlorophenetole
3:3045	4-Chloronaphthol-2	3:6323	m-Chlorophenetole
3:3945	5-Chloronaphthol-2	3:0090	p-Chlorophenetole
3:3500	6-Chloronaphthol-2	3:0165	ω-Chlorophenetole
3:3925	7-Chloronaphthol-2	3:5980	o-Chlorophenol
3:2965	8-Chloronaphthol-2	3:0255	m-Chlorophenol
3:4704	3-Chloro-β-naphthoquinone	3:0475	p-Chlorophenol
3:4704	3-Chloronaphthoquinone-1,2	3:4260	o-Chlorophenoxyacetic acid
3:4000	4-Chloronaphthoquinone-1,2	3:3325	m-Chlorophenoxyacetic acid
3:3580	2-Chloronaphthoquinone-1,4	3: 4 375	p-Chlorophenoxyacetic acid
3:4492	5-Chloronaphthoquinone-1,4	3:2640	2-Chlorophenylacetic acid
3:3145	6-Chloronaphthoquinone-1,4	3:1910	3-Chlorophenylacetic acid
3:8719	1-Chlorononane	3:3135	4-Chlorophenylacetic acid
3:8635	2-Chlorononane	3:1618	α-Chloro-α-phenyl-aceto-
3:9638	3-Chlorononane	0.0004	phenone
3:9640	5-Chlorononane	3:3934	ω-Chloro-p-phenylacetophenone
3:0170	9-Chlorononanol-1	3:9497	o-Chlorophenylacetylene
3:0170	ω-Chloro-n-nonyl alcohol	3:9500 3:0590	m-Chlorophenylacetylene
3:9618 3:0095	1-Chlorononyne-1 1-Chloro-octadecane	3:9494	p-Chlorophenylacetylene
3:0985	18-Chloro-octadecane 18-Chloro-octadecanol-1	3:9494	α-Chloro-β-phenylacetylene ω-Chlorophenylacetylene
3:0985	ω -Chloro- n -octadecyl alcohol	3:9859-A	o-Chlorophenyl m-chlorophenyl
3:9506	3-Chloro-octadiene-1,3	0.0000 12	ketone
3:8585	1-Chloro-octane	3:1565	o-Chlorophenyl p-chlorophenyl
3:8378	2-Chloro-octane		ketone
3:9538	4-Chloro-octane	3:3415	m-Chlorophenyl p-chlorophenyl
3:9590	8-Chloro-octanol-1		ketone
3:8346	2-Chloro-octene-1	3:8735	o-Chlorophenyl ethyl ether
3:9518	3-Chloro-octene-1	3:6323	m-Chlorophenyl ethyl ether
3:8345	2-Chloro-octene-2	3:0090	p-Chlorophenyl ethyl ether
3:8185	4-Chloro-octene-2	3:0340	p-Chlorophenyl ethyl ketone
3:8230	4-Chloro-octene-4	3 : 6255	o-Chlorophenyl methyl ether
3:9590	ω-Chloro-n-octyl alcohol	3:6195	m-Chlorophenyl methyl ether
3:9510	1-Chloro-octyne-1	3 : 6300	p-Chlorophenyl methyl ether

	011 1 1 1 1 1		
3:6615	o-Chlorophenyl methyl ketone	3:8285	γ-Chloro-n-propyl alcohol
3:6815	m-Chlorophenyl methyl ketone	3:8777	γ-Chloro-n-propylbenzene
3:6735	p-Chlorophenyl methyl ketone	3:6010	γ -Chloro- n -propyl
3:1757	" o-Chloro-o'-phenylphenol "		chlorocarbonate
3:8980	4-Chloro-2-phenylphenol	3:6010	γ -Chloro- n -propyl chloroformate
3:1757	6-Chloro-2-phenylphenol	3:903 8	γ-Chloropropylene glycol
3:1900	2-Chloro-4-phenylphenol	3:6775	γ-Chloropropylene glycol
3:0715	o-Chlorophenyl phenyl ketone		α-acetate
3:2160	m-Chlorophenyl phenyl ketone	3:6517	γ-Chloropropylene glycol
3:1914	p-Chlorophenyl phenyl ketone		β -acetate
3:9880	3-Chloro-3-phenylphthalide	3:6840	γ-Chloropropylene glycol
3:9610	2-Chloro-2-phenylpropane		diacetate
3:9604	1-Chloro-1-phenylpropene-1	3:5358	γ-Chloropropylene oxide
3:9606	2-Chloro-1-phenylpropene-1	3:8610	bis-(β-Chloro-n-propyl) ether
3:0010	3-Chloro-1-phenylpropene-1	3:8745	bis-(γ-Chloro-n-propyl) ether
3:8742	1-Chloro-2-phenylpropene-1	3:9742	4-Chloro-4-n-propylheptane
3:8737	1-Chloro-3-phenylpropene-1	3:5630	α-Chloropropylidene (di)-
3:9608	2-Chloro-3-phenylpropene-1		chloride
3:3956	o-Chlorophenylpropiolic acid	3:5660	β-Chloropropylidene (di)-
3:4102	m-Chlorophenylpropiolic acid	3.5550	chloride
3:4265	p-Chlorophenylpropiolic acid	3:7893	α-Chloro-n-propyl methyl ketone
3:4820	3-Chlorophthalic acid	3:8243	β -Chloro- n -propyl methyl ketone
3:4390	4-Chlorophthalic acid	3:9267	γ -Chloro- n -propyl methyl ketone
3:3900	3-Chlorophthalic anhydride	3:8820	
3:2725	4-Chlorophthalic anhydride	3:2650	γ-Chloro-n-propyl phenyl ether
3:0440	Chloropivalic acid	a . 2000	2,4,6-tris-(β-Chloro-n-propyl)-
3:9266	Chloropivallyl chloride	3:7100	trioxane-1,3,5
3:7080			3-Chloropropyne-1
3:5576	Chloroprene	3:0745	3-Chloropyrocatechol
3:7040	3-Chloropropanal-1	3:2470	4-Chloropyrocatechol
	1-Chloropropane	3:1100	Chloroquinone
3:7025	2-Chloropropane	3:2690	2-Chlororesorcinol
3:9038	3-Chloropropanediol-1,2	3:3100	4-Chlororesorcinol
3:9039	2-Chloropropanediol-1,3	3:3530	5-Chlororesorcinol
3:6840	3-Chloropropanediol-1,2	3:1010	3-Chlorosalicylaldehyde
	diacetate	3:0960	4-Chlorosalicylaldehyde
3:6125	2-Chloropropanoic acid	4:2800	5-Chlorosalicylaldehyde
3:0460	3-Chloropropanoic acid	3:4745	3-Chlorosalicylic acid
3:7917	2-Chloropropanol-1	3:4908	4-Chlorosalicylic acid
3:8285	3-Chloropropanol-1	3:4705	5-Chlorosalicylic acid
3:7747	1-Chloropropanol-2	3:4610	6-Chlorosalicylic acid
3:5425	1-Chloropropanone-2	3:0985	ω-Chlorostearyl alcohol
3:9031	2-Chloropropen-2-a1-1	3:8715	α -Chlorostyrene
3:7030	1-Chloropropene-1	3:8717	β -Chlorostyrene
3:7020	2-Chloropropene-1	3:8717	ω-Chlorostyrene
3:7035	3-Chloropropene-1	3: 499 5	Chloroterephthalic acid
3:5635	2-Chloropropen-2-o1-1	3:9874	1-Chlorotetradecane
3:5820	3-Chloropropen-2-o1-1	3:0375	14-Chlorotetradecanol-1
3:5635	2-Chloropropen-1-o1-3	3:0375	ω-Chloro-n-tetradecyl alcohol
3:1685	Chloropropiolic acid	3: 094 5	1-Chloro-2,2,3,3-tetramethyl-
3:51 60	α -Chloropropionaldehyde		butane
3:5576	β -Chloropropionaldehyde	3:1293	p-Chlorothymol
3:9490	β-Chloropropionaldehyde	3:8535	α-Chlorotoluene
	diethylacetal	3:8535	ω-Chlorotoluene
3:6125	α-Chloropropionic acid	3:8245	o-Chlorotoluene
3: 0460	β-Chloropropionic acid	3:8275	m-Chlorotoluene
3:5320	α-Chloropropionyl chloride	3:8287	p-Chlorotoluene
3:5690	β -Chloropropionyl chloride	3:2640	o-Chloro-α-toluie acid
3:9664	α-Chloropropiophenone	3:1910	m -Chloro- α -toluic acid
3:1115	β-Chloropropiophenone	3:3135	p-Chloro-α-toluic acid
3:0340	4-Chloropropiophenone	3:9859	1-Chlorotridecane
3:8180	β-Chloro-n-propyl acetate	3:4855	5-Chlorotrimellitic acid
3:8310	γ-Chloro-m-propyl acetate	3:4975	Chlorotrimesic acid
3:7917	β-Chloro-n-propyl alcohol	3:8725	2-Chloro-1,3,5-trimethylbensene
	to a contract to the second		more riole or minearly increasing

3:4020	3-Chloro-2,2,3-trimethylbutane		D
3:7752	Chloro-trimethylcarbinol	0.0000	
3:9039	β-Chlorotrimethylene glycol	3: 3320 3:18 90	"DDD"
3:6648	β-Chlorotrimethylene glycol	3:1890 3:3320	" o,p'-DDD "
	acetate	3:3298	" p,p'-DDD " " DDT "
3:9744	4-Chloro-2,4,6-trimethylheptane	3:9865	" o,o'-DDT "
3:9654	3-Chloro-2,2,3-trimethylhexane	3:1820	" o,p'-DDT "
3:8113	4-Chloro-2,2,4-trimethylpentane	3:9867	" m,p'-DDT "
3:3560	1-Chloro-1,2,2-triphenylethyl-	3:3298	" p,p'-DDT "
	ene	3:1676	Decachlorodiethyl ether
3:3560	"Chlorotriphenylethylene"	3:9720	Decamethylene (di)chloride
3:3410	α -Chlorotriphenylmethane	3:8800	n-Decanoyl chloride
3:88 9 3	1-Chloroundecane	3:8785	n-Decyl chloride
3:8783	α-Chloro-n-valeric acid	3:1618	Desyl chloride
3:0270	β-Chloro-n-valeric acid	3:8085	Diallylcarbinyl chloride
3:9270	γ-Chloro-n-valeric acid	3:9640	Di-n-butylcarbinyl chloride
3:0075	δ-Chloro-n-valeric acid	3:9732	Di-n-butyl-methyl-carbinyl
3:5860	α-Chloro-n-valeryl chloride		chloride
3:9260	β-Chloro-n-valeryl chloride	3:6110	"Dichloroacetal"
3:9264 3:7070	δ-Chloro-n-valeryl chloride	3:5180	Dichloroacetaldehyde
	1-Chloro-2-vinylacetylene	3:6110	Dichloroacetaldehyde diethyl-
3:8715 3:8717	α-Chlorovinylbenzene		acetal
3:0300	β-Chlorovinylbenzene 2-Chloro-xenene	3:5310	Dichloroacetaldehyde ethyl-
3:8940	3-Chloro-xenene	0.7010	alcoholate
3:1912	4-Chloro-xenene	3:5310	Dichloroacetaldehyde ethyl-
3:8710	ω-Chloro-o-xylene	3:1085	hemiacetal
3:8645	vicChloro-o-xylene	3:6208	Dichloroacetaldehyde hydrate Dichloroacetic acid
3:8675	unsymChloro-o-xylene	3:6430	Dichloroacetic acid anhydride
3:8700	ω-Chloro-m-xylene	3:5430	α, α -Dichloroacetone
3:8590	vicChloro-m-xylene	3:0563	α,α' -Dichloroacetone
3:8665	unsymChloro-m-xylene	3:0563	symDichloroacetone
3:8640	symChloro-m-xylene	3:5430	unsymDichloroacetone
3:8660	ω-Chloro-p-xylene	3:6835	ω,ω-Dichloroacetophenone
3:8600	eso-Chloro-p-xylene	3:5290	Dichloroacetyl chloride
3:2115	5-Chloro-o-3-xylenol	3:5010	Dichloroacetylene
3:2218	6-Chloro-o-3-xylenol	3:2265	α,β -Dichloroacrylic acid
3:1754	5-Chloro-o-4-xylenol	3:1875	β , β -Dichloroacrylic acid
3:2705	6-Chloro-o-4-xylenol	3:4916	9,10-Dichloroanthracene
3:0158	3-Chloro-o-4-xylenol	3:4916	meso-Dichloroanthracene
3:2180	5-Chloro-m-2-xylenol	3:9399	2,4-Dichlorobenzal (di)chloride
3:8784	5-Chloro-m-4-xylenol	3:0490	2,5-Dichlorobenzal (di)chloride
3:2460 3:3505	6-Chloro-m-4-xylenol	3:9898	2,6-Dichlorobenzal (dı)chloride
3:0844	2-Chloro-m-5-xylenol	3:6876	3,4-Dichlorobenzal (di)chloride
3:1822	6-Chloro- <i>m</i> -5-xylenol 5-Chloro- <i>p</i> -2-xylenol	3:0370	3,5-Dichlorobenzal (di)chloride
3:0330	Cinnamoyl chloride	3:1480 3:1800	2,3-Dichlorobenzaldehyde
3:0010	Cinnamyl chloride	3:1145	2,4-Dichlorobenzaldehyde
3:9102	Crotonaldehyde dichloride	3:11 1 5 3:1690	2,5-Dichlorobenzaldehyde 2,6-Dichlorobenzaldehyde
3:5910	Crotonchloral	3:0550	3,4-Dichlorobenzaldehyde
3:1375	Crotonic acid dichloride	3:1475	3,5-Dichlorobenzaldehyde
3:7693	a-Crotonyl chloride	3:6055	o-Dichlorobenzene
3:7205	Crotonyl chloride	3:5960	m-Dichlorobenzene
3:7685	Crotylidene (di)chloride	3:0980	p-Dichlorobenzene
3:8795	Cuminyl chloride	3:4965	4,6-Dichlorobenzenedicarboxylic
3:8580	Cyclohexanecarboxylic acid		acid-1,3
	chloride	3:4985	2,5-Dichlorobenzenedicarboxylic
3:9374	cis-Cyclohexene chlorohydrin		acid-1,4
3:0175	trans-Cyclohexene chlorohydrin	3:4650	2,3-Dichlorobenzoic acid
3:8040	Cyclohexyl chloride	3:4560	2,4-Dichlorobenzoic acid
8:5770	Cyclohexyl chlorocarbonate	3:4340	2,5-Dichlorobenzoic acid
3:5770	Cyclohexyl chloroformate	3:4200	2,6-Dichlorobenzoic acid
3:75 45	Cyclopentyl chloride	3:4925	3,4-Dichlorobensoic acid

3.6-19.00 3.6-				
3:9856	3:4840	3,5-Dichlorobenzoic acid	3:1 90 3	α,β-Dichloro-n-butyric acid
3:19625 2.4-Dichlorobenzophenone 3:2526 2.5-Dichlorobenzophenone 3:2536 2.5-Dichlorobenzophenone 3:2536 3.5-Dichlorobenzophenone 3:2536 3.5-Dichlorobenzophenone 3:2526 3.4-Dichlorobenzophenone 3:2526 3.4-Dichlorobenzophenone 3:2526 3.5-Dichlorobenzophenone 3:2527 3.4-Dichlorobenzophenone 3:2527 3.5-Dichlorobenzophenone 3:2527 3.5-Dichlorobenzophenone 3:2527 3.5-Dichlorobenzophenone 3:2528 3.5-Dichlorobinheny 3:25				
3:2465 2,4'-Dichlorobensophenone 3:2429 3,5-Dichlorocatechol 3:2285 2,5-Dichlorobensophenone 3:2825 2,5-Dichlorobensophenone 3:2825 3,3-Dichlorobensophenone 3:2826 3,3-Dichlorobensophenone 3:2826 3,3-Dichlorobensophenone 3:2826 3,3-Dichlorobensophenone 3:2826 3,3-Dichlorobensophenone 3:2826 3,3-Dichlorobensophenone 3:2825 3,3-Dichlorobinensyl 3:2825 3,3-Di			3:1375	
3:2346 2.5-Dichlorobenzophenone 3:2555 3:2516 3.3-Dichlorobenzophenone 3:3976 3.3-Dichlorobenzophenone 3:3976 3.4-Dichlorobenzophenone 3:275 3.4-Dichlorobenzophenone 3:275 3.5-Dichlorobenzophenone 3:2855 3.5-Dichlorobenzophenone 3:2855 3.5-Dichlorobenzophenone 3:2855 3.5-Dichlorobenzoquinone 3:2855 3.2-Dichlorobenzoquinone 3:2855 3.2-Dichlorobenzoquinone 3:2855 3.2-Dichlorobenzoquinone 3:2855 3.2-Dichlorobenzoquinone 3:2855 3.2-Dichlorobenzoquinone 3:2856 3.2-Dichlorobinal 3:2855 3.2-Dich				
3:2856 2.6-Dichlorobenzophenone 3:3846 3.4-Dichlorobenzophenone 3:3846 3.4-Dichlorobenzophenone 3:415 3.4-Dichlorobenzophenone 3:4275 3.4-Dichlorobenzophenone 3:2855 3.5-Dichlorobenzophenone 3:2855 3.5-Dichlorobenzophenone 3:2855 3.5-Dichlorobenzoquinone 3:2856 3.5-Dichlorobinenzy 3:2856 3.5-Dichlor				
3.3456 3.3-Dichlorobenzophenone 3.3666 3.4-Dichlorobenzophenone 3.4-Dichlorobenzophenone 3.5-Dichlorobenzophenone 3		2,5-Dichlorobenzophenone		4,5-Dichlorocatechol
3.4976 3.4-Dichlorobensophenone 3.2416 3.5-Dichloro-2.2-bie-(chloromens) 3.2416 3.5-Dichlorobensophenone 3.2477 4.4'-Dichlorobensophenone 3.2966 3.5-Dichlorobensophenone 3.2966 3.5-Dichlorobensophenone 3.2966 3.2955 3.5-Dichlorobensoquinone 4.4'-Dichlorobensoquinone 4.4'-Dichlorobensoquinone 4.4'-Dichlorobensoquinone 4.4'-Dichlorobensoquinone 4.4'-Dichlorobensoquinone 4.4'-Dichlorobensoquinone 4.4'-Dichlorobensoquinone 4.4'-Dichlorobensopuinone 4.4'-Dic	3:2285	2,6-Dichlorobenzophenone	3:9218	1,3-Dichloro-2-(chloromethyl)-
3.44.5 3,4 - Dichlorobenzophenone 3.9066 1,3 - Dichloro-2-(chloromethyl) 1,1 - Dichloro-2-(chloromethyl) 1,1 - Dichloro-2-(chloromethyl) 2,2 - Dichlorobenzoquinone 1,3 - Dichloro-2-(chloromethyl) 2,2 - Dichlorobinophyl 3,2 - Dichlor	3:3860	3,3'-Dichlorobenzophenone		butane
3.1-2065 3.5-Dichlorobensophenone	3:3070	3,4-Dichlorobenzophenone	3:2675	1,3-Dichloro-2,2-bis-(chloro-
3:2476	3:3415	3,4'-Dichlorobenzophenone		methyl)propane
3:4276	3:1505	3,5-Dichlorobenzophenone	3:9066	1,3-Dichloro-2-(chloromethyl)-
3:2855 c-Dichlorobensoquinone 3:1896 1,1-Dichloro-2-(c-chlorophenyl)ethane 1,2-Dichlorobensoquinone 3:2855 2,3-Dichlorobensoquinone-1,4 3:3750 2,5-Dichlorobensoquinone-1,4 3:3750 2,5-Dichlorobensoquinone-1,4 3:3750 2,5-Dichlorobensoquinone-1,4 3:3750 2,5-Dichlorobensyl chloride 3,5-Dichlorobensyl chloride 3,5-Dichlorobensyl chloride 3,5-Dichlorobensyl chloride 3,5-Dichlorobensyl chloride 3,5-Dichlorobensyl chloride 3,5-Dichlorobensyl chloride 3:2857 2,2-Dichlorobiphenyl 3:1285 2,2-Dichlorobiphenyl 3:1285 2,2-Dichlorobiphenyl 3:1285 2,2-Dichlorobiphenyl 3:1285 2,3-Dichlorobiphenyl 3:1285 2,3-Dichlorobiphenyl 3:1286 3,5-Dichlorobiphenyl 3:1286 3,5-Dichl	3:4270	4.4'-Dichlorobenzophenone		propene-1
3:3750 m-Dichlorobensoquinone 3:4470 p-Dichlorobensoquinone-1,4 3:4470 2,5-Dichlorobensoquinone-1,4 3:4470 2,5-Dichlorobensoquinone-1,4 3:4470 2,5-Dichlorobensoquinone-1,4 3:4470 2,5-Dichlorobensoquinone-1,4 3:3750 2,5-Dichlorobensoquinone-1,4 3:3750 3,5-Dichlorobensyl chloride 3:3750 3,5-Dichlorobensyl chloride 3:3650 3,5-Dichlorobensyl chloride 3:3863 3,5-Dichlorobensyl chloride 3:3854 meso-a,a'-Dichlorobinensyl 3:1926 4,5-Dichloro-c-c-cesol 3:1935 2,2-Dichlorobinensyl 3:1926 2,5-Dichloro-c-c-cesol 4,5-Dichloro-c-c-c-c-c-c-c-c-c-c-c-c-c-c-c-c-c-c-	3:2855		3:1890	
3:1457	3:3750			
3:2455	3:4470		3:1925	
3.476 2,5-Dichlorobenzoquinone-1,4 3:3863 1,1-Dichloro-2-(m-chlorophenyl)-2-(p-chlorophenyl)-thylene 2,6-Dichlorobenzyl chloride 3:3320 1,1-Dichloro-2,2-bis-(p-chlorophenyl)-thylene 3:0350 3,5-Dichlorobenzyl chloride 3:2438 1,1-Dichloro-2,2-bis-(p-chlorophenyl)-thylene 3:0350 3,5-Dichlorobenzyl chloride 3:2438 1,1-Dichloro-2,2-bis-(p-chlorophenyl)-thylene 2,2-bis-(horobenzyl-thorophenyl)-thylene 2,2-bis-(horobenzyl-thorophenyl-thylene 2,2-bis-(horobenzyl-thorophenzyl				
3.3750 2.6-Dichlorobenzoquinone-1.4 3.3320 1,1-Dichloro-2,2-bis-(p-chlorobenzyl chloride 3.3425 3,4-Dichlorobitenzyl 3.1920 4,6-Dichloro-c-cresol 3.1854 meso-α,α'-Dichlorobitenzyl 3.1920 2,4-Dichloro-c-cresol 3.19350 2,3-Dichlorobitenzyl 3.1936 2,4-Dichloro-c-cresol 3.1936 2,4-Dichloro-bitenzyl 3.1936 2,4-Dichloro-c-cresol 3.1936 3,4-Dichlorobitenzyl 3,4-Dichloro-3,3-dimethy			3:9863	
3.6410			0.0000	
3: 6795 3, 4-Dichlorobenzyl chloride 3: 2438 phenyl)ethane 2: 2570 d.la.a'-Dichlorobinzyl 3: 2940 phenylethylene 3: 2570 d.la.a'-Dichlorobibenzyl 3: 2940 d.la.a'-Dichlorobibenzyl 3: 2940 d.la.a'-Dichlorobibenzyl 3: 2940 d.la.a'-Dichlorobibenzyl 3: 1295 d.la.a'-Dichlorobibenzyl 3: 1295 d.la.a'-Dichlorobibenzyl 3: 1295 d.la.a'-Dichlorobibenzyl 3: 1295 d.la.a'-Dichlorobiphenyl 3: 1295 d.la.a'-Dichlorodecane 3: 1295 d.la.a'-Dichlorobiphenyl 3: 1295 d.la.a'-Dichlorodicthyl ether 3: 1295 d.la.a'-Dichlorobitadiene-1, 3 3: 1295 d.la'-Dichlorobitadiene-1, 3 3: 1295 d.la'-Dichlorobitadiene-1, 3 3: 1295 d.la'-Dichlorobitadiene-1, 3 3: 1295 d.la'-Dichlorobitane 3: 1.1-Dichlorobitane 3: 1.2-Dichlorobitane 3: 1.2-Dichlorobitane 3: 1.2-Dichlorobitane 3: 1.3-Dichlorobitane			3:3320	
3:9440 Dichlorobiacetylene 3:2438 1,1-Dichloro-2,2-bis-(p-chlorobiacetylene 1,4-Dichlorobibenzyl 3:2910 4,5-Dichloro-c-cresol 4,6-Dichloro-c-cresol 4,6-Dichloro-c-c-cresol 4,6-Dichloro-c-c-cresol 4,6-Dichloro-c-c-cresol 4,6-Dichloro-c-c-cresol 4,6-Dichloro-c-c-cresol 4,6-Dichloro-c-c-cresol 4,6-Dichloro-c-c-c-col 4,6-Dichloro-c-c-c-col 4,6-Dichloro-c-c-c-col 4,6-Dichloro-c-c-c-col 4,6-Dichloro-c-c-c-col 4,6-Dichloro-c-c-c-col 4,6-Dichloro-c-c-c-c-c-c-c-c-c-c-c-c-c-c-c-c-c-c-			0.00/10	
3:9040 Dichlorobiacetylene 3:2970 d.l-α.α'-Dichlorobibenzyl 3:2910 4,5-Dichloro-c-cresol 4,5-Dichloro-c-cresol 4,5-Dichloro-c-cresol 4,5-Dichloro-c-cresol 4,5-Dichloro-c-cresol 3:1325 2,2'-Dichlorobiphenyl 3:1205 2,4-Dichloro-m-cresol 2,4'-Dichlorobiphenyl 3:1745 4,6-Dichloro-m-cresol 2,6-Dichloro-m-cresol 2,6-Dichloro-dexene 2,6-Dichloro-dicthyl ether 2,6-Dichloro-dicthyl ether 2,6-Dichloro-dicthyl ether 2,6-Dichloro-3,4-diethylhexane 3,4-Dichloro-dexene 3,4-Dichloro-2,2-dimethylbutane 3,4-Dichloro-2,2-dimethylbutane 3,4-Dichloro-dexene 3,4-Dichloro-2,3-dimethylbutane 3,4-Dichloro-2,3-dimethylbutane 3,4-Dichloro-2,3-dimethylbutane 2,6-Dichloro-2,6-dimethyl-kexane 2,			3 . 2438	
3: 2570 d,l-α,α'-Dichlorobibenzyl 3: 2910 4,5-Dichloro-α-cresol 3: 1825 2,2'-Dichlorobiphenyl 3: 1825 2,2'-Dichlorobiphenyl 3: 1826 2,4-Dichloro-m-cresol 2,4-Dichloro-m-cresol 2,4-Dichloro-m-cresol 2,4-Dichloro-m-cresol 2,5-Dichloro-m-cresol 2,5-Dichloro-p-cresol 2,5-Dichloro-m-cresol			U . NEUG	
3:4854 meso-α,α'-Dichlorobibenzyl 3:1026 4,6-Dichloro-o-cresol 3:1325 2,2'-Dichlorobiphenyl 3:1056 2,4-Dichloro-m-cresol 3:1936 2,6-Dichloro-m-cresol 3:0160 2,4'-Dichlorobiphenyl 3:1745 4,6-Dichloro-m-cresol 3:0160 3,3'-Dichlorobiphenyl 3:0400 2,6-Dichloro-m-cresol 3:0150 3,3'-Dichlorobiphenyl 3:0400 2,6-Dichloro-m-cresol 1,10-Dichlorodecane α,α'-Dichlorodecane α,α'-Dichlorodecane α,α'-Dichlorodecane α,α'-Dichlorodecane α,α'-Dichlorodecane α,α'-Dichlorodecane α,α'-Dichlorodecane α,α'-Dichlorodecane α,α'-Dichlorodecane α,β'-Dichlorodecane α,β			3.2010	
3:1325 2.2'-Dichlorobiphenyl 3:1245 2.4-Dichloro-m-cresol 3:9850 2.3-Dichlorobiphenyl 3:1745 4.6-Dichloro-m-cresol 4.6-Dichloro-m-cresol 3:9854 2.5-Dichlorobiphenyl 3:1745 4.6-Dichloro-m-cresol 3:0858 2.5-Dichlorobiphenyl 3:9720 1,10-Dichlorodecane α.α'-Dichlorodiethyl ether α.β-Dichlorodiethyl ether β.β-Dichlorodiethyl ether α.β-Dichlorodiethyl ether α				
3:9850 2,3-Dichlorobiphenyl 3:1745 4,6-Dichloro-m-cresol 3:0870 2,4'-Dichlorobiphenyl 3:1745 4,6-Dichloro-m-cresol 3:0870 2,4'-Dichlorobiphenyl 3:1745 4,6-Dichloro-m-cresol 3:0885 3,4-Dichlorobiphenyl 3:9720 1,10-Dichlorodesane α,α'-Dichlorobiphenyl 3:9730 α,α'-Dichlorodiethyl ether α,β-Dichlorodiethyl ether α,β-Dichlorodiethyl ether α,β-Dichlorodiethyl ether α,β-Dichlorodiethyl ether 3:9657 1,2-Dichlorobutadiene-1,3 3:9724 3,4-Dichlorodiethyl ether 3:9527 2,3-Dichlorobutadiene-1,3 3:9724 3,4-Dichloro-3,4-diethylhexane 3:9162 2,3-Dichlorobutane 3:4326 3,3-Dichloro-3,4-diethylhexane 3:7680 1,2-Dichlorobutane 3:4326 3,3-Dichloro-2,2-dimethylbutane 3:7415 2,2-Dichlorobutane 3:4326 3,3-Dichloro-2,2-dimethylbutane 3:5835 1,4-Dichlorobutane 3:4326 3,3-Dichloro-2,2-dimethylbutane 3:5836 1,3-Dichlorobutane 3:54520 2,3-Dichlorobutane 3:54520 2,3-Dichloro-2,3-dimethylbutane 3:54520 1,3-Dichlorobutane 3:54520 2,3-Dichloro-2,2-dimethylbutane 3:54520 1,3-Dichlorobutane 3:54520 2,3-Dichloro-2,2-dimethylbutane 3:54520 1,3-Dichlorobutane 3:54520 2,3-Dichloro-2,2-dimethylbutane 3:54520 1,3-Dichlorobutane 3:54520 1,3-Dichlorobu				
3: 9854 2,5-Dichlorobiphenyl 3: 9400 2,6-Dichloro-m-cresol 3: 9854 2,5-Dichlorobiphenyl 3: 9400 1,10-Dichlorodecane 3: 9720 1,10-Dichlorodecane 3: 9720 2,3-Dichlorobiphenyl 3: 5544 α,β-Dichlorodichtyl ether α,β-Dichloro-3,β-diintyl dray-y-benzoquinone-1,4 α,β-Dichloro-3,β-diintyl dray-y-benzoquinone-1,4 α,β-Dichloro-3,β-diintyl dray-y-benzoquinone-1,4 α,β-Dichloro-2,2-dimethyl butane 3: 4520 3,3-Dichloro-2,2-dimethyl butane 3: 4520 3,3-Dichloro-2,2-dimethyl butane 3: 4520 3,3-Dichloro-2,2-dimethyl-beptane 3: 5324 3,3-Dichloro-2,3-dimethyl butane 3: 5324 3,3-Dichloro-2,3-dimethyl butane 3: 5324 3,3-Dichloro-2,3-dimethyl butane 3: 5324 3,3-Dichloro-2,3-dimethyl butane 3: 5324 3,3-Dichloro-2,3-dimethyl benzoquinone-2 3: 5330 3,3-Dichloro-2,3-dimethyl benzoquinone-2 3: 5330 3,3-Dichloro-2,3-dimethyl benzoquinone-2 3: 5330 3,3-Dichloro-2,3-dimethyl-benzoquinone-2 3: 5330 3,3-Dichloro-2,3-dimethyl-benzoquinone-1,4 3: 5330 3,3-Dichloro-2,3-dimethyl-benzoquinone-3 3: 5330 3,3-Dichloro-2,3-dimethyl-benz				
3:9854 2,5-Dichlorobiphenyl 3:9720 1,10-Dichlorodecane 3.693 3,4-Dichlorobiphenyl 3:9720 1,10-Dichlorodecane 3.7595 3,4-Dichlorobiphenyl 3:5640 α,β-Dichlorodiethyl ether α,β-Dichloro-3,4-diethylhexane 3:9122 2,3-Dichlorobutane 3:9224 3,4-Dichloro-3,4-diethylhutane 3:9325 1,3-Dichlorobutane 3:8325 3,3-Dichloro-2,2-dimethylbutane 3:4326 3,3-Dichloro-2,2-dimethylbutane 3:4326 3,3-Dichloro-2,3-dimethylbutane 3:4526 2,3-Dichlorobutane 3:8132 1,1-Dichlorodiethyl ether 3:9145 1,3-Dichlorobutane 3:8132 1,1-Dichlorodiethyl ether 3:9145 1,3-Dichlorobutane 3:8132 1,1-Dichlorodiethyl ether 3:9145 1,3-Dichlorobutane 3:9145 1,3-Dichlorobutane 3:9145 1,3-Dichlorobutane 3:9145 1,3-Dichlorobutane 3:9145 1,3-Dichlorobutane 3:9145 1,3-Dichlorobutene-1 3:9145 1,3-Dichlorobutene-1 3:9145 1,3-Dichlorobutene-1 3:9145 1,3-Dichlorobutene-2				
3.0180 3,3'-Dichlorobiphenyl 3:7595 a, α'-Dichlorodethyl ether α.α'-Dichlorodethyl ether α.α'-Dichloro-3.4-diethylbexane 3:6324 3.4-Dichloro-3.4-diethylbexane 3:6324 3.4-Dichloro-3.4-diethylbexane 3:6324 3.4-Dichloro-3.4-dimethylbexane 3:6324 3.4-Dichlorodethyl ether 3:6324 3.3-Dichlorodethyl ether 3				
3.0685 3,4-Dichlorobiphenyl 3:5646 α,β-Dichlorodiethyl ether α,β-Dichloro-3,4-diethylhexane 3:6025 β,β'-Dichloro-3,4-diethylhexane 3:9040 1,4-Dichlorobutane-1,3 3:9724 3,4-Dichloro-3,4-diethylhexane 3:9162 2,3-Dichlorobutane-1,4 bensoquinone-1,4 μ-Dichloro-2,2-dimethylbutane 3:4326 3,3-Dichloro-2,2-dimethylbutane 3:4326 3,3-Dichloro-2,2-dimethylbutane 3:4326 3,3-Dichloro-2,2-dimethylbutane 3:4520 2,3-Dichloro-2,3-dimethylbutane 3:4520 2,3-Dichlorobutane 3:54520 2,3-Dichlorobutane 3:54520 2,3-Dichlorobutane 3:54520 2,3-Dichlorobutane 3:54520 2,3-Dichlorobutane-2 3:5550 1,3-Dichlorobutane-2 3:5550 1,3-Dichlorobutene-1 3:5550 1,3-Dichlorobutene-1 3:5550 1,3-Dichlorobutene-2 3:5550 1,3-Dichlorobutene-2 2 3:5550 1,3-Dichlorobutene-2 3:5550 1,3-				
3:0360 3,5-Dichlorobiphenyl 3:5640 α,β-Dichlorodiethyl ether 3:4300 4,4'-Dichlorobutadiene-1,3 3:6025 β,β'-Dichlorodiethyl ether 3:9057 1,2-Dichlorobutadiene-1,3 3:6025 β,β'-Dichlorodiethyl ether 3:5220 2,3-Dichlorobutadiene-1,3 3:9724 3,4-Dichloro-3,4-diethylhexane 3:9040 1,4-Dichlorobutane-1,3 3:4970 2,5-Dichloro-3,6-dihydroxy-benzoquinone-1,4 benzoquinone-1,4 benzoquinone-1				
3:4300				
3:9057 1,2-Dichlorobutadiene-1,3 3:9724 3,4-Dichloro-3,4-diethylhexane 3:9040 1,4-Dichlorobutadiyne-1,3 3:4970 2,3-Dichlorobutaniyne-1,3 3:4970 2,5-Dichloro-3,6-dihydroxy-benzoquinone-1,4 5:7550 1,1-Dichlorobutane 3:4826 3,3-Dichloro-2,2-dimethylbutane 3:4826 1,2-Dichlorobutane 3:4826 3,3-Dichloro-2,2-dimethylbutane 3:5835 1,4-Dichlorobutane 3:4520 2,3-Dichloro-2,2-dimethylbutane 3:7615 4,2-3-Dichlorobutane 3:4520 2,3-Dichloro-2,3-dimethylbutane 3:7615 4,2-3-Dichlorobutane 3:5245 2,6-Dichloro-3,3-dimethylbutane 3:5836 1,3-Dichlorobutane 3:6536 1,3-Dichlorobutane 3:6536 1,3-Dichlorobutane 3:6536 1,3-Dichlorobutane 3:6536 1,3-Dichlorobutane 3:6536 1,2-Dichlorobutene-1 3:6536 1,2-Dichlorobutene-2 3:6536 1,2-Dichlorobutene-2 (low-boilg. isomer) 3:6536 1,2-Dichlorobutene-2 (low-boilg. isomer) 3:6536 1,3-Dichlorobutene-2 3:6536 1,3-Dichlorobutene-2 3:6536 1,3-Dichlorobutene-2 3:6536 1,2-Dichlorobutene-2 3:6536 1,2-Dic				
3:5229 2,3-Dichlorobutadiene-1,3 3:9724 3,4-Dichloro-3,4-diethylhexane 3:9102 2,3-Dichlorobutanil-1 2,3-Dichlorobutanal-1 3:1952 1,1-Dichlorobutane 3:4325 3,3-Dichloro-2,2-dimethylbutane 3:4325 3,3-Dichloro-2,2-dimethylbutane 3:5335 1,4-Dichlorobutane 3:4529 2,3-Dichloro-2,2-dimethylbutane 3:5335 1,4-Dichlorobutane 3:5535 1,3-Dichlorobutane 3:5535 1,2-Dichlorobutene-1 3:5535 1,2-Dichlorobutene-2 3:5535 1,3-Dichlorobutene-2 3:5535 1,3-Dichlorobutene-2 3:5535 1,3-Dichlorobutene-2 3:5535 1,3-Dichlorobutene-2 3:5535 1,3-Dichlorobutene-2 3:5535 1,3-Dichlorobutene-2 3:5535 1,2-Dichlorobutene-2 3:5535 1,2-Dichlorobutene-2 3:5535 1,3-Dichlorobutene-2 3:5535				
3:9040 1,4-Dichlorobutaniyne-1,3 3:9102 2,3-Dichlorobutanie 3:8505 1,1-Dichlorobutane 3:4325 3,3-Dichloro-2,2-dimethylbutane 3:5835 1,4-Dichlorobutane 3:4325 4,4-Dichloro-2,2-dimethylbutane 3:5835 1,4-Dichlorobutane 3:4520 2,3-Dichloro-2,3-dimethylbutane 3:5835 1,4-Dichlorobutane 3:4520 2,3-Dichloro-2,3-dimethylbutane 3:5835 1,4-Dichlorobutane 3:5325 3,3-Dichloro-2,3-dimethylbutane 3:5835 1,4-Dichlorobutane 3:5325 3,3-Dichloro-2,3-dimethylbutane 3:5835 3,3-Dichloro-2,3-dimethylbutane 3:5836 3:5836 3,3-Dichlorobutane 3:5245 3,3-Dichlorobutane 3:5845 3,3-Dichloro-2,3-dimethylbutane 3:5836 3,3-Dichlorobutane 3:5835 3,3-Dichlorobutane 3:5836 1,1-Dichlorobutane 2 3:5836 1,2-Dichlorobutane 2 3:5836 1,2-Dichlorobutane 2 3:5836 1,3-Dichlorobutane				
3:9102 2,3-Dichlorobutanal-1				
3:7550 1,1-Dichlorobutane 3:8605 β,β'-Dichloro-di-isopropyl ether 3:7680 1,2-Dichlorobutane 3:4325 3,3-Dichloro-2,2-dimethylbutane 3:7855 1,3-Dichlorobutane 3:8132 4,4-Dichloro-2,2-dimethylbutane 3:5835 1,4-Dichlorobutane 3:4520 2,3-Dichloro-2,3-dimethylbutane 3:7415 2,2-Dichlorobutane 3:8132 1,1-Dichloro-3,3-dimethylbutane 3:7615 d,L-2,3-Dichlorobutane 3:5245 symDichlorodimethyl ether 3:7616 d,L-2,3-Dichlorobutanol-2 3:5455 symDichlorodimethyl ether 3:7616 d,L-2,3-Dichlorobutanol-2 3:1550 2,6-Dichloro-2,6-dimethyl-hexane 3:7650 1,3-Dichlorobutene-1 3:8315 3,4-Dichloro-3,4-dimethylhexane 3:7685 1,1-Dichlorobutene-2 3:8316 2,6-Dichloro-2,5-dimethyl-hexane 3:5860 1,2-Dichlorobutene-2 (low-boilg, isomer) 3:8516 4,5-Dichloro-2,7-dimethyl-pentane 3:5850 1,3-Dichlorobutene-2 3:7610 3:9428 2,4-Dichloro-2,4-dimethyl-pentane 3:5850 1,3-Dichlorobutene-2 3:9430 3:9430 3:9400			3:4976	
3:7680 1,2-Dichlorobutane 3:4325 3,3-Dichloro-2,2-dimethylbutane 3:7925 1,3-Dichlorobutane 3:8132 4,4-Dichloro-2,2-dimethylbutane 3:5835 1,4-Dichlorobutane 3:4520 2,3-Dichloro-2,3-dimethylbutane 3:7415 2,2-Dichlorobutane 3:8132 1,1-Dichloro-2,3-dimethylbutane 3:7415 2,2-Dichlorobutane 3:63245 2,3-Dichlorobutane 3:5245 2,4-Dichloro-2,3-dimethylbutane 3:5245 2,5-Dichloro-2,5-dimethylbutane 2,5-Dichloro-2,7-dimethylbutane 2,5-Dichloro-2,7-dimethylbutane 2,5-Dichloro-2,4-dimethylbutane 3:5245 2,4-Dichlorobutene-2				
3:7925 1,3-Dichlorobutane 3:8132 4,4-Dichloro-2,2-dimethylbutane 3:5835 1,4-Dichlorobutane 3:4529 2,3-Dichloro-2,3-dimethylbutane 3:7415 2,2-Dichlorobutane 3:8132 1,1-Dichloro-3,3-dimethylbutane 3:7515 d,2-3-Dichlorobutane 3:8245 symDichlorodimethyl ether 3:7580 mesc-2,3-Dichlorobutane 3:6245 symDichlorodimethyl ether 3:5945 1,3-Dichlorobutane-2 3:1550 2,5-Dichloro-2,5-dimethylhexane 3:9074 2,3-Dichlorobutene-1 3:8315 3,4-Dichloro-2,5-dimethylhexane 3:9074 2,3-Dichlorobutene-1 3:9504 2,5-Dichloro-2,5-dimethylhexane 3:9074 2,3-Dichlorobutene-2 3:9504 2,5-Dichloro-2,5-dimethylhexane 3:7685 1,1-Dichlorobutene-2 (low-boilg. 3:9640 2,7-Dichloro-2,7-dimethyloctane 2,7-Dichloro-2,2-dimethyl-pentane 3:5515 1,2-Dichlorobutene-2 (high-boilg 3:9428 2,4-Dichloro-2,4-dimethyl-pentane 3:5550 1,3-Dichlorobutene-2 3:7616 3,3-Dichloro-2,4-dimethyl-pentane 3:5550 cis-2,3-Dichlorobutene-2 3:6550 cis-2,3-Dichlorobutene-2 3:6550 2,4-Dichloro-2,4-dimethyl-pentane 1,2-Dichloro-4,4-dimethyl-pentane 3:5550 2,4-Dichloro-4er-butyl alcohol 3:2442 5,6-Dichloro-2,3-dimethyl-pentane 2,3-Dichloro-4,4-dimethyl-pentane 2,3-Dichloro-4,4-dimethyl-pentane 2,3-Dichloro-3,3-dimethyl-pentane 2,3-Dichloro-3,4-dimethyl-pentane 2,5-Dichloro-3,4-dimethyl-pentane 3,5-Dichloro-3,4-dimethyl-pentane 3,5-Dichloro-3,4-dimethyl-pentane 3,5-Dichloro-3,4-dime				
3:5835 1,4-Dichlorobutane 3:4520 2,3-Dichloro-2,3-dimethylbutane 3:7415 2,2-Dichlorobutane 3:5132 1,1-Dichloro-3,3-dimethylbutane 3:7615 d,l-2,3-Dichlorobutane 3:5245 2,6-Dichloro-2,8-dimethylbutane 3:5285 2,6-Dichlorobutane 3:6455 2,6-Dichloro-2,8-dimethyl-heptane 3:5850 1,3-Dichlorobutanen-2 3:1550 1,3-Dichlorobutene-1 3:8515 3,4-Dichlorobutene-1 3:8515 3,4-Dichlorobutene-1 3:8550 1,1-Dichlorobutene-2 3:6560 1,2-Dichlorobutene-2 (low-boilg. isomer) 3:5550 1,3-Dichlorobutene-2 (low-boilg. isomer) 3:5550 1,3-Dichlorobutene-2 (low-boilg. isomer) 3:5550 1,3-Dichlorobutene-2 (high-boilg 3:9428 2,4-Dichloro-2,4-dimethyl-pentane 3:5550 1,3-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:5550 1,2-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:5550 2,4-Dic				
3:7415 2,2-Dichlorobutane 3:8132 1,1-Dichloro-3,3-dimethylbutane 3:7515 d,2-3-Dichlorobutane 3:6245 2,6-Dichlorodimethyl ether 3:58145 1,3-Dichlorobutane-2 3:455 2,6-Dichloro-2,6-dimethyl-hexane 3:5900 1,3-Dichlorobutane-2 3:1550 2,5-Dichlorobutane-1 3:8315 3,4-Dichloro-2,5-dimethylhexane 3:9074 2,3-Dichlorobutene-1 3:8315 3,4-Dichloro-2,5-dimethylhexane 3:9074 2,3-Dichlorobutene-1 3:9564 2,5-Dichloro-2,5-dimethylhexane 3:5350 3,4-Dichlorobutene-2 3:6545 1,2-Dichlorobutene-2 (low-boilg. isomer) 3:5550 1,2-Dichlorobutene-2 (low-boilg isomer) 3:5550 1,3-Dichlorobutene-2 3:6550 1,3-Dichlorobutene-2 3:6550 1,3-Dichlorobutene-2 3:6550 1,3-Dichlorobutene-2 3:6550 2,4-Dichlorobutene-2 3:6550 2,4-Dichlorobutene-2 3:6550 2,4-Dichlorobutene-2 3:6550 1,2-Dichlorobutene-2 3:6550 1,2-Dichlorobutene-2 3:6550 2,4-Dichlorobutene-2 3:6550 1,2-Dichlorobutene-2 3:6550 2,4-Dichlorobutene-2 3:6550 2,5-Dichlorobutene-2 3:6550 2,5-Dich				
3:7615				
3:7580				
1,3-Dichlorobutanon-2 3:1550 1,3-Dichlorobutanon-2 3:1550 1,3-Dichlorobutene-1 3:8315 3,4-Dichlorobutene-1 3:9504 2,5-Dichloro-2,5-dimethylhexane 2,5-Dichloro-2,5-dimethylhexane 2,5-Dichloro-3,4-dimethylhexane 2,5-Dichloro-2,5-dimethylhexane 2,5-Dichloro-2,4-dimethylhexane 2,5-Dichloro-2,4-dimethylhexane 2,5-Dichloro-3,3-dimethylhexane 2,5-Dichloro-3,4-dimethylhexane 2,5-Dichloro-3,3-dimethylhexane 2,5-Dichloro-3,3-dimethylhexane 2,5-Dichloro-3,4-dimethylhexane 2,5-Dichloro-3,4-dimethylhexane 2,5-Dichloro-3,4-dimethylhexane 2,5-Dichloro-3,4-dimethylhexane 2,5-Dichloro-3,4-dimethylhexane 2,5-Dichloro-3,4-dimethylhexane 2,5-Dichlorodixane 2				
3:5900 1,3-Dichlorobutanone-2 3:1850 2,5-Dichloro-2,5-dimethylhexane 3:7650 1,3-Dichlorobutene-1 3:8315 3,4-Dichloro-3,4-dimethylhexane 3:9504 2,3-Dichlorobutene-1 3:9504 2,5-Dichloro-2,5-dimethylhexane 3:500 3,4-Dichlorobutene-2 3:9504 2,5-Dichloro-2,5-dimethylhexane 3:500 1,2-Dichlorobutene-2 (low-boilg, isomer) 3:8516 1,2-Dichlorobutene-2 (low-boilg isomer) 3:5550 1,3-Dichlorobutene-2 3:5550 1,3-Dichlorobutene-2 3:5500 cis-2,3-Dichlorobutene-2 3:5500 cis-2,3-Dichlorobutene-2 3:5500 2,4-Dichlorobutene-2 3:5500 2,4-Dichlorobute			3: 04 55	
3:7650 1,3-Dichlorobutene-1 3:8315 3,4-Dichloro-3,4-dimethylhexane 3:9074 2,3-Dichlorobutene-1 3:9564 2,5-Dichloro-2,5-dimethylhexane 2,5-Dichlorobutene-2 3:9565 1,1-Dichlorobutene-2 (low-boilg. isomer) 3:8516 1,2-Dichlorobutene-2 (high-boilg isomer) 3:9428 2,4-Dichloro-2,4-dimethylexane 3:5550 1,3-Dichlorobutene-2 3:7516 3,3-Dichlorobutene-2 3:5550 cis-2,3-Dichlorobutene-2 3:5550 cis-2,3-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:5550 2,4-Di				
3:9674 2,3-Dichlorobutene-1 3:5356 3,4-Dichlorobutene-1 3:7685 1,1-Dichlorobutene-2 (low-boilg. isomer) 3:5615 1,2-Dichlorobutene-2 (high-boilg isomer) 3:5550 1,3-Dichlorobutene-2 (high-boilg isomer) 3:5550 1,4-Dichlorobutene-2 (high-boilg isomer) 3:5550 2,4-Dichlorobutene-2 (high-boilg isomer) 3:5550 2,4-Dichlorobutene-2 (high-boilg isomer) 3:5550 2,4-Dichlorobutene-2 (high-boilg isomer) 3:5550 2,4-Dichlorobutene-2 (high-boilg isomer) 3:5555 1,4-Dichlorobutene-2 (high-boilg isomer) 3:5550 2,4-Dichlorobutene-2 (high-boilg isomer) 3:5560 2,4-Dichlorobutene-2 (high-boilg isomer) 3:5570 2,4-Dichlorobutene-2 (high-boilg isomer) 3:5560 2,4-Dichlorobutene-2 (high-boilg isomer) 3:5570 2,4-Dichloro-2,4-dimethyl-pentane 3:5570 2,4-Dichloro-4,4-dimethyl-pentane 3:5570 2,5-Dichlorodioxane-1,4 3:5771 2,5-Dichloro-4,4-dimethyl-pentane 3:5772 2,5-Dichloro-3,4-dimethyl-pentane 3:5773 2,5-Dichloro-3,4-dimethyl-pentane 3:5773 2,5-Dichlorodioxane-1,4 3:5773 2,5-Dichlorodioxane-1,4 3:5773 2,5-Dichlorodioxane-1,4 3:5773 2,5-Dichlorodioxane-1,4 3:5774 2,5-Dichlorodioxane-1,4 3:5775 2,5-Dichlorodioxane-1,4 3:5776 2,5-Dichlorodioxane-1,4 3:5777 2,5-Dichlorodioxane-1,4 3:5778 2,5-Dichlorodioxane-1,4 3:5779 2,5-Dichlorodioxane-1,4 3:5770 2,5-Dichlorodioxane-1,4 3:5771 2,5-Dichlorodioxane-1,4 3:5772 2,5-Dichlorodioxane-1,4 3:5773 2,5-Dichlorodioxane-1,4 3:5773 2,5-Dichlorodioxane-1,4 3:5774 2,5-Dichlorodioxane-1,4 3:5775 2,5-Dichlorodioxane-1,4 3:5775 2,5-Dichlorodioxane-1,4 3:5775 2,5-Dichlorodioxane-1,4 3:5775 2,5-Dichlorodioxane-1,4 3:5785 2,5-Dichlorodioxane-1,4				
3: 5350 3,4-Dichlorobutene-1 3: 6846 2,7-Dichloro-2,7-dimethyloctane 3: 5360 1,2-Dichlorobutene-2 (low-boilg. isomer) 3: 5815 1,2-Dichlorobutene-2 (high-boilg isomer) 3: 5855 1,3-Dichlorobutene-2 3: 5550 1,3-Dichlorobutene-2 3: 5560 cis-2,3-Dichlorobutene-2 3: 5560 2,4-Dichlorobutene-2 3: 5550 2,4-Dichlorobutene-2 3: 5550 1,2-Dichlorobutene-2 3: 5550 1,2-Dichlorobutene-2 3: 5550 1,2-Dichlorobutene-2 3: 5550 2,4-Dichlorobutene-2 3: 5550 2,4-Dichlorobutene-2 3: 5550 2,4-Dichlorobutene-2 3: 5550 3,3-Dichlorobutene-2 3: 5550 3,3-Dichlor				
3:7685 1,1-Dichlorobutene-2 3:6846 2,7-Dichloro-2,7-dimethyloctane 4,5-Dichloro-2,2-dimethyloctane 4,5-Dichloro-2,2-dimethyloctane 4,5-Dichloro-2,2-dimethyloctane 4,5-Dichloro-2,2-dimethyloctane 4,5-Dichloro-2,2-dimethyloctane 2,4-Dichlorobutene-2 3:7616 3:7616 3,3-Dichloro-2,4-dimethyloctane 3,3-Dichloro-2,4-dimethyloctane 3,3-Dichloro-2,4-dimethyloctane 2,3-Dichlorobutene-2 3:5500 cis-2,3-Dichlorobutene-2 3:5500 cis-2,3-Dichlorobutene-2 3:5500 cis-2,3-Dichlorobutene-2 3:5500 2,4-Dichlorobutene-2 3:6500 2,4-Dichlorobutene-2 3:6			3:95 04	
3:5360 1,2-Dichlorobutene-2 (low-boilg. isomer) 3:5615 1,2-Dichlorobutene-2 (high-boilg isomer) 3:5550 1,3-Dichlorobutene-2 3:5550 1,4-Dichlorobutene-2 3:5550 1,4-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:5550 3,3-Dichloro-2,4-dimethyl-pentane 1,5-Dichloro-3,3-dimethyl-pentane 1,2-Dichloro-3,3-dimethyl-pentane 2,3-Dichloro-4,4-dimethyl-pentane 3:5577 3:5772 3:5772 3:5773 3:5773 3:5773 3:5774 3:5775 3:5775 3:5775 3:5776 3:5776 3:5776 3:5776 3:5776 3:5776 3:5777 3:5776 3:5777 3:5777 3:5777 3:5777 3:5777 3:5778 3:5788 3				
isomer) 3:5615 1,2-Dichlorobutene-2 (high-boilg isomer) 3:5550 1,3-Dichlorobutene-2 3:5725 1,4-Dichlorobutene-2 3:5500 cis-2,3-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:5550 1,2-Dichlorobutene-2 3:5550 1,2-Dichlorobutene-2 3:5550 1,2-Dichlorobutene-2 3:5550 1,2-Dichlorobutene-2 3:5550 1,2-Dichlorobutene-2 3:5550 1,2-Dichlorobutene-3 3:5577 2	3:7685			
3:5615 1,2-Dichlorobutene-2 (high-boilg isomer) 3:5428 2,4-Dichloro-2,4-dimethylpentane 3,3-Dichlorobutene-2 3:5550 1,3-Dichlorobutene-2 pentane 3,3-Dichlorobutene-2 pentane 1,5-Dichloro-3,3-dimethylpentane 1,5-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:6550 2,4-Dichlorobutene-2 3:6550 1,2-Dichlorobutene-2 3:6550 1,2-Dichlorobutene-3 3:6577 symDichloro-ter-butyl alcohol 3:2442 5,6-Dichloro-2,3-dimethylphenol alcohol 3:2216 2,5-Dichloro-3,4-dimethylphenol	3:5360		3:8516	
isomer) 3:5550 1,3-Dichlorobutene-2 3:5725 1,4-Dichlorobutene-2 3:5500 2:5500 3:7355 1,4-Dichlorobutene-2 3:5550 3:7355 1,4-Dichlorobutene-2 3:7395 3:7355 2,4-Dichlorobutene-2 3:5550 3:5550 3:5550 3:5577 3:5772 3:5772 3:5773				
3:5550 1,3-Dichlorobutene-2 3:7610 3,3-Dichloro-2,4-dimethyl- 3:5725 1,4-Dichlorobutene-2 pentane 1,5-Dichloro-3,3-dimethyl- 3:5500 cis-2,3-Dichlorobutene-2 2,4-Dichlorobutene-2 3:5550 2,4-Dichlorobutene-2 3:5550 1,2-Dichlorobutene-3 3:5570 symDichloro-ter-butyl alcohol 3:7216 2,5-Dichloro-3,4-dimethylphenol 2,5-Dichloro-3,4-dimethylphenol 3:7216 2,5-Dichloro-3,4-dimethylphenol	3:5615	1,2-Dichlorobutene-2 (high-boilg	3:9428	
3: 5725				
3:5500 cis-2,3-Dichlorobutene-2 3:9430 1,5-Dichloro-3,3-dimethyl-pentane 3:7395 trans-2,3-Dichlorobutene-2 pentane 1,2-Dichloro-4,4-dimethyl-pentane 3:5550 2,4-Dichloro-butene-2 3:8516 1,2-Dichloro-4,4-dimethyl-pentane 3:5977 symDichloro-ter-butyl alcohol 3:9195 2,3-Dichlorodioxane-1,4 3:5773 unsymDichloro-ter-butyl 3:2443 5,6-Dichloro-2,3-dimethylphenol alcohol 3:2216 2,5-Dichloro-3,4-dimethylphenol	3:5550	1,3-Dichlorobutene-2	3:7610	3,3-Dichloro-2,4-dimethyl-
3: 7395	3:5725	1,4-Dichlorobutene-2		
3:5550 2,4-Dichlorobutene-2 3:8556 1,2-Dichloro-4,4-dimethyl- 3:6350 1,2-Dichlorobutene-3 pentane 3:5577 symDichloro-ter-butyl alcohol 3:2442 5,6-Dichloro-2,3-dimethylphenol alcohol 3:2316 2,5-Dichloro-3,4-dimethylphenol	3:5500	cis-2,3-Dichlorobutene-2	3:9430	1,5-Dichloro-3,3-dimethyl-
3:5559 2,4-Dichlorobutene-2 3:8516 1,2-Dichloro-4,4-dimethyl- 3:6359 1,2-Dichlorobutene-3 pentane 3:5577 symDichloro-ter-butyl alcohol 3:2442 5,6-Dichloro-2,3-dimethylphenol alcohol 3:2216	3:7395	trans-2,3-Dichlorobutene-2		pentane
3:5356	3:5550		3:8516	1,2-Dichloro-4,4-dimethyl-
3:5977 symDichloro-ter-butyl alcohol 3:9165 2,3-Dichlorodioxane-1,4 3:5772 unsymDichloro-ter-butyl 3:2443 5,6-Dichloro-2,3-dimethylphenol 2,5-Dichloro-3,4-dimethylphenol				pentane
3: 5772 unsymDichloro-ter-butyl 3: 2443 5,6-Dichloro-2,3-dimethylphenol alcohol 3: 2216 2,5-Dichloro-3,4-dimethylphenol			3:9105	2,3-Dichlorodioxane-1,4
alcohol 3:2216 2,5-Dichloro-3,4-dimethylphenol			3:2442	5,6-Dichloro-2,3-dimethylphenol
	3:9103	α,β-Dichloro-n-butyraldehyde	3:0935	

3:3 00 5	5,6-Dichloro-3,4-dimethylphenol	3:2637	3,5-Dichloro-2-hydroxy-
3:2182	2,4-Dichloro-3,5-dimethylphenol		benzaldehyde
3:2638	2,6-Dichloro-3,5-dimethylphenol	3:4140	2.4-Dichloro-3-hydroxy-
3:2570	d,l-1,2-Dichloro-1,2-diphenyl-	011110	benzaldehyde
0.2010		0.4400	
	ethane	3:4160	2,6-Dichloro-3-hydroxy-
3:4854	meso-1,2-Dichloro-1,2-diphenyl-		benzaldehyde
	ethane	3:3952	4,6-Dichloro-3-hydroxy-
3:1940	1,1-Dichloro-2,2-diphenylethane		benzaldehyde
3:1380	cis-1,2-Dichloro-1,2-diphenyl-	3:4400	3.5-Dichloro-4-hydroxy-
0.1000		0:2200	
0.4040	ethylene		benzaldehyde
3: 4210	trans-1,2-Dichloro-1,2-diphenyl-	3:4935	3,5-Dichloro-2-hydroxybenzoic
	ethylene		acid
3:1938	1,1-Dichloro-2,2-diphenyl-	8:4950	3,5-Dichloro-4-hydroxybenzoic
	ethylene		acid
3:1057	4,4'-Dichlorodiphenylmethane	3:2145	β,β -Dichloro- α -hydroxyiso-
		9:5140	
3:6960	α, α -Dichlorodiphenylmethane		butyric acid
3:8610	β,β' -Dichloro-di-n-propyl ether	3:2565	β,β' -Dichloro- α -hydroxyiso-
3:8745	γ, γ -Dichloro-di-n-propyl ether		butyric acid
3:6960	α,α-Dichloroditan	3:5300	α,α-Dichloroisobutylene
3:5035	1,1-Dichloroethane	3:5590	α,γ-Dichloroisobutylene
3:5130	1,2-Dichloroethane		
		3:5633	γ, γ' -Dichloroisobutylene
3:5130	symDichloroethane	3: 496 5	4,6-Dichloroisophthalic acid
3:5035	unsymDichloroethane	3:6318	β,β' -Dichloroisopropyl acetate
3:5745	2,2-Dichloroethanol-1	3:5755	β,β -Dichloroisopropyl alcohol
3:5540	α,β -Dichloro- α -ethoxyethylene	3:5985	β, β' -Dichloroisopropyl alcohol
3:5745	β,β-Dichloroethyl alcohol	3:9394	β, β' -Dichloroisopropyl-ethyl-
3:6685		9:9994	
	α, β -Dichloroethylbenzene		formal
3:6790	$Di(\beta$ -chloroethyl) carbonate	3:363 4	Dichloromaleic acid
3:6790	β,β-Dichloroethyl carbonate	3:3635	Dichloromaleic anhydride
3:5005	1,1-Dichloroethylene	3:6197	Dichloromalevl (di)chloride
3:5030	1,2-Dichloroethylene (ordinary	3:5020	Dichloromethane
0.0000	mixt.)	3:7920	1,2-Dichloro-2-methylbutane
3:5005			
	unsymDichloroethylene	3:9228	1,3-Dichloro-2-methylbutane
3:5042	cis-1,2-Dichlorethylene	3:8360	1,4-Dichloro-2-methylbutane
3:5028	trans-1,2-Dichloroethylene	3:7975	2,3-Dichloro-2-methylbutane
3:5 640	α,β-Dichloroethyl ethyl eth er	3:8105	2.4-Dichloro-2-methylbutane
3:9534	1,3-Dichloro-2-ethylhexane	3:9230	3,3-Dichloro-2-methylbutane
3:0572	Di-(β-chloroethyl) oxalate	3:8075	3,4-Dichloro-2-methylbutane
3:5010	1,2-Dichloroethyne		
		3:7885	4,4-Dichloro-2-methylbutane
3:8650	1,1-Dichloroheptane	3:7690	3,3-Dichloro-2-methylbutene-1
3:9420	1,2-Dichloroheptane	3:8170	1,3-Dichloro-2-methylbutene-2
3: 94 22	1,7-Dichloroheptane	3:92 04	1,4-Dichloro-2-methylbutene-2
3:9424	2,2-Dichloroheptane	3:5315	Dichloromethyl chlorocarbonate
3:9426	4.4-Dichloroheptane	3:5315	Dichloromethyl chloroformate
3:9310	1,3-Dichlorohexadiene-2,4	3:5772	
3:8380		0.0118	Dichloromethyl-dimethyl-
	1,2-Dichlorohexane		carbinol
3:9340	1,5-Dichlorohexane	3:5755	Dichloromethyl-methyl-carbinol
3:8720	1,6-Dichlorohexane	3:5430	Dichloromethyl methyl ketone
3:934 2	2,2-Dichlorohexane	3:934 6	2,3-Dichloro-2-methylpentane
3:8300	2,3-Dichlorohexane	3:8550	2,5-Dichloro-2-methylpentane
3:8525	2.5-Dichlorohexane	3:2910	4,5-Dichloro-2-methylphenol
3:9344	3,4-Dichlorohexane	3:1020	4.6 Dichlers 0 moderate laborat
			4,6-Dichloro-2-methylphenol
3:9300	3,4-Dichlorohexatetraene-1,2,4,5	8:1205	2,4-Dichloro-3-methylphenol
3:9304 ,	3.6-Dichlorohexatriene-1,3,4	3:0150	2,6-Dichloro-3-methylphenol
8:9330	1,2-Dichlorohexene-1	8:1745	4,6-Dichloro-3-methylphenol
3:5985	" a-Dichlorohydrin "	3:0400	2,6-Dichloro-4-methylphenol
3:6060	"β-Dichlorohydrin "	3:7425	1,1-Dichloro-2-methylpropane
3:4220	b zatomoromy arm	8:7430	1.9 Dickless 0
	2,3-Dichlorohydroquinone		1,2-Dichloro-2-methylpropane
3:4690	2,5-Dichlorohydroquinone	3:7960	1,3-Dichloro-2-methylpropane
3:4600	2,6-Dichlorohydroquinone	8:5772	1,1-Dichloro-2-methylpropanol-2
3:4220	o-Dichlorohydroquinone	3:5977	1,3-Dichloro-2-methylpropanol-2
3:4600	m-Dichlorohydroquinone	3:5300	1,1-Dichloro-2-methylpropene-1
3:4690	p-Dichlorohydroquinone	3:5590	1,3-Dichloro-2-methylpropene-1
J. 2000	5	J. 3000	-,

3:7480	3,3-Dichloro-2-methylpropene-1	3:2285	2,6-Dichlorophenyl phenyl
3:7480	1,1-Dichloro-2-methylpropene-2	5. AROS	ketone
3:0320	1,2-Dichloronaphthalene	3:3070	3,4-Dichlorophenyl phenyl
3:1310	1,3-Dichloronaphthalene	0.00.0	ketone
3:1655	1,4-Dichloronaphthalene	3:1505	3,5-Dichlorophenyl phenyl
3:3200	1.5-Dichloronaphthalene	012000	ketone
3:0810	1.6-Dichloronaphthalene	3:4880	3.4-Dichlorophthalic acid
3:1385	1.7-Dichloronaphthalene	3:4580	3,5-Dichlorophthalic acid
3:2435	1,8-Dichloronaphthalene	3:4870	3,6-Dichlorophthalic acid
3:3665	2.3-Dichloronaphthalene	3:4890	4,5-Dichlorophthalic acid
3:0810	2,5-Dichloronaphthalene	3:3695	3,4-Dichlorophthalic anhydride
3:4040	2,6-Dichloronaphthalene	3:2375	3,5-Dichlorophthalic anhydride
3:3445	2.7-Dichloronaphthalene	3:4860	3,6-Dichlorophthalic anhydride
3:1385	2,8-Dichloronaphthalene	3:4830	4,5-Dichlorophthalic anhydride
3:2935	2,3-Dichloronaphthol-1	3:2395	3,3-Dichlorophthalide
3:3250	2,4-Dichloronaphthol-1	3:9033-A	2,2-Dichloropropanal-1
3:3985	5,7-Dichloronaphthol-1	3:903 4	2,3-Dichloropropanal-1
3:3420	5,8-Dichloronaphthol-1	3:7230	1,1-Dichloropropane
3:4315	6,7-Dichloronaphthol-1	3:5200	1,2-Dichloropropane
3:2635	7,8-Dichloronaphthol-1	3:5450	1,3-Dichloropropane
3:1990	1,3-Dichloronaphthol-2	3:71 40	2,2-Dichloropropane
3:3840	1,4-Dichloronaphthol-2	3:6060	2,3-Dichloropropanol-1
3:360 0	1,6-Dichloronaphthol-2	3:5755	1,1-Dichloropropanol-2
3:3295	3,4-Dichloronaphthol-2	3:5985	1,3-Dichloropropanol-2
3: 44 20	4,8-Dichloronaphthol-2	3:5430	1,1-Dichloropropanone-2
3:4155	5,8-Dichloronaphthol-2	3:0563	1,3-Dichloropropanone-2
3:4857	2,3-Dichloronaphthoquinone-1,4	3:5120	1,1-Dichloropropene-1
3:4775	3,4-Dichloronaphthoquinone-1,2	3:5150	1,2-Dichloropropene-1 (hb.
3:9632	1,2-Dichlorononane		isomer)
3:8880	1,9-Dichlorononane	3:5110	1,2-Dichloropropene-1 (lb.
3:9530	1,6-Dichloro-octane		isomer)
3:9532	1,7-Dichloro-octane	3:5280	1,3-Dichloropropene-1
3:8805	1,8-Dichloro-octane	3:5190	2,3-Dichloropropene-1
3:8670	2,2-Dichloro-octane	3:5140	3,3-Dichloropropene-1
3:8015	1,1-Dichloropentane	3:5140	1,1-Dichloropropene-2
3:8140	1,2-Dichloropentane	3:9033-A	α,α-Dichloropropionaldehyde
3:9220	1,3-Dichloropentane	3:9034	α,β-Dichloropropionaldehyde
3:9224	1,4-Dichloropentane	3:6162.	α,α-Dichloropropionic acid
3:8575	1,5-Dichloropentane	3:0855 3:1058	α,β-Dichloropropionic acid
3:7755	2,2-Dichloropentane	3:5372	β,β-Dichloropropionic acid
3:8010 3:8120	2,3-Dichloropentane	3:9032	α,α-Dichloropropionyl chloride
3:7895	2,4-Dichloropentane 3,3-Dichloropentane	3:9032-A	α,β -Dichloropropionyl chloride β,β -Dichloropropionyl chloride
3:8045	3,4-Dichloropentene-2	3:6220	β, γ -Dichloro-n-propyl acetate
3:9202	2,5-Dichloropentene-2	3:6895	Di-(γ-chloropropyl) carbonate
3:1175	2,3-Dichlorophenol	3:6895	γ, γ' -Dichloropropyl carbonate
3:0560	2,4-Dichlorophenol	3:5280	α, γ -Dichloropropylene
3:1190	2,5-Dichlorophenol	3:2192	3,5-Dichloropyrocatechol
3:1595	2,6-Dichlorophenol	3:3525	4,5-Dichloropyrocatechol
3:1460	3,4-Dichlorophenol	3:4220	2,3-Dichloroquinol
3:1670	3,5-Dichlorophenol	3:3380	4,6-Dichlororesorcinol
3:4095	2,4-Dichlorophenoxyacetic acid	3:2637	3,5-Dichlorosalicylaldehyde
3:4612	Di-(p-chlorophenyl)acetic acid	3:4935	3,5-Dichlorosalicylic acid
3:6685	1,2-Dichloro-1-phenylethane	3:1380	cis-\alpha,\alpha'-Dichlorostilbene
3:0995	1,1-Di-(p-chlorophenyl)ethane	3:4210	trans-a, a'-Dichlorostilbene
3:2475	1,1-Di-(p-chlorophenyl)ethylene	3:4711	d,l-α,α'-Dichlorosuccinic acid
3:0717	Di-(o-chlorophenyl) ketone	3:4930	meso-a.a'-Dichlorosuccinic
3:3860	Di-(m-chlorophenyl) ketone		acid
3:4270	Di-(p-chlorophenyl) ketone	3:4711	allo-Dichlorosuccinic acid
3:1057	Di-(p-chlorophenyl)methane	3:0395	d,l-α,α'-Dichlorosuccinyl (di)-
3:0825	2,4-Dichlorophenyl phenyl ketone		chloride
3:2340	2,5-Dichlorophenyl phenyl	3:9087	meso-α,α'-Dichlorosuccinyl (di)-
	ketone		chloride

3:4985	2,5-Dichloroterephthalic acid	3:7900	Dimethyl-ethyl-acetyl chloride
3:6327	α,α-Dichlorotoluene	8:7220	Dimethyl-ethyl-carbinyl chloride
3:6327	ω,ω-Dichlorotoluene	3:9287	Dimethyl-ethyl-carbinyl hypo-
3:6345	2,3-Dichlorotoluene		chlorite
3:6290 3:6245	2,4-Dichlorotoluene	3:7752	α,α-Dimethylethylene α-chloro-
3:0245	2,5-Dichlorotoluene		hydrin
3:6355	2,6-Dichlorotoluene	3:7750	Dimethyl-isobutyl-carbinyl
3:6310	3,4-Dichlorotoluene 3,5-Dichlorotoluene	9.0405	chloride
3:9536	3,3-Dichloro-2,2,4-trimethyl-	3:0485 3:8145	Dimethyl isodichlorosuccinate
0.000	pentane	9:0149	Dimethyl-isopropyl-acetyl chloride
3:5540	α,β-Dichlorovinyl ethyl ether	3:7600	Dimethyl-isopropyl-carbinyl
3:1040	ω,ω'-Dichloro-o-xylene	0.1000	chloride
3:0310	ω,ω' -Dichloro-m-xylene	3:1355	2,4-Dimethylphenacyl chloride
3:2825	ω,ω' -Dichloro-p-xylene	3:0245	2,5-Dimethylphenacyl chloride
3:2442	4,5-Dichloro-o-3-xylenol	3:1775	3,4-Dimethylphenacyl chloride
3:0935	3,5-Dichloro-o-4-xylenol	3:9610	Dimethyl-phonyl-carbinyl
3:2216	3,6-Dichloro-o-4-xylenol		chloride
3:3005	5,6-Dichloro-o-4-xylenol	3:7450	α,α -Dimethylpropionyl chloride
3:2182	2,4-Dichloro-m-5-xylenol	3:9456	Dimethyl- n -propyl-acetyl
3:2638	2,6-Dichloro-m-5-xylenol		chloride
3:7990 3:7330	Diethylacetyl chloride	3:7490	Dimethyl-n-propyl-carbinyl
3:6864	Diethylcarbinyl chloride		chloride
3:6697	Diethyl chlorofumarate Diethyl chloromaleate	3:9456	α, α -Dimethyl-n-valeryl chloride
2:9578	Diethyl $d_i l - \alpha_i \alpha'$ -dichloro-	3:9458 3:9460	α,β -Dimethyl- <i>n</i> -valeryl chloride
0.00.0	succinate	3:7120 3:7120	γ,γ-Dimethyl-n-valeryl chloride
3:9578	Diethyl allo-dichlorosuccinate	3:9402	β,β-Dimethylvinyl chloride Dimethyl-vinylethynyl-carbinyl
3:1364	Diethyl meso-a, a'-dichloro-	0.0±0%	chloride
	succinate	3:0060	Diphenylcarbinyl chlorido
3:9390	Diethylene glycol mono(chloro-	3:3585	Diphenylchloroacetic acid .
	acetate)	3:0885	Diphenyl-chloro-acetyl chloride
3:9185	Diethylene glycol chlorohydrin	3:0060	Diphenyl-chloromethane
3:9578	Diethyl isodichlorosuccinate	3:9870	1,1-Diphenylethyl chloride
3:8210	Diethyl-isopropyl-carbinyl	3:9871	2,2-Diphenylethyl chloride
	chloride	3:0060	Diphenylmethyl chloride
3:7585	Diethyl-methyl-carbinyl	3:5515	" Diphosgene "
3:8223	chloride .	3:8095	Di-n-propyl-carbinyl chloride
o. Grro	Diethyl-n-propyl-carbinyl chloride	3:1915	Di-(trichloromethyl) carbonate
3:9092	Diglycoloyl dichloride	3:6373	Di-(trichlorovinyl) ether
3:9039	β, β' -Dihydroxyisopropyl chloride	3:9310 3:9858	Divinylacetylene dihydrochloride
3:8113	Di-isobutylene hydrochloride	3:8810	n-Dodecanoyl chloride n-Dodecyl chloride
3:9744	Di-isobutyl-methyl-carbinyl	0.0010	n-Dodecyr emoride
	chloride		E
3:9527	Di-isocrotyl hydrochloride		F.
3:1550	Di-isocrotyl bis-hydrochloride	3:9950	Elaidyl chloride
3:9240	cis-α,β-Dimethyl-acryloyl	3:8520	Enanthoyl chloride
	chloride	3:5358	"Epichlorohydrin"
3:7300	α, β -Dimethylallyl chloride	3:9082	Erythrene tetrachloride (liquid
8:7400	α,γ-Dimethylallyl chloride		isomer)
3:7485 3:7465	β,γ-Dimethylallyl chloride	3:1760	Erythrene tetrachloride (solid
8:7900	γ,γ-Dimethylallyl chloride α,α-Dimethyl-n-butyryl chloride	9.7007	isomer)
3:7965	α,β -Dimethyl- n -butyryl chloride	3 : 7065 3 : 5625	Ethanoyl chloride
3:7880	β,β-Dimethyl-n-butyryl chloride	3:7745	Ethoxalyl chloride
3:6582	Dimethyl chlorofumarate	3:7305	Ethoxyacetyl chloride
3:9251	Dimethyl chloromaleate	3:7463	α-Ethoxyethyl chloride β-Ethoxyethyl chloride
3:0485	Dimethyl d,l-\alpha,\alpha'-dichloro-	3:9280	β-Ethoxyethyl chlorocarbonate
	succinate	3:9280	β-Ethoxyethyl chloroformate
3:0485	Dimethyl allo-dichlorosuccinate	3:7260	α-Ethylallyl chloride
8:0240	Dimethyl meso-\alpha,\alpha'-dichloro-	3:9214	β-Ethylallyl chloride
	succinate	3:7470	γ-Ethylallyl chloride
			•

0.0000	Walnut or housest and the St. 11. 19		
3:8080	Ethyl-n-butyl-carbinyl chloride	3:9462	α -Ethyl-isovaleryl chloride
3:7720	2-Ethylbutyl chloride	3:7603	Ethyl-methyl-acetyl chloride
3:7990	α-Ethyl-n-butyryl chloride	3:7660	α -Ethyl- β -methylallyl chloride
3:7015	Ethyl chloride	3:7675	α -Ethyl- γ -methylallyl chloride
3:5700	Ethyl chloroacetate	3: 946 2	α -Ethyl- β -methyl- n -butyryl
3:6207	Ethyl α-chloroacetoacetate		chloride
3:6375	Ethyl γ-chloroacetoacetate	3:7125	Ethyl-methyl-carbinyl chloride
3:9242	Ethyl a-chloroacrylate	3:8175	unsymEthyl-methyl-ethylene
3:6800	Ethyl o-chlorobenzoate		chlorohydrin
3:6770	Ethyl m-chlorobenzoate	3:8010	symEthyl-methyl-ethylene
3:6750	Ethyl p-chlorobenzoate		dichloride
3:8307	Ethyl a-chloro-n-butyrate	3:7950	Ethyl-methyl-n-propyl-carbinyl
3:8373	Ethyl β -chloro- n -butyrate		chloride
3:8597	Ethyl γ -chloro- n -butyrate	3:8235	Ethyl-n-propyl-acetyl chloride
3:7295	"Ethyl chlorocarbonate"	3:7670	Ethyl-n-propyl-carbinyl chloride
3:8523	Ethyl α-chlorocrotonate	3:5950	Ethyl trichloroacetate
3:8538	Ethyl β-chlorocrotonate	3:6380	Ethyl α, α, β -trichloro-n-butyrate
3:8657	Ethyl γ-chlorocrotonate	3:5955	Ethyl-trichloromethyl-carbinol
3:5270	"Ethyl chloroform"	3:8235	α -Ethyl- n -valeryl chloride
3:7295	Ethyl chloroformate		F
3:9246	Ethyl (chloroformyl)acetate	9.0004	-
3:8147	Ethyl α-chloro-isobutyrate	3:9394	Formaldehyde β,β'-dichloro-
3:9368	Ethyl α-chloroisocrotonate		isopropyl-ethyl-acetal
3:8325	Ethyl β -chloroisocrotonate	3:5875	Fumaryl (di)chloride
3:8528	Ethyl α-chloro-isovalerate	3:8515	Furan 2-carboxylic acid chloride
3:6207	Ethyl α -chloro- β -keto- n -butyrate	3:8515	Furoyl chloride
3:6375	Ethyl γ -chloro- β -keto- n -butyrate		G
3:8518	Ethyl α -chloro- α -methyl- n - butyrate	3:6500	Glutaryl (di)chloride
3:8528		3:6775	Glycerol a-chlorohydrin a'-
3:39/6	Ethyl α-chloro-β-methyl-n-	3.9713	acetate
0.0105	butyrate	3:6517	Glycerol α-chlorohydrin β-
3:8125 3:8290	Ethyl α -chloropropionate Ethyl β -chloropropionate	6.0011	acetate
3:8596	Ethyl α -chloro- n -valerate	3:6648	Glycerol β -chlorohydrin α -
3:8629	Ethyl β -chloro-n-valerate.	0.0020	acetate
3:8703	Ethyl γ -chloro- n -valerate	3:5985	Glycerol α,α' -dichlorohydrin
3:8727	Ethyl δ-chloro-n-valerate	3:6060	Glycerol α, β -dichlorohydrin
3:7675	α-Ethylcrotyl chloride	3:6318	Glycerol a,a'-dichlorohydrin
3:5850	Ethyl dichloroacetate		β-acetate
3:6090	Ethyl α,β-dichloropropionate	3:6220	Glycerol α-β-dichlorohydrin α'-
3:9648	Ethyl-di-n-propyl-carbinyl		acetate
0.0020	chloride	3:9038	Glycerol a-monochlorohydrin
3:5130	Ethylene (di)chloride	3:9039	Glycerol β-monochlorohydrin
3:5552	Ethylene chlorohydrin	3:6840	Glycerol a-monochlorohydrin
3:6780	Ethylene glycol mono(chloro-		diacetate
	acetate)	3:5840	Glycerol trichlorohydrin
3:0720	Ethylene glycol bis-(chloro-	3:5552	" Glycol chlorohydrin "
	acetate)		
3:9185	Ethylene glycol mono-(β-		H
	chloroethyl) ether	3:9800	n-Hendecanoyl chloride
3:6655	Ethylene glycol bis-(β-chloro-	3:9800	n-Hendecoyl chloride
	ethyl) ether	3:9056	1,1,2,2,3,4,4-Heptachlorobutane
3:9322	Ethyl-ethynyl-methyl-carbinyl	3:6860	symHeptachloropropane
	chloride	3:0200	unsymHeptachloropropane
3:8370	2-Ethylhexyl chloride	3:0200	1,1,1,2,2,3,3-Heptachloropropane
3:7022	Ethyl hypochlorite	3:6860	1,1,1,2,3,3,3-Heptachloropropane
3:5 9 35	Ethylidene (di)chloride	3:9925	n-Heptadecanoyl chloride
3:9652	Ethyl-isoamyl-methyl-carbinyl	3:0100	n-Heptadecyl chloride
	chloride	3:9422	Heptamethylene dichloride
3:9462	Ethyl-isopropyl-acetyl chloride	3:8520	n-Heptanoyl chloride
3:7565	Ethyl-isopropyl-carbinyl chloride	3:8250	n-Heptyl chloride
3:7970	Ethyl-isopropyl-methyl-carbinyl	3:8 63 5	n-Heptyl-methyl-carbinyl chlo-
	chloride		ride

0.0040	77 13 1		
3:6312 3:4939	Hexachloroacetone Hexachlorobenzene	3:8215	Isoamyl chlorocarbonate
3:6425	Hexachlorobutadiene-1,3	3:8215 3:9580	Isoamyl chloroformate
3:3155	1.1.2.3.4.4-Hexachlorobutane	3:873 0	Isoamyl α -chloropropionate Isoamyl β -chloropropionate
3:1945	1,1,2,3,4,4-Hexachlorobutene-2	3:9556	Isoamyl-dimethyl-carbinyl
VV.	(solid isomer)	0.000	chloride
3:9046	1,1,2,3,4,4-Hexachlorobutene-2	3:7985	Isoamyl-methyl-carbinyl chloride
	(liquid isomer)	3:9628	Isoamyl-propenyl-carbinyl
3:9048	Hexachlorobutene-X		chloride
3:9050	Hexachlorobutene-Y	3:6490	Isoamyl trichloroacetate
3:318 0	Hexachlorocyclohexadien-2,5-	3:7145	Isobutenyl chloride
0.4440	one-1	3:8090	Isobutyl-acetyl chloride
3:4410	cis-1,2,3,4,5,6-Hexachlorocyclo-	3:7135	Isobutyl chloride
3:4990	hexane	3:8375	Isobutyl chloroacetate
0.2000	trans-1,2,3,4,5,6-Hexachloro- cyclohexane	3:7760 3:9216	Isobutyl chlorocarbonate "Isobutylchloroform"
3:3470	1,2,4,4,6,6-Hexachlorocyclo-	3:7760	Isobutyl chloroformate
0.02.0	hexen-1-dione-3,5	3:9470	Isobutyl a-chloropropionate
3:2360	2,3,5,5,6,6-Hexachlorocyclo-	3:8655	Isobutyl β-chloropropionate
	hexen-5-dione-1,4	3:7752	Isobutylene α -chlorohydrin
3:1915	Hexachlorodimethyl carbonate	3:7905	"β-Isobutylene chlorohydrin"
3:4835	Hexachloroethane	3:7 430	Isobutylene dichloride
3:1220	1,2,3,4,5,6-Hexachlorohexene-3	3:7425	Isobutylidene (di)chloride
3:3180	"Hexachlorophenol"	3:7495	Isobutyl-methyl-carbinyl
3:6460 3:6525	1,1,1,2,3,3-Hexachloropropane	0.0110	chloride
3:6525	1,1,2,2,3,3-Hexachloropropane symHexachloropropane	3:6140 3:7270	Isobutyl trichloroacetate
3:6460	unsymHexachloropropane	3:8090	Isobutyryl chloride Isocaproyl chloride
3:6312	Hexachloropropanone-2	3:1903	Isocrotonic acid dichloride
3:6370	Hexachloropropene	3:7120	Isocrotyl chloride
3:3470	"Hexachlororesorcinol"	3:4711	Isodichlorosuccinic acid
3:9912	n-Hexadecanoyl chloride	3:9750	β-Isodurylyl chloride
3:0015	n-Hexadecyl chloride	3:8365	Isoheptanoyl chloride
3:8580	Hexahydrobenzoyl chloride	3:7695	Isohexyl chloride
3:8720	Hexamethylene dichloride	3:9540	Isohexyl-methyl-carbinyl
3:8168	n-Hexanoyl chloride	0.0700	chloride
3:7955 3:7715	n-Hexyl chloride sec(2)-Hexyl chloride	3:0520 3:0520	Isophthaloyl (di)chloride Isophthalyl (di)chloride
3:7670	sec(3)-Hexyl chloride	3:0846	"Isopral"
3:8378	n-Hexyl-methyl-carbinyl chloride	3:8105	Isoprene bis-hydrochloride
3:8787	Hydrocinnamoyl chloride	3:7465	Isoprene hydrochloride
3:8777	Hydrocinnamyl chloride	3:9200	"Isoprene monochloride"
3:0085	2-Hydroxybenzoyl chloride	3:7020	Isopropenyl chloride
3:9446	3-Hydroxybenzoyl chloride	3:7358	Isopropenyl chlorocarbonate
3:9447	4-Hydroxybenzoyl chloride	3:7358	Isopropenyl chloroformate
3:9107	2-Hydroxy-2-(dichloromethyl)-	3:8795	4-Isopropylbenzyl chloride
3:9588	1,3-dioxolane β -[(β -Hydroxyethoxy)ethoxy]-	3:7135 3:7025	Isopropylcarbinyl chloride Isopropyl chloride
0:5000	ethyl chloroacetate	3:8160	Isopropyl chloroacetate
3:9390	β -(β -Hydroxyethoxy)ethyl	3:7405	Isopropyl chlorocarbonate
0.000	chloroacetate	3:7405	Isopropyl chloroformate
3:6780	β-Hydroxyethyl chloroacetate	3:8165	Isopropyl a-chloropropionate
3:9107	β -Hydroxyethyl dichloroacetate	3:9388	Isopropyl β -chloropropionate
3:9099	β-Hydroxyethyl trichloroacetate	3:5890	Isopropyl dichloroacetate
3:9570	β-Hydroxy-β-phenyl-ethyl chlo-	3:8075	Isopropylethylene dichoride
0.0000	ride	3:7140	Isopropylidene (di)chloride
3:9099	2-Hydroxy-2-(trichloromethyl)-	3:7965	Isopropyl-methyl-acetyl chloride
	1,3-dioxolane	3:7275	Isopropyl-methyl-carbinyl chlo- ride
3:8365	I Isoamylacetyl chloride	3:9554	Isopropyl-methyl-n-propyl- carbinyl chloride
3:7865	Isoamyl chloride	3:5975	Isopropyl tirchloroacetate
8:7275	secIsoamyl chloride	3:7560	Isovaleryl chloride

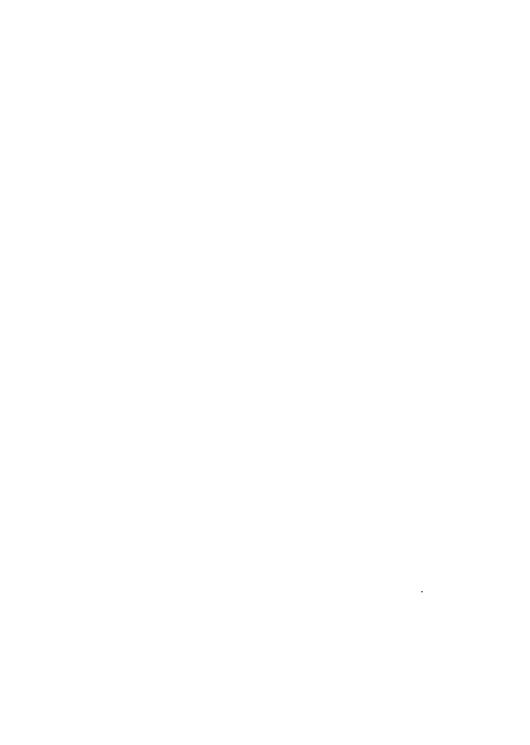
	ĸ	3:9792	Mothyl (c. (abloroformyl)
3:9098	β-Keto-n-butyryl chloride	U. 318A	Methyl ω-(chloroformyl)- pelargonate
21000	•	3:9247	Methyl β -(chloroformyl)-
	L		propionate
3:9858	n-Lauroyl chloride	3:7918	Methyl α-chloroisobutyrate
3:8810	n-Lauryl chloride	3:8028 3:7360	Methyl β-chloroisocrotonate "Methylchloroprene"
	M	3:7908	Methyl α-chloropropionate
3:9030	Malonyl dichloride	3:5765	Methyl β-chloropropionate
3:9925	n-Margaroyl chloride	3:8264	Methyl α -chloro-n-valerate
3:0250	α-Menaphthyl chloride	3:9240	cis-a-Methylcrotonoyl chloride
3:0747	β-Menaphthyl chloride	3:7400 3:5655	a-Methylcrotyl chloride
3:9750	Mesitoyl chloride	3:9103	Methyl dichloroacetate Methyl α,β-dichloropropionate
3:71 4 5 3:5225	Methallyl chloride Methoxyacetyl chloride	3:9550	Methyl-di-n-propyl-carbinyl
3:6870	2-Methoxybenzoyl chloride		chloride
3:6797	3-Methoxybenzoyl chloride	3:5020	Methylene (di)chloride
3:6890	4-Methoxybenzoyl chloride	3:1960	3,4-Methylenedioxybenzoyl
3:7150	α-Methoxyethyl chloride	3:7657	chloride
3:7265	β-Methoxyethyl chloride	3:9190	"β-Methylepichlorohydrin" β-Methylglycerol α-monochloro-
3:9285 3:9140	β-Methoxyethyl chloroacetate β-Methoxyethyl chlorocarbonate	0.0100	hydrin
3:9140	β-Methoxyethyl chloroformate	3:9440	Methyl-neopentyl-carbinyl
3:9250	β-Methoxyethyl trichloroacetate		chloride
3:7085	Methoxymethyl chloride	3:9660	o-Methylphenacyl chloride
3:7090	α -Methylallyl chloride	3:1130 3:8667	p-Methylphenacyl chloride
3:7145	β-Methylallyl chloride	3:7175	Methyl-phenyl-carbinyl chloride γ-Methylpropargyl chloride
3:7205 3:8740	γ-Methylallyl chloride o-Methylbenzoyl chloride	3:8020	Methyl-n-propyl-acetyl chloride
3:6535	m-Methylbenzoyl chloride	3:7325	Methyl-n-propyl-carbinyl
3:6600	p-Methylbenzoyl chloride		chloride
3:8710	o-Methylbenzyl chloride	3:5800	Methyl trichloroacetate
3:8700	m-Methylbenzyl chloride	3 : 5620 3 : 8020	Methyl trichloromethyl ketone
3:8660	p-Methylbenzyl chloride	3:8035	α-Methyl-n-valeryl chloride β-Methyl-n-valeryl chloride
3:7603 3:7560	α-Methyl-n-butyryl chloride β-Methyl-n-butyryl chloride	3:8090	γ -Methyl- n -valeryl chloride
3:9452	α -Methyl- n -caproyl chloride	3:7020	α-Methylvinyl chloride
3:8305	β-Methyl-n-caproyl chloride	3:7030	β -Methylvinyl chloride
3:8355	γ -Methyl- n -caproyl chloride	3:9038	"α-Monochlorohydrin"
3:8365	δ-Methyl-n-caproyl chloride	3:9039 3:6840	"β-Monochlorohydrin" "α-Monochlorohydrin"
3:9285	"Methylcellosolve"	0.0020	diacetate
3:9140	chloroacetate "Methylcellosolve"	3:9885	n-Myristoyl chloride
0.0120	chloroformate	3:9874	n-Myristyl chloride
3:9250	"Methylcellosolve"		N
	trichloroacetate	9.4750	-
3:7005	Methyl chloride	3 : 4750 3 : 6930	Napthalene tetrachloride α-Naphthoyl chloride
3:5585 3:9096	Methyl chloroacetate Methyl α-chloroacrylate	3:0900	β-Naphthoyl chloride
3:6695	Methyl o-chlorobenzoate	3:9856	α-Naphthylacetyl chloride
3:6670	Methyl m-chlorobenzoate	3:0250	α-Naphthylmethyl chloride
3:0535	Methyl p-chlorobenzoate	3:0747	β -Naphthylmethyl chloride
3:8103	Methyl α -chloro- n -butyrate	3:7590 3:9460	Neohexyl chloride
3:8224	Methyl β-chloro-n-butyrate	3:7555	Neopentylacetyl chloride Neopentylcarbinyl chloride
3:8517	Methyl γ-chloro-n-butyrate " Methyl chlorocarbonate"	3:7200	Neopentyl chloride
3:5075 3:5870	Methyl α-chlorocrotonate	3:8780	Neophyl chloride
3:9244	Methyl β -chlorocrotonate	3:8765	<i>n</i> -Nonanoyl chloride
3:5085	Methylchloroform	3:8719	n-Nonyl chloride
3:5075	Methyl chloroformate		0
3:9998-A	Methyl (chloroformyl)acetate	0.0000	0
3:9373	Methyl γ-(chloroformyl)-n-	3:2000 3:0422	1,1,2,2,3,3,4,4-Octachlorobutane Octachlorocyclopentene
	butyrate	U.VZAA	Consenior ocy cropertiente

3:073 8	$\alpha,\alpha,\beta,\beta,\beta,\beta',\beta',\beta'$ -Octachlorodi-	3:483 5	Perchloroethane
	ethyl ether	3:1676	" Perchloroether "
3:4893	Octachloronaphthalene	3:5460	Perchloroethylene
3:4450	Octachloropropane	3:0290	Perchloromethyl acetate
3:9960	n-Octadecanoyl chloride	3:48 9 3	Perchloronaphthalene
3:9940	n-Octadecen-9-oyl chloride	3: 4450	Perchloropropane
3:0095	n-Octadecyl chloride	3:6373	"Perchlorovinyl ether"
3:8805	Octamethylene dichloride	3:97 40	Perhydrogeranyl chloride
3:8680	n-Octanoyl chloride	3:1212	Phenacyl chloride
3:8585	n-Octyl chloride	3:8790	Phenoxyacetyl chloride
3:9940	n-Oleoyl chloride	3:9770	β -(β -Phenoxyethoxy)ethyl
3: <i>5</i> 060	Oxalyl (di)chloride		chloride
	P	3:0165	β -Phenoxyethyl chloride
0.0010	_	3:9448	Phenoxymethyl chloride
3:9912	n-Palmitoyl chloride	3:8820	γ-Phenoxy-n-propyl chloride
3:2650	Para-β-chloro-n-butyraldehyde	3:9567	Phenylacetyl chloride
3:3220 3:8766	Para-α-chloro-isobutyraldehyde	3:7 90 3	Phenyl chloride
3:62 0 5	Pelagonyl chloride	3:0565	Phenyl chloroacetate
3:3590	Pentachloroacetone	3:6540	Phenylchloroform
3:4892	Pentachlorobenzal (di)chloride Pentachlorobenzaldehyde	3:8712 3:9494	β-Phenylethyl chloride
3:2290	Pentachlorobenzene	3:3934	Phenylethynyl chloride
3:4910	Pentachlorobenzoic acid	3:9658	p-Phenylphenacyl chloride Phenylpropiolyl chloride
3:2295	Pentachlorobenzovi chloride	3:8787	β-Phenylpropionyl chloride
3:9044	1.1.2.3.4-Pentachlorobutadiene-	3:8777	γ -Phenyl- n -propyl chloride
0.00xx	1,3	3:6874	Phenyl trichloromethyl ketone
3:0750	1,1,2,3,4-Pentachlorobutane	3:5000	Phosgene
0.0.00	(solid isomer)	3:6900	symo-Phthaloyl dichloride
3:9068	1,1,2,3,4-Pentachlorobutane	3:2395	unsymo-Phthaloyl dichloride
0.000	(liquid isomer)	3:6900	symo-Phthalyl dichloride
3:9070	1,2,2,3,4-Pentachlorobutane	3:2395	unsymo-Phthalyl dichloride
3:9070	1,2,3,3,4-Pentachlorobutane	3:9450	Pimelyl (di)chloride
3:0750	1.2.3.4.4-Pentachlorobutane	3:7475	Pinacolyl chloride
	(solid isomer)	3:1960	Piperonyloyl chloride
3:9068	1,2,3,4,4-Pentachlorobutane	3:7400	Piperylene hydrochloride
	(liquid isomer)	3:7360	Pirylene monohydrochloride
3:9054	1,1,1,4,4-Pentachlorobutene-2	3:7450	Pivalyl chloride
3:5880	Pentachloroethane	3:7100	Propargyl chloride
3:1676	bis-(Pentachloroethyl) ether	3:7153	Propencyl chloride
3:9328	1,1,1,2,2-Pentachlorohexane	3:7030	Propenyl chloride
3:6725	3,3,4,4,4-Pentachloro-2-methyl-	3:8050	Propenyl-n-propyl-carbinyl
	butane		chloride
3:1265	1,1,1,2,3-Pentachloro-2-methyl-	3:7170	Propionyl chloride
	propane	3:7620	γ-(n-Propyl)allyl chloride
3:4850	Pentachlorophenol	3:7160	n-Propylcarbinyl chloride
3:4740	1,1,1,2,3-Pentachloropropane	3:7040	n-Propyl chloride
3:6280	1,1,2,3,3-Pentachloropropane	3:8295	n-Propyl chloroacetate
3:6280 3:4740	symPentachloropropane unsymPentachloropropane	3:7540 3:7540	n-Propyl chlorocarbonate n-Propyl chloroformate
3:4740 3:6205		3:9384	
3:6075	Pentachloropropanone-2 1,1,2,3,3-Pentachloropropene-1	3:8545	n -Propyl α -chloropropionate n -Propyl β -chloropropionate
3:4895	Pentachloropropionic acid	3:6000	n-Propyl dichloroacetate
3:0470	Pentachloropropionyl chloride	3:5200	Propylene (di)chloride
3:4937	2.3.4.5.6-Pentachlorotoluene	3:7747	Propylene (al/chloride Propylene α -chlorohydrin
3:4937 3:4937	eso-Pentachlorotoluene	3:7727	Propylene β -chlorohydrin
3:9900	Pentadecanoyl chloride	3:8225	n-Propylethylene chlorohydrin
3:9890	n-Pentadecyl chloride	3:7230	Propylidene (di)chloride
3:2675	Pentaerythrityl tetrachloride	3:6135	n-Propyl trichloroacetate
3:5880	"Pentalin"	3:8515	Pyromucyl chloride
3:9536	Pentamethylacetone dichloride	G . COTA	- J. J. J. OHIOITAG
3:8575	Pentamethylene dichloride		Q
3:1915	Perchlorodimethyl carbonate	3:9376	Quinitol chlorohydrin
	J v von nvenuv	50.0	

	8	3:5555	unsymTetrachloroethane
3:0085	Salicyloyl chloride	3:5460	Tetrachloroethylene
3:6870	Salicyloyl chloride methyl ether	3:0738	$bis-(\alpha,\beta,\beta,\beta-\text{Tetrachloroethyl})$
3:9789	Sebacyl (di)chloride		ether
3:9960	n-Stearoyl chloride	3:9306	1,3,4,6-Tetrachlorohexadiene-2,4
3:0095	Stearyl chloride	3:9332	1,1,2,2-Tetrachlorohexane
3:4854	"α"-Stilbene dichloride	3:4941	2,3,5,6-Tetrachlorohydroquinone
3:2570	"β"-Stilbene dichloride	3:90 36	$\beta, \beta, \beta, \beta'$ -Tetrachloroisopropyl
3:9570	Styrene chlorohydrin	3:9037	alcohol
3:6685	Styrene dichloride	3:8037	β,β,β',β'-Tetrachloroisopropyl alcohol
3:8717	Styryl chloride	3:5100	Tetrachloromethane
3:9576 3:6200	Suberyl (di)chloride Succinyl (di)chloride	3:4725	1,1,1,2-Tetrachloro-2-methyl-
3:5515	"Superpalite"	012170	propane
0.0010	Duperpante	3:6165	1,1,2,3-Tetrachloro-2-methyl-
	${f T}$		propane
3:2205	Terephthaloyl (di)chloride	3:3523	2,3,4,5-Tetrachlorophenol
3:2205	Terephthalyl (di)chloride	3:1687	2,3,4,6-Tetrachlorophenol
3:6050	symTetrachloroacetone	3:3460	2,3,5,6-Tetrachlorophenol
3:6085	unsymTetrachloroacetone	3:4946	Tetrachlorophthalic acid
3:9397	2,3,4,5-Tetrachlorobenzal (di)-	3:4947 3:5785	Tetrachlorophthalic anhydride
	chloride	3:5825	1,1,1,2-Tetrachloropropane 1,1,2,2-Tetrachloropropane
3:6980	2,3,4,6-(or 2,3,5,6-)Tetrachloro-	3:0035	1,1,2,3-Tetrachloropropane
3:3140	benzal (di)chloride 2,3,4,5-Tetrachlorobenzaldehyde	3:5895	1,2,2,3-Tetrachloropropane
3:2700	2,3,4,6-(or 2,3,5,6-) Tetrachloro-	3:9036	1,1,1,3-Tetrachloropropanol-2
0.2100	benzaldehyde	3:9037	1,1,3,3-Tetrachloropropanol-2
3:0655	1,2,3,4-Tetrachlorobenzene	3:6085	1,1,1,3-Tetrachloropropanone-2
3:0915	1,2,3,5-Tetrachlorobenzene	3:6050	1,1,3,3-Tetrachloropropanone-2
3:4115	1,2,4,5-Tetrachlorobenzene	3:5920	1,2,3,3-Tetrachloropropene-1
3:4790	2,3,4,5-Tetrachlorobenzoic acid	3:1850	$\alpha, \alpha, \beta, \beta$ -Tetrachloropropionic
3:3965	Tetrachlorobenzoquinone-1,2	3:4875	acid
3:4978	2,3,5,6-Tetrachlorobenzoquinone-	3:3965	Tetrachloropyrocatechol Tetrachloro-o-quinone
3:4496	1,4	3:4978	Tetrachloro-p-quinone
3:4490 3:0870	α,α,α',α',-Tetrachlorobibenzyl 1,2,3,4-Tetrachlorobutadiene-	3:4135	Tetrachlororesorcinol
0.0010	1,3 (solid isomer)	3:4750	1,2,3,4-Tetrachloro-1,2,3,4-
3:6150	1,2,3,4-Tetrachorobutadiene-		tetrahydronaphthalene
	1,3 (liquid isomer)	3:4703	5,6,7,8-Tetrachloro-1,2,3,4-
3:5622	1,1,1,2-Tetrachlorobutane		tetrahydronaphthalene
3:9078	1,2,2,3-Tetrachlorobutane	3:4750	1,2,3,4-Tetrachlorotetralin
3:9080	1,2,3,3-Tetracholorobutane	3:47 03 3:2710	5,6,7,8-Tetrachlorotetralin
3:1760	1,2,3,4-Tetrachlorobutane (solid	3:2480	2,3,4,5-Tetrachlorotoluene 2,3,4,6-Tetrachlorotoluene
3:9082	isomer) 1,2,3,4-Tetrachlorobutane (liquid	3:2575	2,3,5,6-Tetrachlorotoluene
9:5006	isomer)	3:9885	n-Tetradecanoyl chloride
3:9058	1,3,4,4-Tetrachlorobutene-1	3:9874	n-Tetradecyl chloride
3:9060	2,3,3,4-Tetrachlorobutene-1	3:8152	Tetrahydro-α-furfuryl chloride
3:9058	1,1,2,4-Tetrachlorobutene-3	3:9740	Tetrahydrogeranyl chloride
3:9060	1,2,2,3-Tetrachlorobutene-3	3:9170	Tetramethylene chlorohydrin
3:4875	Tetrachlorocatechol	3:5835	Tetramethylene (di)chloride
3:9072	1,1,2,3-Tetrachloro-2-(chloro-	3:4520 3:9240	Tetramethylethylene dichloride
	methyl) propane	3:1380	Tiglyl chloride cis-Tolane dichloride
3:2477	1,1,1,2-Tetrachloro-2,2-bis-	3:421 0	trans-Tolane dichloride
3:4875	(p-chlorophenyl)ethane Tetrachloro-1,2-dihydroxyben-	3:4496	Tolane tetrachloride
0:20/0	zene	3:9567	a-Toluyl chloride
3:4496	1,1,2,2-Tetrachloro-1,2-diphenyl-	3:8740	o-Toluyl chloride
J. 2200	ethane	3:6535	m-Toluyl chloride
3:5555	1,1,1,2-Tetrachloroethane	8:6600	p-Toluyl chloride
3:5750	1,1,2,2-Tetrachloroethane	3:6317	β, β, β -Trichloroacetal
8:5750	symTetrachloroethane	8:5210	Trichloroacetaldehyde

			m / 11
3:0843	Trichloroacetaldehyde n-	3:9094	α,α,γ-Trichloro-n-butyraldehyde
9.0947	butylhemiacetal	3:1905	α, α, β -Trichloro- <i>n</i> -butyraldehyde
3:6317	Trichloroacetaldehyde di-	3:1280	hydrate
3:0860	ethylacetal Trichloroacetaldehyde (mono)-	3:1831	α,α,β-Trichloro-n-butyric acid α,α,γ-Trichloro-n-butyric acid
9:0000	ethylacetal	3:0925	α, β, β -Trichloro- <i>n</i> -butyric acid
3:1270	Trichloroacetaldehyde hydrate	3:1000	γ, γ, γ -Trichloro-n-butyric acid
3:1270 3:1150	Trichloroacetic acid	3:3448	3.4.5-Trichlorocatechol
3:6575	Trichloroacetic acid anhydride	3:5230	1,2,3-Trichloro-2-(chloromethyl)-
3:5620	α,α,α -Trichloroacetone	0.000	butane
3:5957	α,α,γ -Trichloroacetone	3:9084	1,1,3-Trichloro-2-(chloromethyl)-
3:6874	ω,ω,ω-Trichloroacetophenone	0.0002	propane
3:5420	Trichloroacetyl chloride	3:6335	1,2,3-Trichloro-2-(chloromethyl)-
3:1840	α, β, β -Trichloroacrylic acid		propane
3:5845	Trichloroscryloyl chloride	3:1820	1,1,1-Trichloro-2-(o-chloro-
3:2212	2,3,4-Trichlorobenzal (di)-		phenyl)-2-(p-chlorophenyl)-
	chloride		ethane
3:2178	2,3,6-Trichlorobenzal (di)-	3:9867	1,1,1-Trichloro-2-(m-chloro-
	chloride		phenyl)- 2 -(p -chlorophenyl)-
3:6910	2,4,5-Trichlorobenzal (di)-		ethane
	chloride	3:9865	1,1,1-Trichloro-2,2-bis-(o-chloro-
3:0142	2,4,6-Trichlorobenzal (di-		phenyl)ethane
	chloride	3:329 8	1,1,1-Trichloro-2,2-bis-(p-chloro-
3:2445	2,3,4-Trichlorobenzaldehyde	0.000	phenyl)ethane
3:1060	2,3,5-Trichlorobenzaldehyde	3:0618	2,4,6-Trichloro-m-cresol
3:2287	2,3,6-Trichlorobenzaldehyde	3:1280	"Trichlorocrotonic acid"
8:3375	2,4,5-Trichlorobenzaldehyde	3:4742	4,5,6-Trichloro-2,3-dimethyl-
3:1200 3:2440	2,4,6-Trichlorobenzaldehyde 3,4,5-Trichlorobenzaldehyde	3:4707	phenol 3,5,6-Trichloro-2,4-dimethyl-
3:0990	1,2,3-Trichlorobenzene	0.2101	phenol
3:6420	1,2,4-Trichlorobenzene	3:4709	3,4,6-Trichloro-2,5-dimethyl-
3:1400	1,3,5-Trichlorobenzene	0.2100	phenol
3:1400	symTrichlorobenzene	3:4747	2,5,6-Trichloro-3,4-dimethyl-
3:6420	unsymTrichlorobenzene		phenol
3:0990	vicTrichlorobenzene	3:4713	2,4,6-Trichloro-3,5-dimethyl-
3:4810	2,3,4-Trichlorobenzoic acid		phenol
3:4485	2,3,5-Trichlorobenzoic acid	3:1420	1,1,1-Trichloro-2,2-diphenyl-
3:4500	2,3,6-Trichlorobenzoic acid		ethane
3:4630	2,4,5-Trichlorobenzoic acid	3:5760	3,3,3-Trichloro-1,2-epoxypropane
3:454 5	2,4,6-Trichlorobenzoic acid	3:5085	1,1,1-Trichloroethane
8:4920	3,4,5-Trichlorobenzoic acid	3:5330	1,1,2-Trichloroethane
8:4672	2,3,5-Trichlorobenzoquinone-1,4	3:5330	unsymTrichloroethane
8:2212	2,3,4-Trichlorobenzylidene (di)-	3:5775	2,2,2-Trichloroethanol-1
9.9470	chloride	3:5775 3:5170	β,β,β-Trichloroethyl alcohol 1,1,2-Trichloroethylene
3:2178	2,3,6-Trichlorobenzylidene (di)- chloride	3:9308	3,3,6-Trichlorohexadiene-1,4
3:6910	2,4,5-Trichlorobenzylidene (di)-	3:9302	3,4,6-Trichlorohexatriene-1,2,4
9.4814	chloride	3:9326	1,1,2-Trichlorohexene-1
3:0142	2,4,6-Trichlorobenzylidene (di)-	3:5840	"Trichlorohydrin"
	chloride	3:4052	2,3,5-Trichlorohydroquinone
3:9052	1,2,3-Trichlorobutadiene-1,3	3:3520	2,4,6-Trichloro-3-hydroxy-
3:9086	1,1,3-Trichlorobutane		benzaldehyde
3:5935	1,2,3-Trichlorobutane	3:4444	3,5,6-Trichloro-2-hydroxy-
3:5680	2,2,3-Trichlorobutane		hydroquinone
3:1336	2,2,3-Trichlorobutanol-1	3:0846	β, β, β -Trichloroisopropyl alcohol
3:5955	1,1,1-Trichlorobutanol-2	3:5785	β, β, β -Trichloroisopropyl chloride
3:9064	2,3,4-Trichlorobutene-1	3:5050	Trichloromethane
8:9062	1,2,4-Trichlorobutene-2	3:6100	1,2,3-Trichloro-2-methylbutane
8:9062	1,3,4-Trichlorobutene-2	3:4755	2,3,3-Trichloro-2-methylbutane
8:9064	1,2,3-Trichlorobutene-3	3:9216	4,4,4-Trichloro-2-methylbutane
3:6180	β,β,β-Trichloro-ter-butyl acetate	3:1915 3:5515	bis-(Trichloromethyl) carbonate
3:2662 3:5910	β,β,β-Trichloro-ter-butyl alcohol	3:5515 3:5515	Trichloromethyl chlorocarbonate
●: 0ATA	α, α, β -Trichloro- n -butyraldehyde	o . Jolu	Trichloromethyl chloroformate

3:351 0	2.5-bis-(Trichloromethyl)-1,3-	3:0425	2,3,4-Trichlorotoluene
	dioxolanone-4	3:0610	2,3,5-Trichlorotoluene
3:0618	2,4,6-Trichloro-3-methylphenol	3:0625	2,3,6-Trichlorotoluene
3:5710	1,1,2-Trichloro-2-methylpropane	3:2100	2.4.5-Trichlorotoluene
3:5885	1,2,3-Trichloro-2-methylpropane	3:0380	2,4,6-Trichlorotoluene
3:2662	1,1,1-Trichloro-2-methyl-	3:0580	3,4,5-Trichlorotoluene
	propanol-2	3:4742	Trichloro-o-3-xylenol
3:5025	1,1,3-Trichloro-2-methyl-	3:4747	Trichloro-o-4-xylenol
	propene-1	3:4707	Trichloro-m-4-xylenol
3:5605	3,3,3-Trichloro-2-methyl-	3:4713	Trichloro-m-5-xylenol
	propene-1	3:4709	Trichloro-p-xylenol
3:5605	1,1,1-Trichloro-2-methyl-	3:9860	Tridecanoyl chloride
	propene-2	3:9859	n-Tridecyl chloride
3:0290	Trichloromethyl trichloroacetate	3:8055	Triethylcarbinyl chloride
3:2125	1,2,3-Trichloronaphthalene	3:9588	Triethylene glycol mono(chloro-
3:2490	1,2,4-Trichloronaphthalene	0.0000	acetate)
3:1930	1,2,5-Trichloronaphthalene	3:6655	"Triglycol dichloride"
3:2515	1,2,6-Trichloronaphthalene	3:7450	Trimethylacetyl chloride
3:2325	1,2,7-Trichloronaphthalene	3:9338	α, β, γ -Trimethylallyl chloride
3:2220	1,2,8-Trichloronaphthalene	3:7520	β, γ, γ -Trimethylallyl chloride
3:3015	1,3,5-Trichloronaphthalene	3:9750	2,4,6-Trimethylbenzoyl chloride
3:1975	1,3,6-Trichloronaphthalene	3:9701	2,3,6-Trimethylbenzyl chloride
3:3400	1,3,7-Trichloronaphthalene	3:9702	2,4,5-Trimethylbenzyl chloride
3:2420		3:0372	
3:4005	1,3,8-Tric iloronaphthalene	3:8145	2,4,6-Trimethylbenzyl chloride
3:1625	1,4,5-Trichloronaphthalene	9:0149	α, α, β -Trimethyl- n -butyryl
	1,4,6-Trichloronaphthalene	0.7047	chloride
3:3300	2,3,5-Trichloronaphthalene	3:7045	Trimethylcarbinyl chloride
3:2455	2,3,6-Trichloronaphthalene	3:7165	Trimethylcarbinyl hypochlorite
3:2300	Trichloroparaldehyde	3:9418	Trimethylcrotyl chloride
3:2185	2,3,4-Trichlorophenol	3:5450	Trimethylene (di)chloride
3:13 40	2,3,5-Trichlorophenol	3:8285	Trimethylene chlorohydrin
3:1160	2,3,6-Trichlorophenol	3:8310	Trimethylene chlorohydrin
3:1620	2,4,5-Trichlorophenol		acetate
3:1673	2,4,6-Trichlorophenol	3:8030	Trimethylethylene chlorohydrin
3:2885	3,4,5-Trichlorophenol	3:7975	Trimethylethylene dichloride
3:4335	2,4,5-Trichlorophenoxyacetic	3:9324	Trimethylpropargyl chloride
	acid	3:7335	Trimethylvinyl chloride
3:4030	2,4,6-Trichlorophloroglucinol	3:3410	Triphenylchloromethane
3:9033	2,2,3-Trichloropropanal-1	3:3410	Triphenylmethyl chloride
3:5270	1,1,1-Trichloropropane	3:1915	Triphosgene
3:5630	1,1,2-Trichloropropane	3:9742	Tri-n-propylcarbinyl chloride
3:5660	1,1,3-Trichloropropane	3:3410	Trityl chloride
3:5475	1,2,2-Trichloropropane		U
3:5840	1,2,3-Trichloropropane		
3:0846	1,1,1-Trichloropropanol-2	3:9800	n-Undecanoyl chloride
3:5620	1,1,1-Trichloropropanone-2	3:8803	n-Undecyl chloride
3:5957	1,1,3-Trichloropropanone-2		v
3:5395	1,1,2-Trichloropropene-1		•
3:5650	1,2,3-Trichloropropene-1	3:7740	n-Valeryl chloride
3:5345	3,3,3-Trichloropropene-1	3:7010	Vinyl chloride
3:5345	1,1,1-Trichloropropene-2	3:5005	Vinylidene (di)chloride
3:9033	α, α, β -Trichloropropionaldehyde		x
3:1275	α, α, β -Trichloropropionic acid		
3:5760	ω,ω,ω -Trichloropropylene oxide	3:8710	o-Xylyl chloride
3:3 44 8	3,4,5-Trichloropyrocatechol	3:8700	m-Xylyl chloride
3:4782	4,5,6-Trichloropyrogallol	3:8660	p-Xylyl chloride
3:4672	Trichloroquinone	3:1 04 0	o-Xylylene (di)chloride
3:2174	2,4,6-Trichlororesorcinol	3:0310	m-Xylylene (di)chloride
3:6540	ω,ω,ω -Trichlorotoluene	3:2825	p-Xylylene (di)chloride



1246.13 Hayyp

Perhandring properties chemical

behavior & identification of

Organic Chemical

Organi